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Drug Science
and Technology

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Oxidation of Food Components

Unit 1 -> Oxidation in food

Proteins and carbohydrates - mechanisms of oxidation
Insights on the cross reactivity between oxidized food components

Unit 2 -> Anti-oxidants

Molecular basis of protection to oxidation
Native antioxidants (tocopherols, polyphenols, ascorbic acid, carotenoids)
Antioxidants formed during processing (reductones from Maillard reaction)
Syntetic antioxidants

Case studies:

Polyphenols-myoproteins interactions

Unit 1 Oxidation of Food Components

Proteins oxidation

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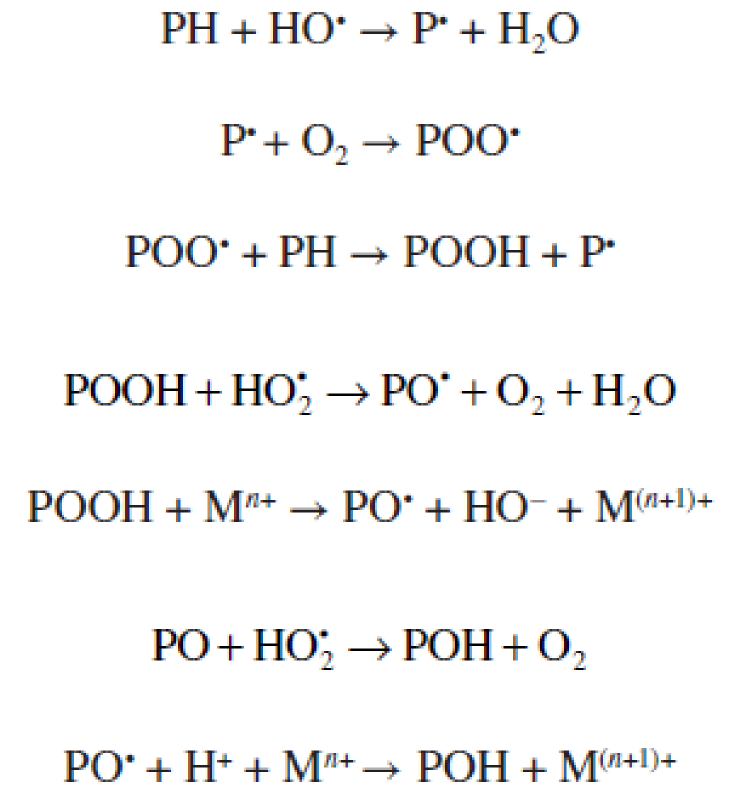
Reactive oxidants generated continuously in biological systems are expected to react mainly with proteins (P) as a result of the high abundance of proteins (approximately 70% of the dry mass of cells) and rapid rates of their reactions with many oxidants.

Protein oxidation occurs as a result of either **direct attack** by **ROS** or **photooxidation** or **indirectly through peroxidation** of **lipids** that further degrade and attack proteins.

The **common targets** for ROS are the **peptide backbone** and the **functional groups in the side chains** of amino acid residues. **A single hydroxyl radical is capable of causing damage of up to 15 amino acids of a peptide chain.**

Certain amino acids, such as Cys and Met, would be first oxidized because of the high susceptibility of their sulfur centers. Trp residues are also promptly oxidized. Susceptible to oxidation are also amino acids with a free amino, amide, and hydroxyl group (Lys, Arg, and Tyr).



$$PH + HO^{\bullet} \rightarrow P^{\bullet} + H_2O$$

$$P^{\bullet} + O_2 \rightarrow POO^{\bullet}$$

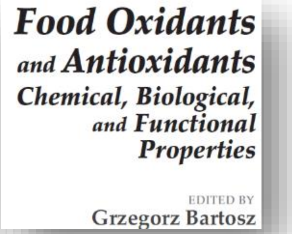
$$POO^{\bullet} + PH \rightarrow POOH + P^{\bullet}$$

$$POOH + HO_2^{\bullet} \rightarrow PO^{\bullet} + O_2 + H_2O$$

$$POOH + M^{n+} \rightarrow PO^{\bullet} + HO^{-} + M^{(n+1)+}$$

$$PO + HO_2^{\bullet} \rightarrow POH + O_2$$

$$PO^{\bullet} + H^{+} + M^{n+} \rightarrow POH + M^{(n+1)+}$$



Food Oxidants and Antioxidants
Chemical, Biological, and Functional Properties
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Proteins oxidation

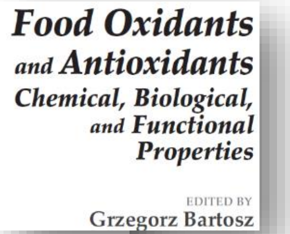
Lipid radicals abstract hydrogen mainly from the side chains of the protein molecule, in particular, **from lysine**, **arginine**, **histidine**, **tryptophan**, **cysteine**, and **cystine residues**, to form protein radicals (P•) **that initiate formation** of **further radicals** interacting with the **protein, causing formation of protein radicals or protein–protein and protein–lipid adducts**, or they react also with other food components.

$$P + L^{\bullet} \rightarrow P^{\bullet} + L$$

$$P + LO^{\bullet} \rightarrow P^{\bullet} + LOH,\ LO^{\bullet}P$$

$$P + LOO^{\bullet} \rightarrow P^{\bullet} + LOOH,\ LOO^{\bullet}P$$

$$P + LOH \rightarrow LO^{\bullet} + P^{\bullet} + {}^{\bullet}OH + H^{\bullet}$$



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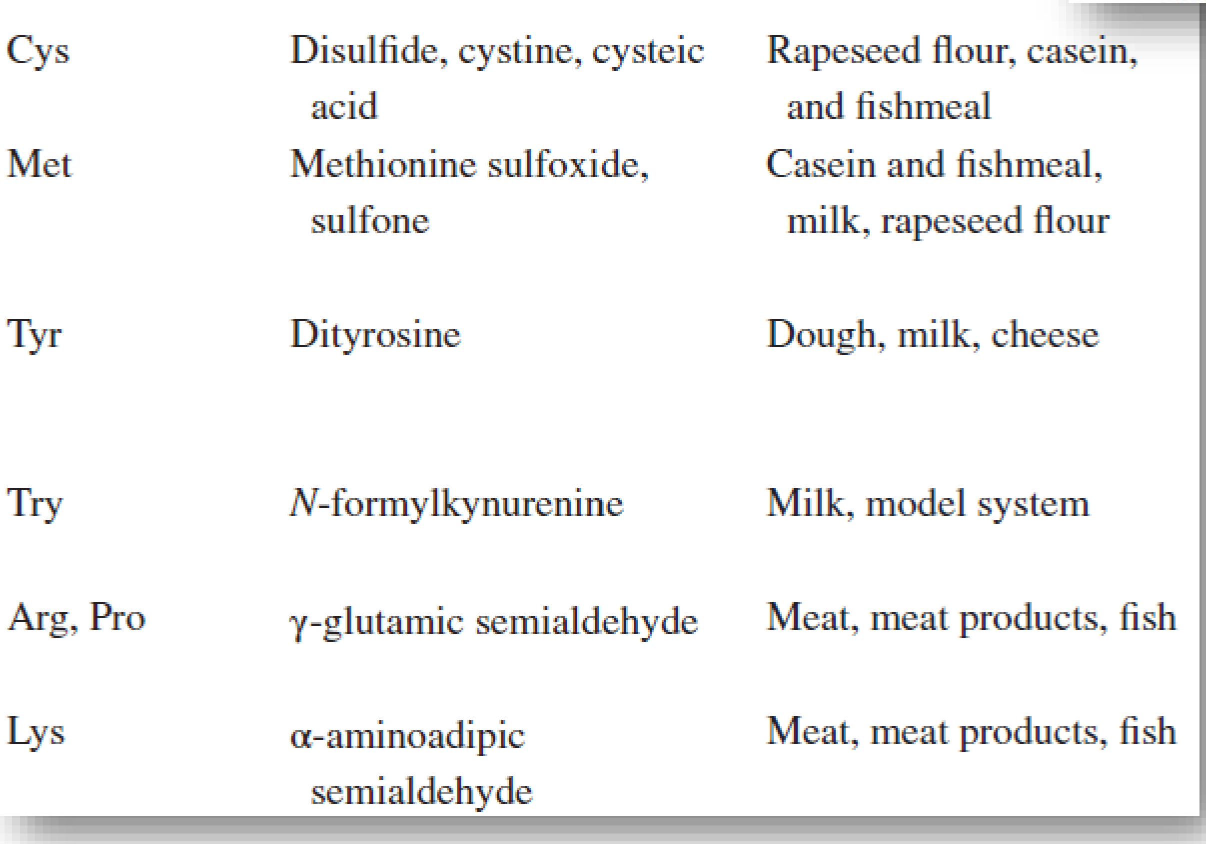
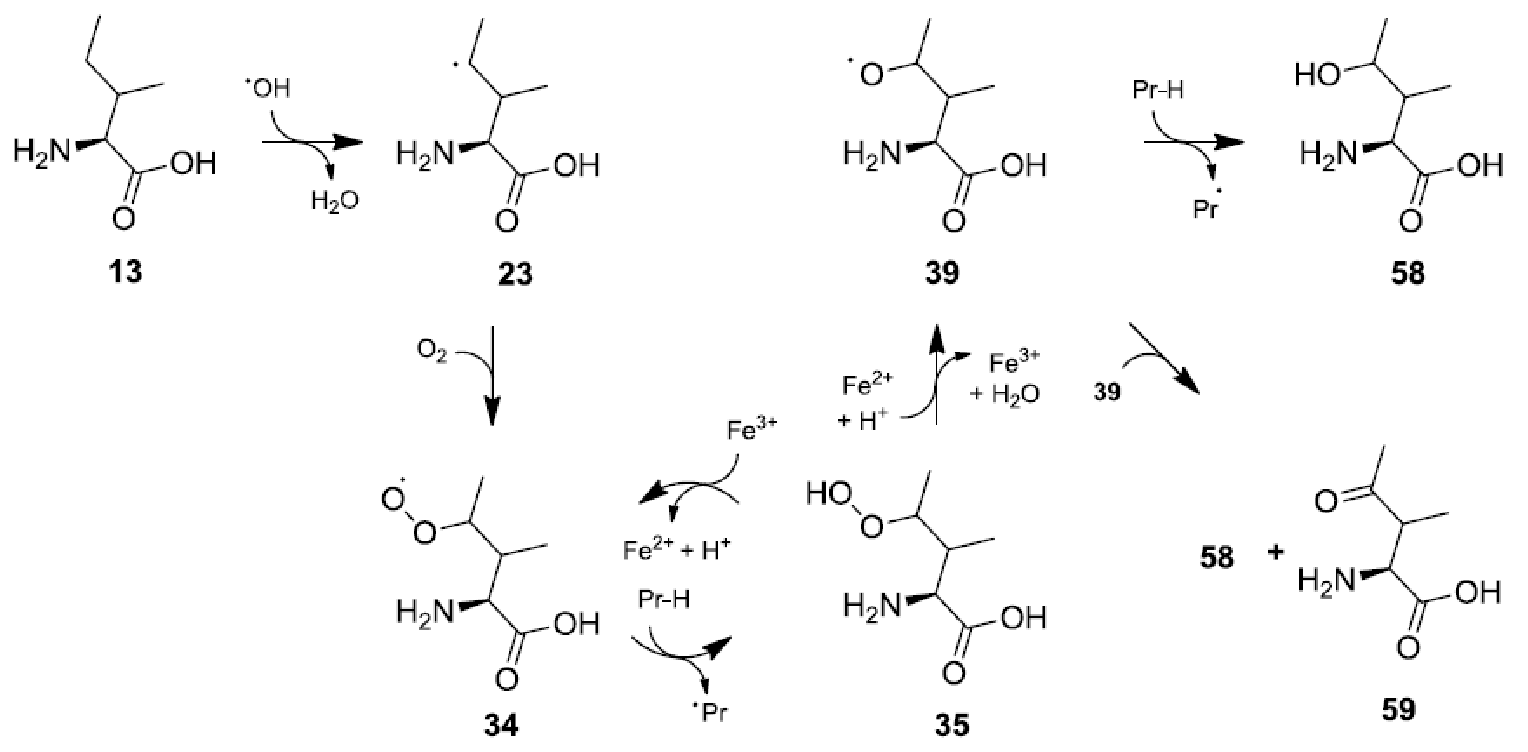


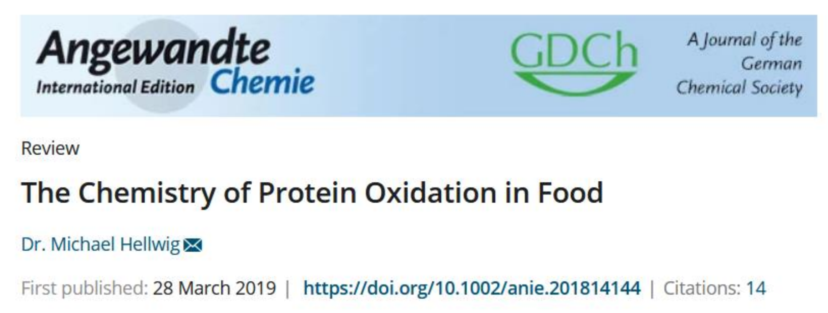
Amino Acid	Oxidation Products	Food
Cys	Disulfide, cystine, cysteic acid	Rapeseed flour, casein, and fishmeal
Met	Methionine sulfoxide, sulfone	Casein and fishmeal, milk, rapeseed flour
Tyr	Dityrosine	Dough, milk, cheese
Try	*N*-formylkynurenine	Milk, model system
Arg, Pro	γ-glutamic semialdehyde	Meat, meat products, fish
Lys	α-aminoadipic semialdehyde	Meat, meat products, fish

Proteins oxidation



13: Ile
23: side-chain radical from Ile
34: peroxyl radical
35: hydroperoxide
39: alkoxyl radical

58: alcohol derivative
59: carbonyl derivative



Review

The Chemistry of Protein Oxidation in Food

Dr. Michael Hellwig

First published: 28 March 2019 | https://doi.org/10.1002/anie.201814144 | Citations: 14

Oxidation reactions in the aliphatic side-chain of amino acids using the example of isoleucine (Pr, protein).

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Proteins oxidation

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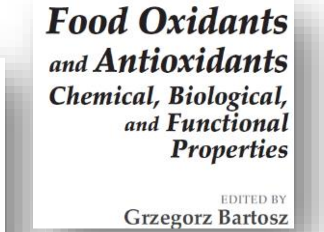

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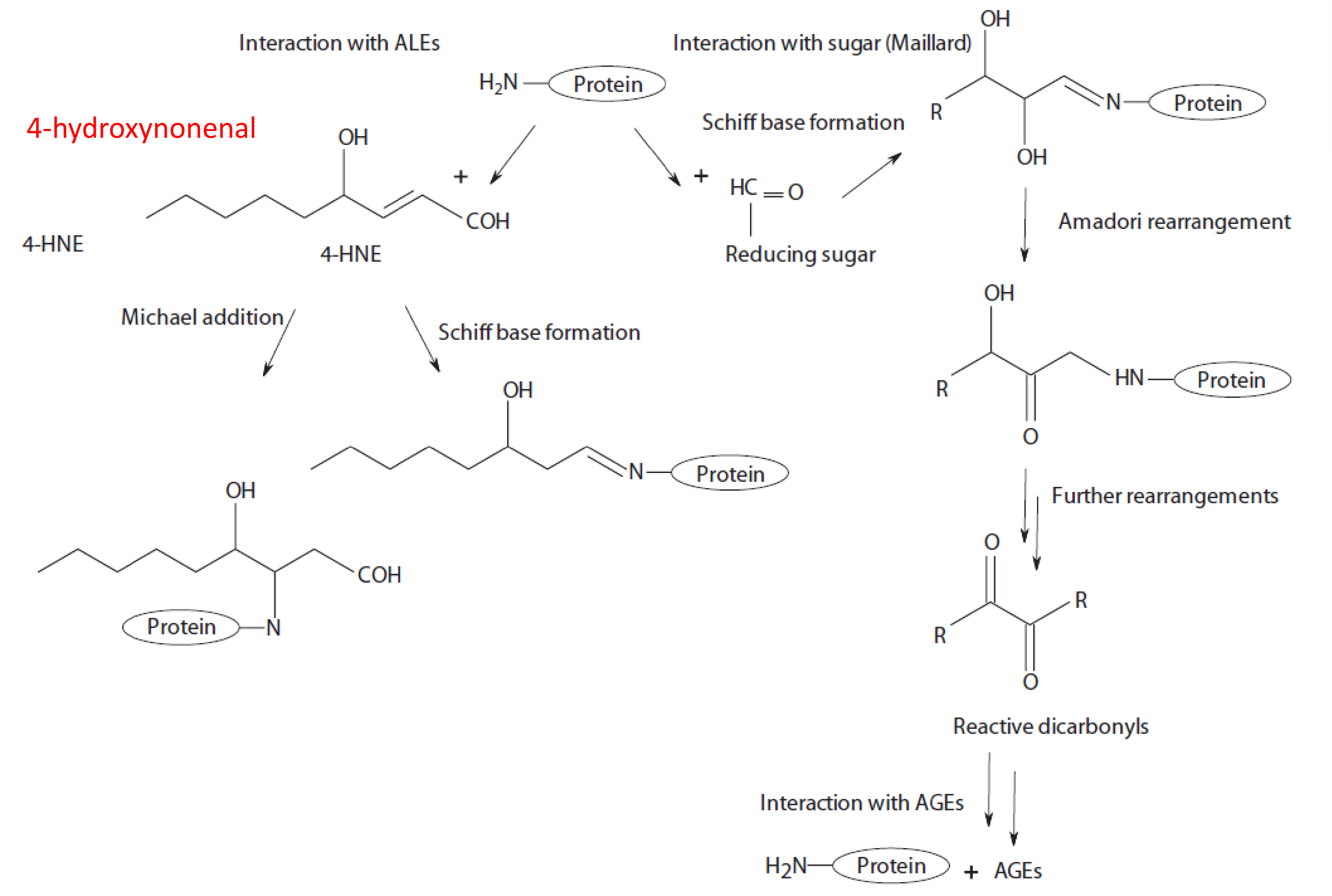
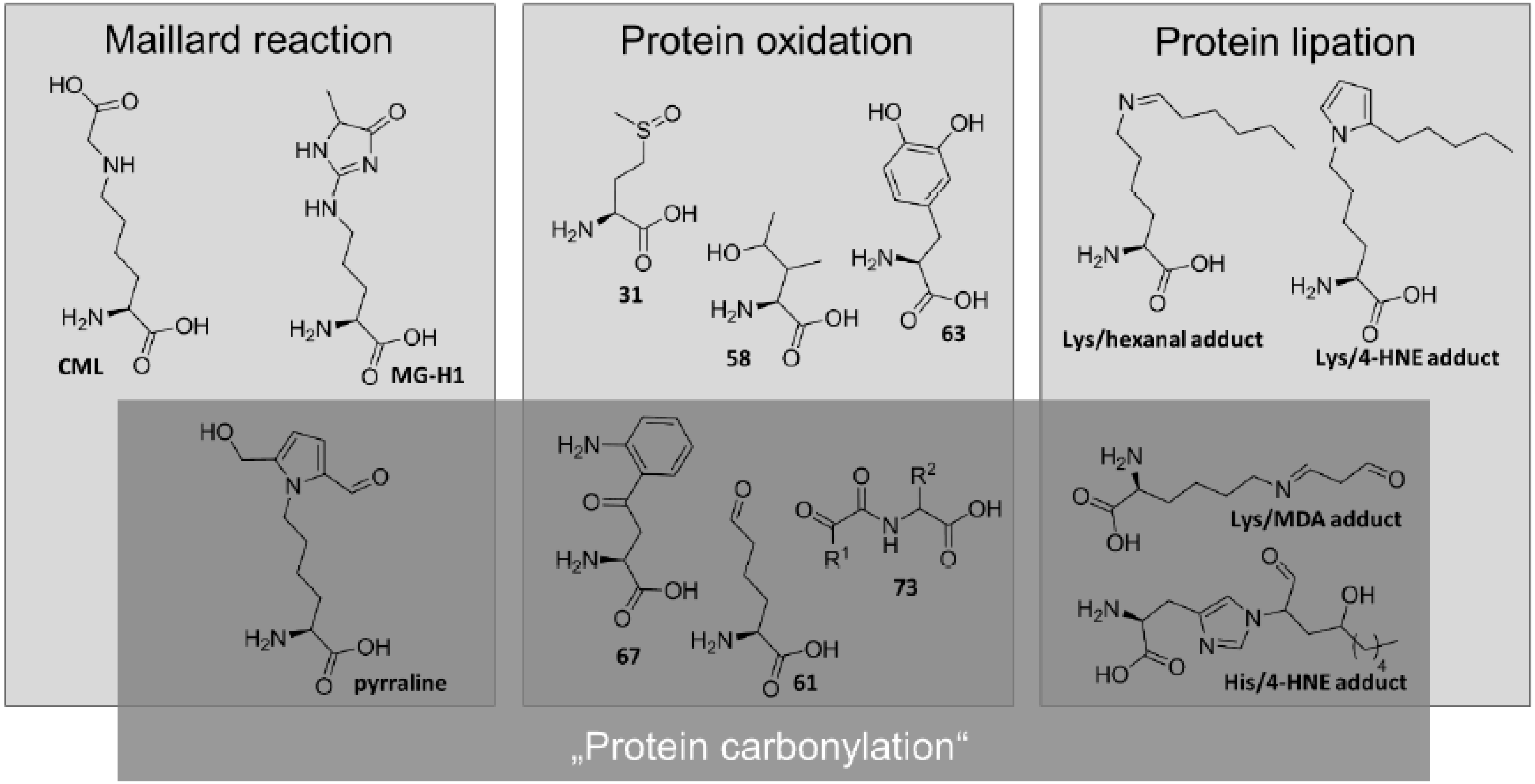
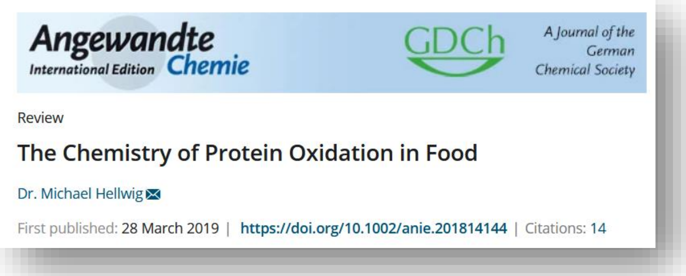


Carbonylation of protein via interaction of protein with advanced lipid oxidation end products (ALEs) and with reducing sugar leading to formation of advanced glycation end products (AGEs).

Proteins oxidation

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Review

The Chemistry of Protein Oxidation in Food

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Positioning of “protein carbonylation” between defined protein deterioration reactions in food. 4-HNE, 4-hydroxynonenal; CML, N-ε-carboxymethyllysine; MDA, malondialdehyde; MG-H1, methylglyoxal-derived hydroimidazolone 1.

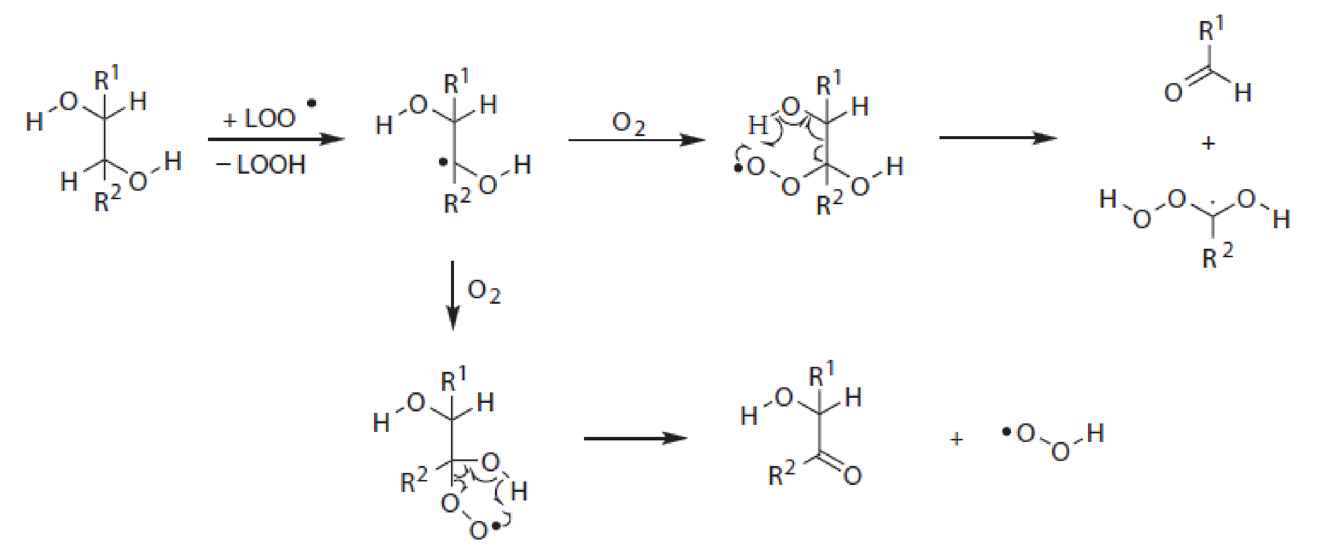
Carbohydrates oxidation

Classical nonenzymatic browning (Maillard reaction) is traditionally attributed to reactions of reducing sugars with amine-containing compounds, and it is uncertain whether these free-radical reactions are accompanied by the oxidative processes of saccharides.

Free radicals do not play a significant role in the browning reactions of amine groups of ethanolamine and PUFA and in a saccharide–lecithin system. The presence of radicals and the oxidation of saccharides have been shown in an oxidative model system copper–carbohydrate and in the iron-containing xanthine oxidase and hypoxanthine (Fe-XO/HX)–saccharide system. Saccharide molecules, such as glucose, fructose, and sucrose, are essential for generating radicals (R•) as no R• were detected in the absence of saccharides.

$$\text{Saccharide chain (R)} - \text{H} + \text{OH}^{\bullet} \rightarrow \text{saccharide derivatives} + \text{R}^{\bullet} + \text{H}_2\text{O}$$

Carbohydrates oxidation



The reaction pathway for the carbohydrate degradation produced by lipid peroxyl radicals is shown in Figure.

In the first step of the reaction, the C–H bond of the secondary alcoholic group is cleaved to generate a carbon-centered radical. This radical adds oxygen instantly to produce a peroxyl radical. This new radical can either release the hydrogen peroxyl radical to produce oxo derivatives of sugars or suffer an electronic rearrangement to fractionate the carbohydrate carbon chain and produce an aldehyde and a new carbon-centered radical. This new radical may finally add oxygen and an abstract hydrogen radical to produce an acid and oxygen peroxide after hydrolysis. Different monocarbonyl and dicarbonyl compounds are produced in these reactions, depending on the site of attack by the lipid peroxyl.

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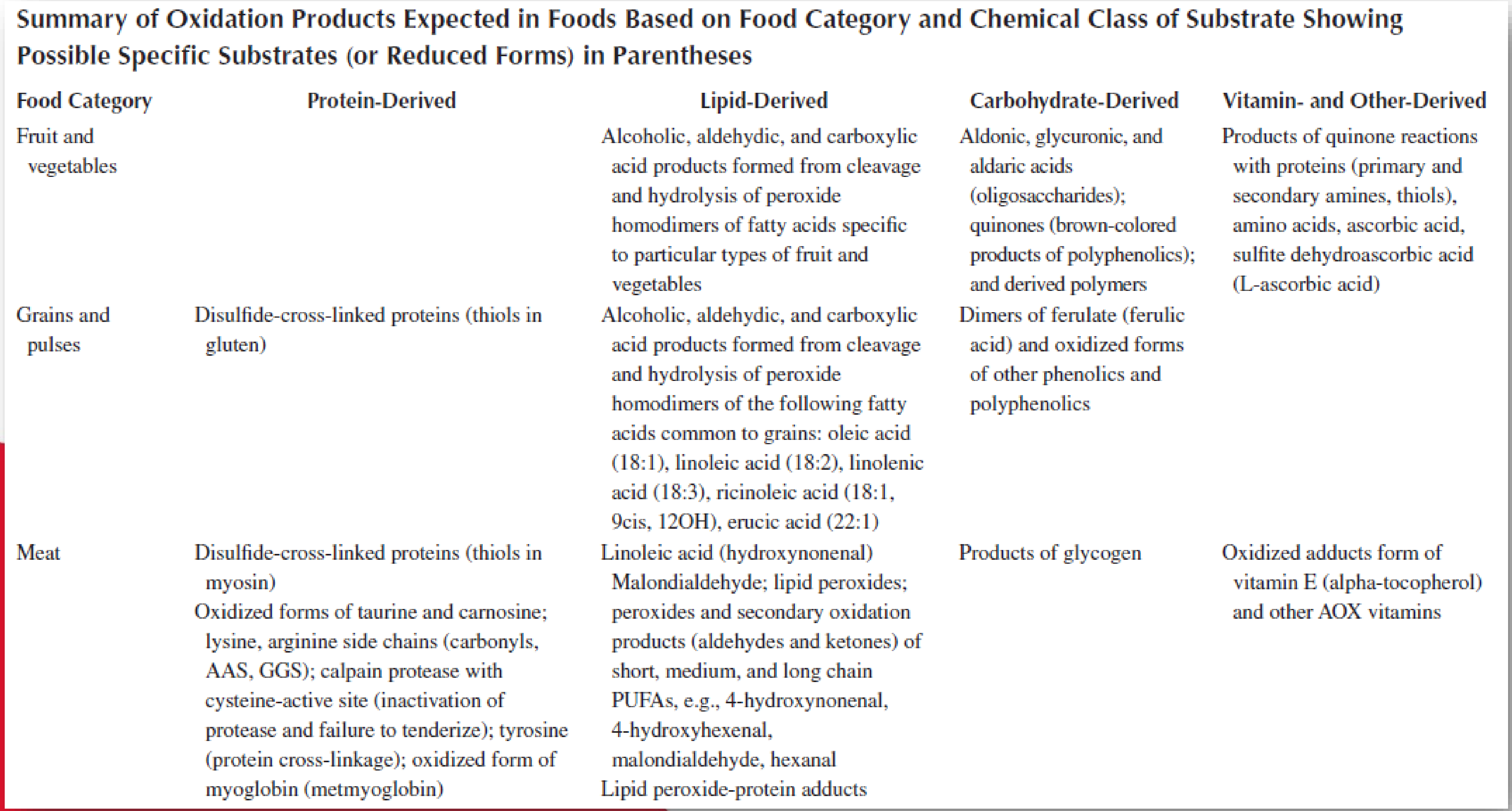
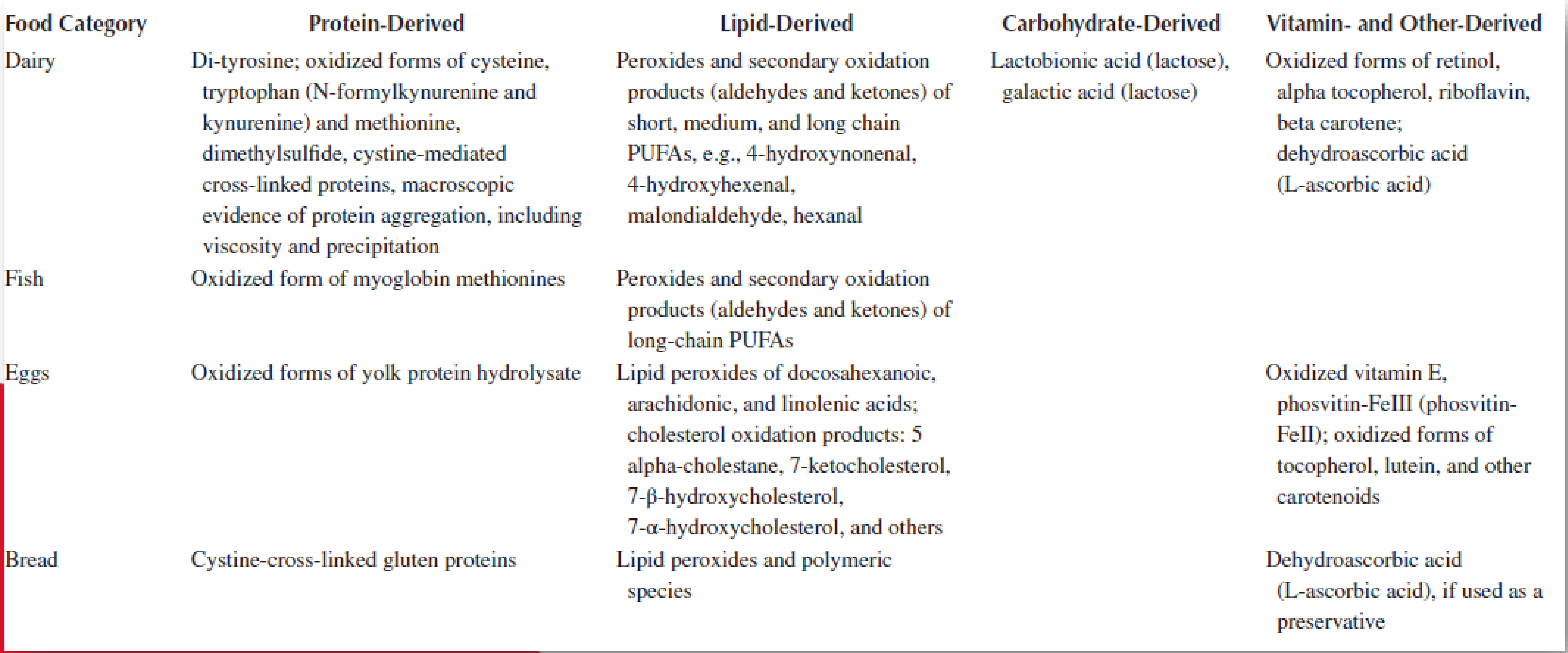


Summary of Oxidation Products Expected in Foods Based on Food Category and Chemical Class of Substrate Showing Possible Specific Substrates (or Reduced Forms) in Parentheses

Food Category	Protein-Derived	Lipid-Derived	Carbohydrate-Derived	Vitamin- and Other-Derived
Fruit and vegetables		Alcoholic, aldehydic, and carboxylic acid products formed from cleavage and hydrolysis of peroxide homodimers of fatty acids specific to particular types of fruit and vegetables	Aldonic, glycuronic, and aldaric acids (oligosaccharides); quinones (brown-colored products of polyphenolics); and derived polymers	Products of quinone reactions with proteins (primary and secondary amines, thiols), amino acids, ascorbic acid, sulfite dehydroascorbic acid (L-ascorbic acid)
Grains and pulses	Disulfide-cross-linked proteins (thiols in gluten)	Alcoholic, aldehydic, and carboxylic acid products formed from cleavage and hydrolysis of peroxide homodimers of the following fatty acids common to grains: oleic acid (18:1), linoleic acid (18:2), linolenic acid (18:3), ricinoleic acid (18:1, 9cis, 12OH), erucic acid (22:1)	Dimers of ferulate (ferulic acid) and oxidized forms of other phenolics and polyphenolics	
Meat	Disulfide-cross-linked proteins (thiols in myosin) Oxidized forms of taurine and carnosine; lysine, arginine side chains (carbonyls, AAS, GGS); calpain protease with cysteine-active site (inactivation of protease and failure to tenderize); tyrosine (protein cross-linkage); oxidized form of myoglobin (metmyoglobin)	Linoleic acid (hydroxynonenal) Malondialdehyde; lipid peroxides; peroxides and secondary oxidation products (aldehydes and ketones) of short, medium, and long chain PUFAs, e.g., 4-hydroxynonenal, 4-hydroxyhexenal, malondialdehyde, hexanal Lipid peroxide-protein adducts	Products of glycogen	Oxidized adducts form of vitamin E (alpha-tocopherol) and other AOX vitamins

Unit 1 Oxidation of Food Components



Food Category	Protein-Derived	Lipid-Derived	Carbohydrate-Derived	Vitamin- and Other-Derived
Dairy	Di-tyrosine; oxidized forms of cysteine, tryptophan (N-formylkynurenine and kynurenine) and methionine, dimethylsulfide, cystine-mediated cross-linked proteins, macroscopic evidence of protein aggregation, including viscosity and precipitation	Peroxides and secondary oxidation products (aldehydes and ketones) of short, medium, and long chain PUFAs, e.g., 4-hydroxynonenal, 4-hydroxyhexenal, malondialdehyde, hexanal	Lactobionic acid (lactose), galactic acid (lactose)	Oxidized forms of retinol, alpha tocopherol, riboflavin, beta carotene; dehydroascorbic acid (L-ascorbic acid)
Fish	Oxidized form of myoglobin methionines	Peroxides and secondary oxidation products (aldehydes and ketones) of long-chain PUFAs		
Eggs	Oxidized forms of yolk protein hydrolysate	Lipid peroxides of docosahexanoic, arachidonic, and linolenic acids; cholesterol oxidation products: 5 alpha-cholestane, 7-ketocholesterol, 7-β-hydroxycholesterol, 7-α-hydroxycholesterol, and others		Oxidized vitamin E, phosvitin-FeIII (phosvitin-FeII); oxidized forms of tocopherol, lutein, and other carotenoids
Bread	Cystine-cross-linked gluten proteins	Lipid peroxides and polymeric species		Dehydroascorbic acid (L-ascorbic acid), if used as a preservative

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Antioxidants: phenols and polyphenols

Antioxidants are substances that when present in foods at low concentrations compared to that of an oxidizable substrate markedly delay or prevent the oxidation of the substrate.

The antioxidant activity of a particular compound, a mixture of compounds, or a natural source containing such compounds, is generally related to its (their) ability to **scavenge free radicals**, **decompose free radicals**, or to **quench singlet oxygen** or possibly **act as metal chelators** or a **synergists with other components present**.

Next sections will present natural food components with antioxidant activity by illustrating molecular mechanisms and synergic interactions with other components.
A brief insight on syntetic antioxidants is provided although it will be the object of another integrated module (Prof. Erica Liberto).

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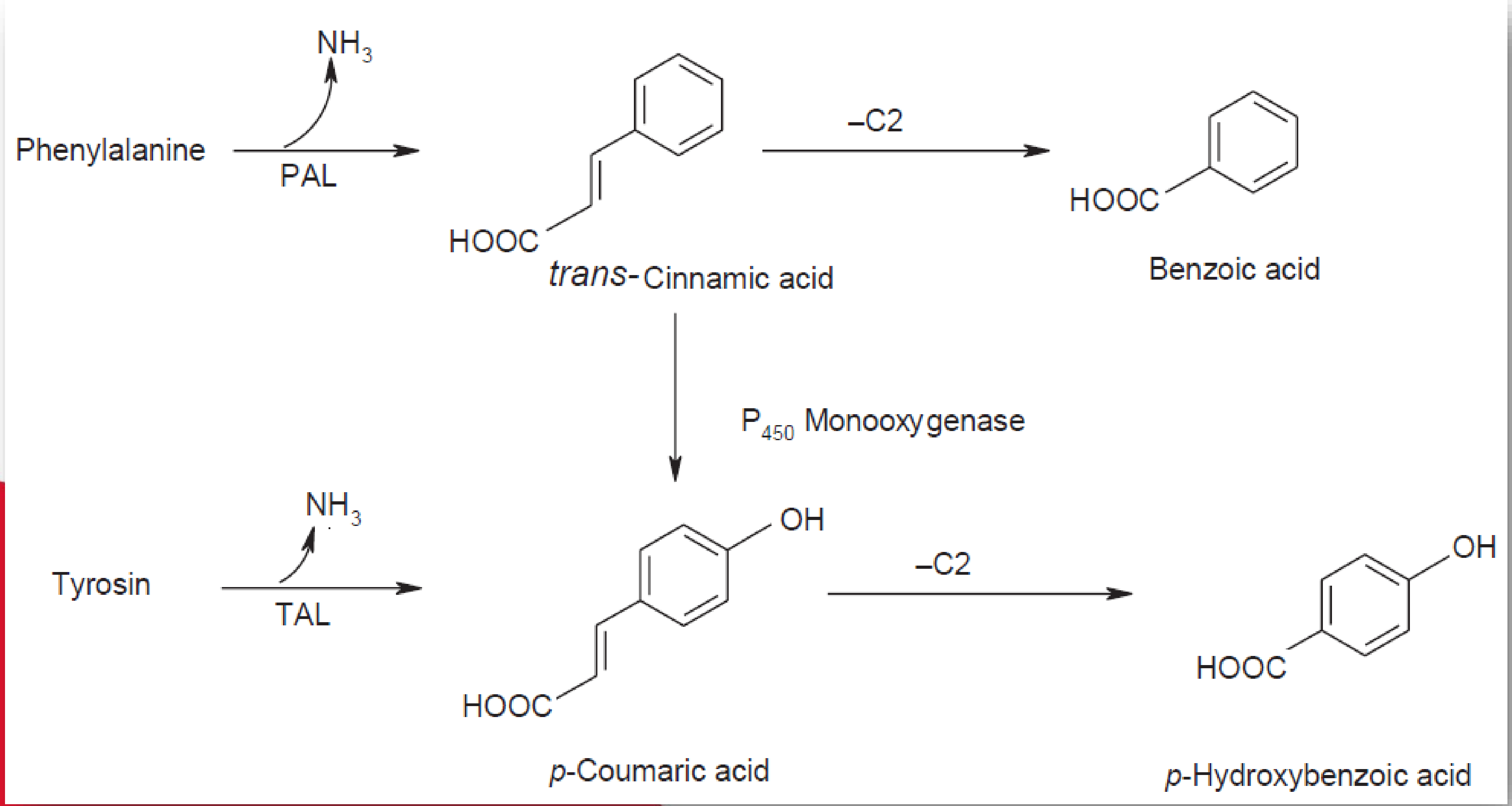
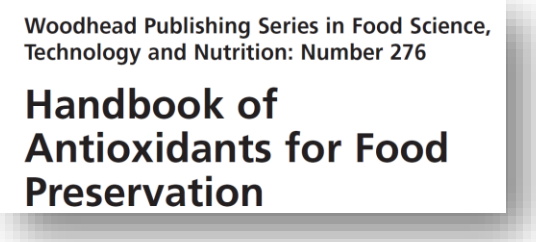
Antioxidants: phenols and polyphenols



Simplified biosynthetic pathway of phenolic acids from phenylalanine and tyrosine

Phenolic and polyphenolic compounds are specialized metabolites occurring in plants and are produced via shikimic acid pathway. The precursors to phenolic compounds are phenylalanine and, to a lesser extent, tyrosine.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Handbook of Antioxidants for Food Preservation

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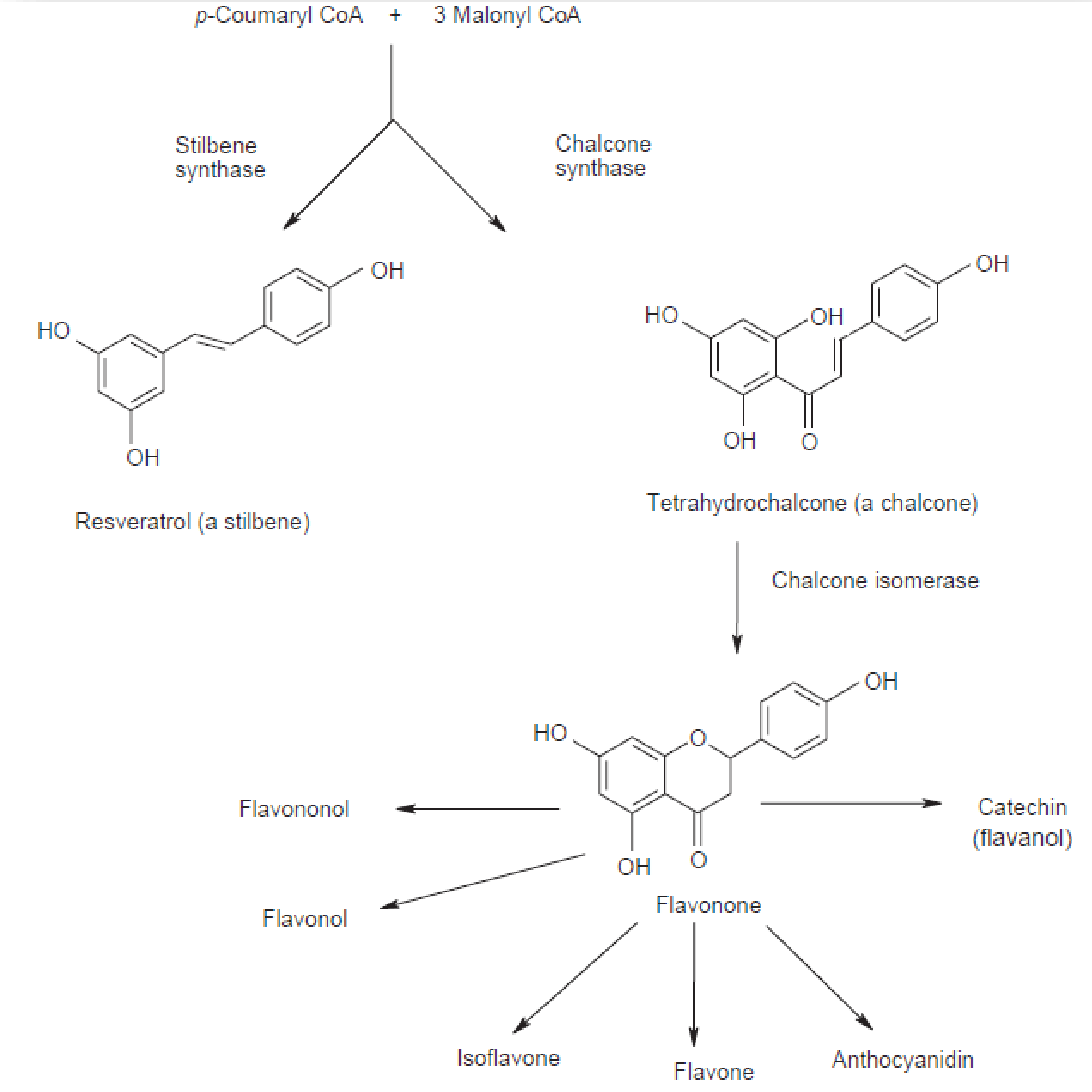
Antioxidants: phenols and polyphenols



Simplified biosynthetic pathway of flavonoids from phenyl propanoids.

Phenylpropanoids may react with three molecules of malonyl coenzyme A to produce chalcones that can subsequently cyclize to afford different subclasses of flavonoids. Condensation of phenolics may lead to the formation of tannins, both hydrolyzable (lignanes) and condensed nonhydrolyzable (proanthocyanidins, flavan-3-ols derivatives - see tea extracts) tannins.

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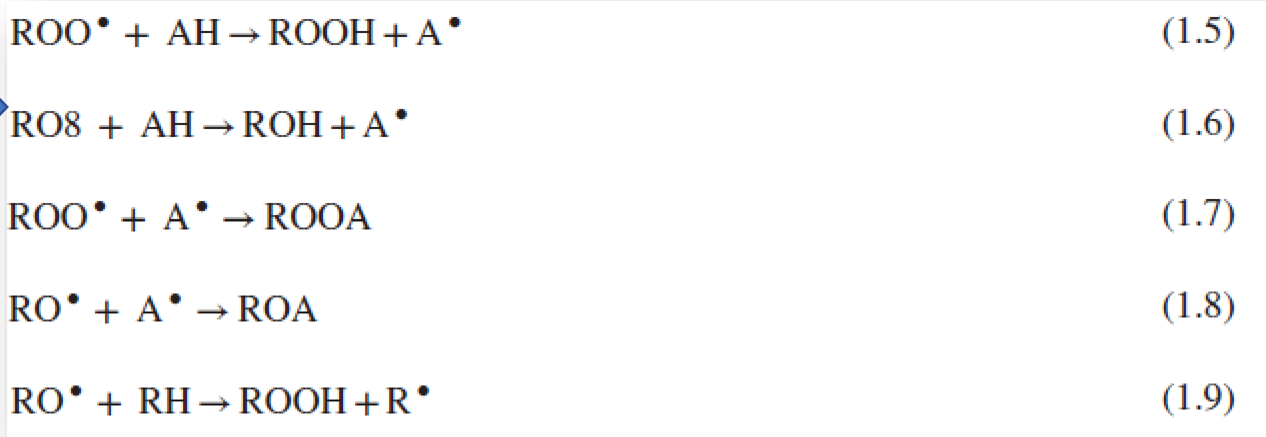
The initial detailed kinetic study of antioxidant activity postulated reactions (1.5) and (1.6) as their mode of action as free radical terminators. Phenolic antioxidants (AH) interfere with lipid oxidation by rapid donation of a hydrogen atom to lipid radicals [reactions (1.5) and (1.6)]. The latter reactions compete with chain propagation reactions.

The above reactions are exothermic in nature. The activation energy increases with increasing A–H and R–H bond dissociation energy. Therefore, the efficiency of the antioxidants (AH) increases with decreasing A–H bond strength. The resulting phenoxyl radical itself must not initiate a new free radical reaction or be subject to rapid oxidation by a chain reaction.

In this regard, phenolic antioxidants are excellent hydrogen or electron donors and, in addition, their radical intermediates are relatively stable due to resonance delocalization and lack of suitable sites for attack by molecular oxygen.

Antioxidants: phenols and polyphenols



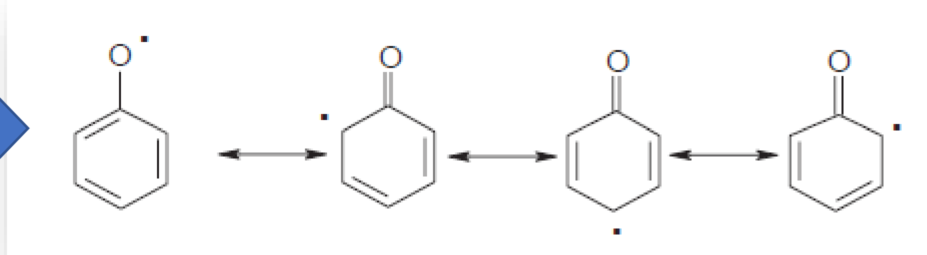
$$ROO^{\bullet} + AH \rightarrow ROOH + A^{\bullet} \quad (1.5)$$

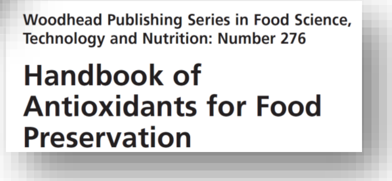
$$RO8 + AH \rightarrow ROH + A^{\bullet} \quad (1.6)$$

$$ROO^{\bullet} + A^{\bullet} \rightarrow ROOA \quad (1.7)$$

$$RO^{\bullet} + A^{\bullet} \rightarrow ROA \quad (1.8)$$

$$RO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (1.9)$$





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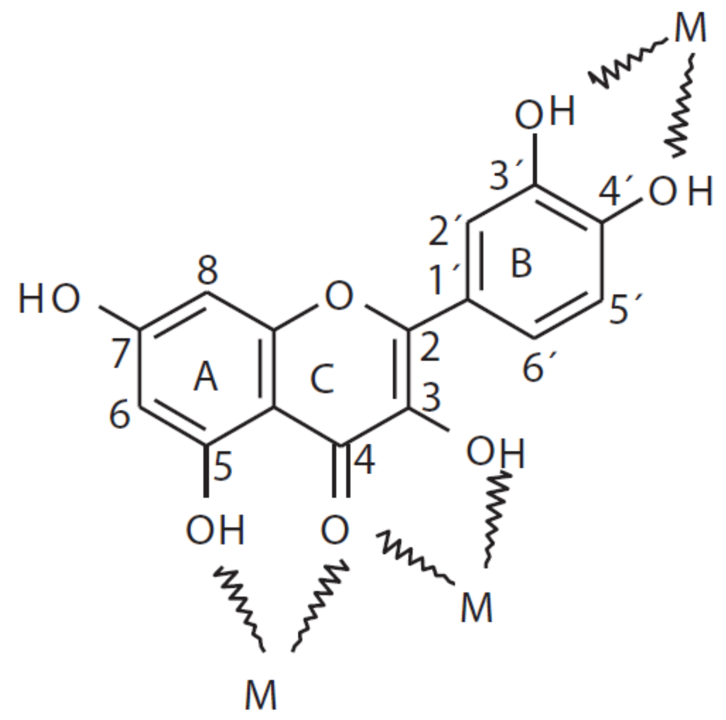
Antioxidants: phenols and polyphenols

Flavonoids

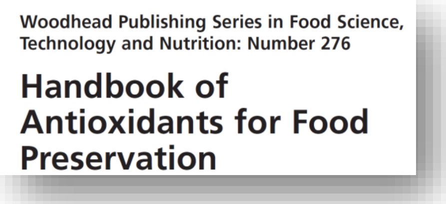


Structure of flavonoid quercetin (M = coordinated metal ion)

The molecular structure of flavonoids consists of two aromatic carbon rings and benzopyran (A and C rings) and benzene (B ring).

Flavonoids can be classified into several subgroups on the basis of degree of the oxidation of the C ring, the hydroxylation pattern of the ring structure, and the substitution of the three-position.

The protective effects of flavonoids in biological systems are substantiated by their antioxidant capacity to terminate free radicals, chelate redox-active metal, activate various antioxi… enzymes, and inhibit oxidases.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Unit 2 Anti-oxidants

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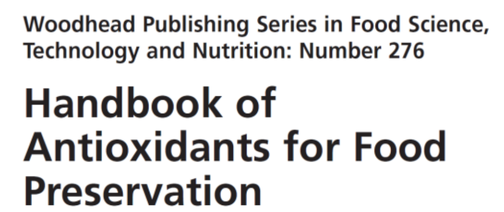
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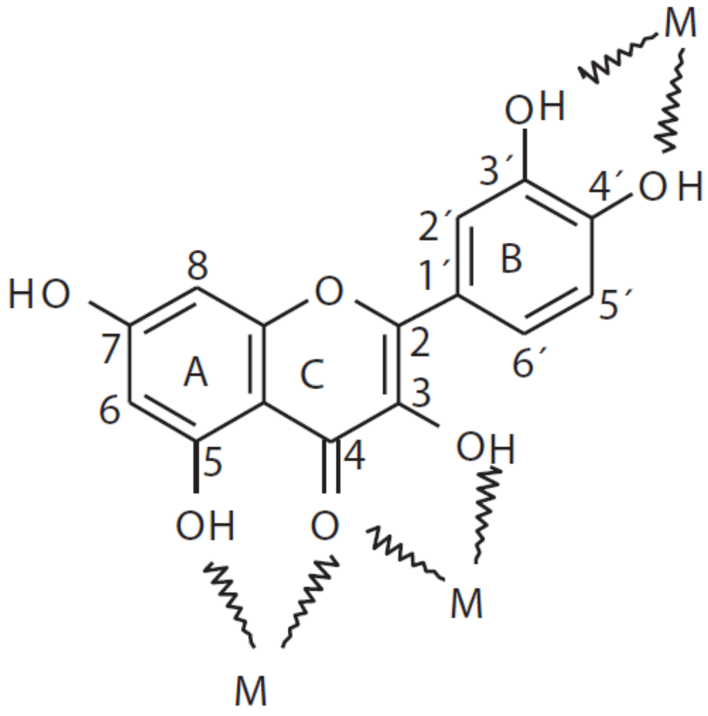
Flavonoids



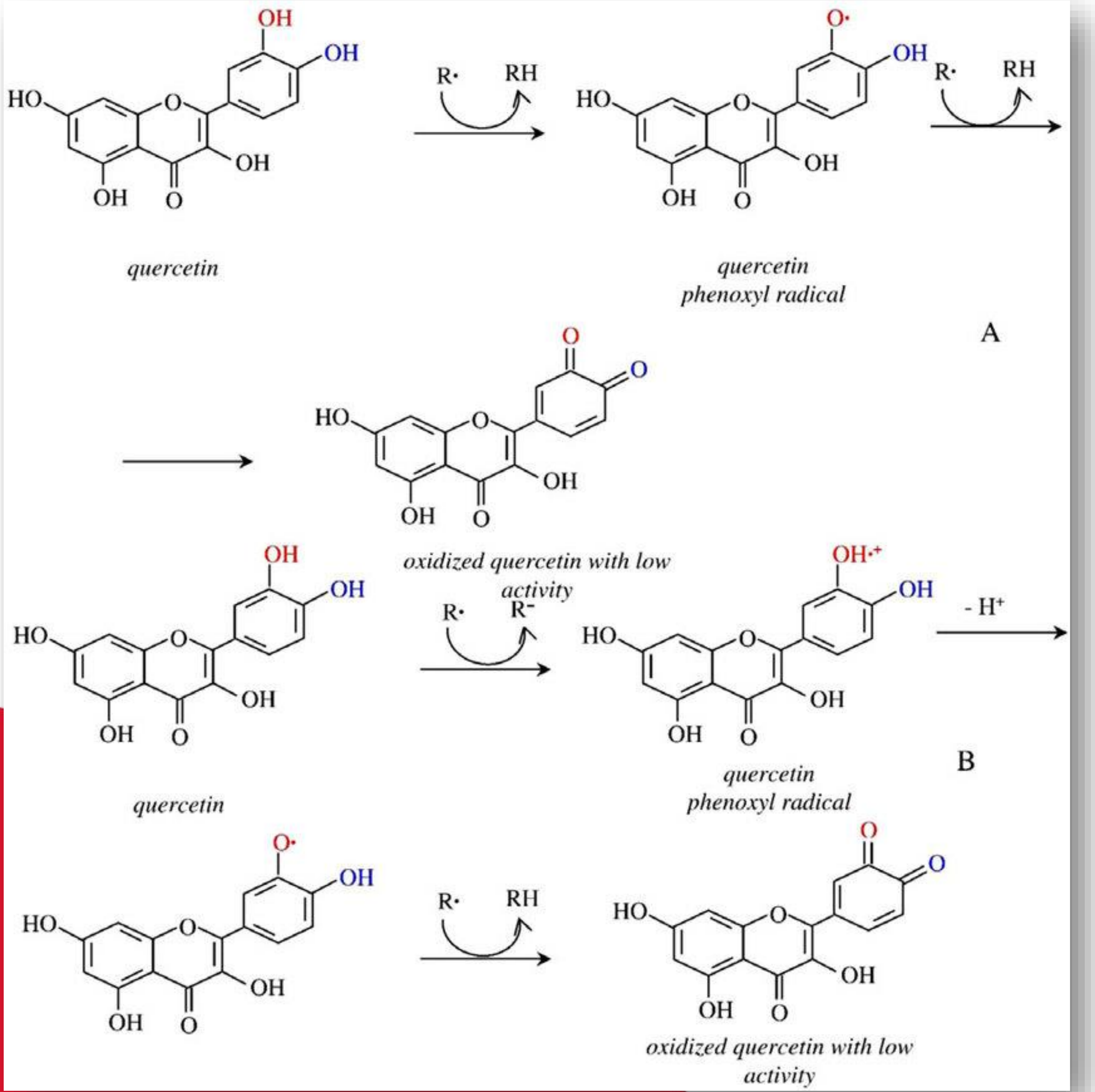
Structure of flavonoid quercetin (M = coordinated metal ion)

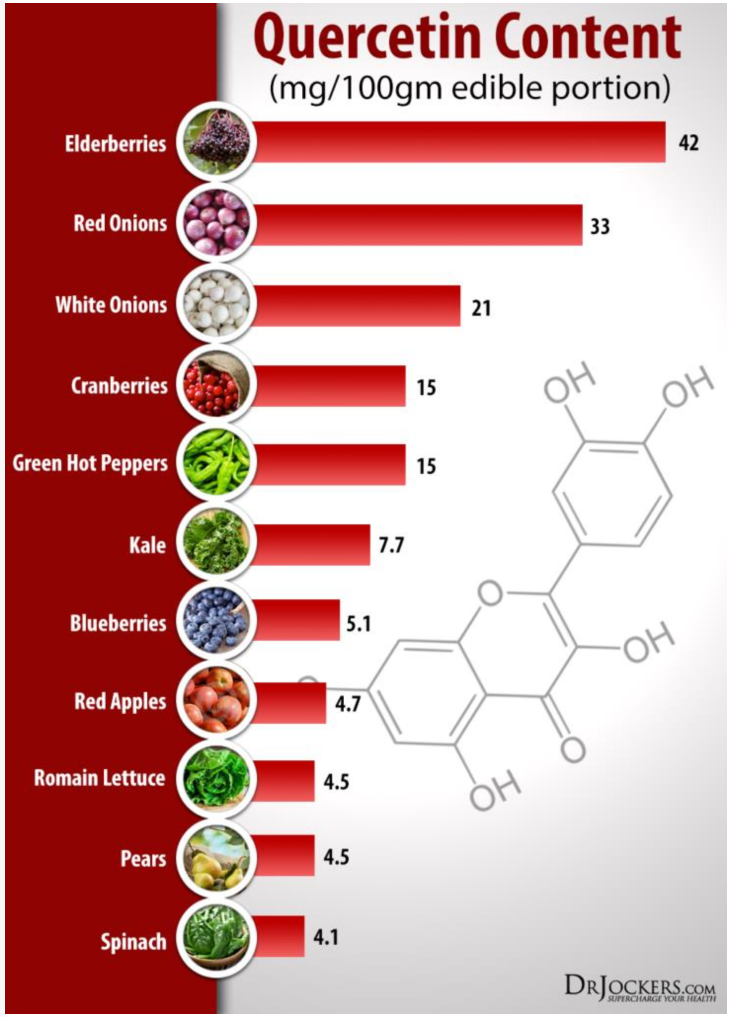
Antioxidants: phenols and polyphenols

The configuration and total number of hydroxyl groups influence the total antioxidant activity of flavonoids.

- ✓ Free radical-scavenging activity is primarily attributed to the reactivity of hydroxyl groups participating in the reactions of hydrogen abstraction.
- ✓ The arrangement of hydroxyl groups located on the B ring most significantly affects the ROS scavenging properties.
- ✓ Hydroxyl groups on the B ring donate hydrogen atoms (electrons) to various free radicals, such as hydroxyl radicals, peroxyl radicals, and peroxynitrite, thus stabilizing them and leaving behind a relatively stable flavonoid radical.
- ✓ A 3′4′-catechol structure in the B ring promotes inhibition of peroxidation of lipids.

Antioxidants: phenols and polyphenols





Unit 2 Anti-oxidants

Antioxidants: tocopherols

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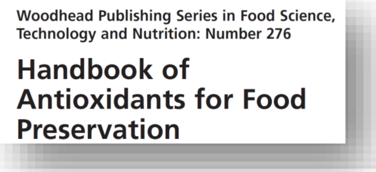

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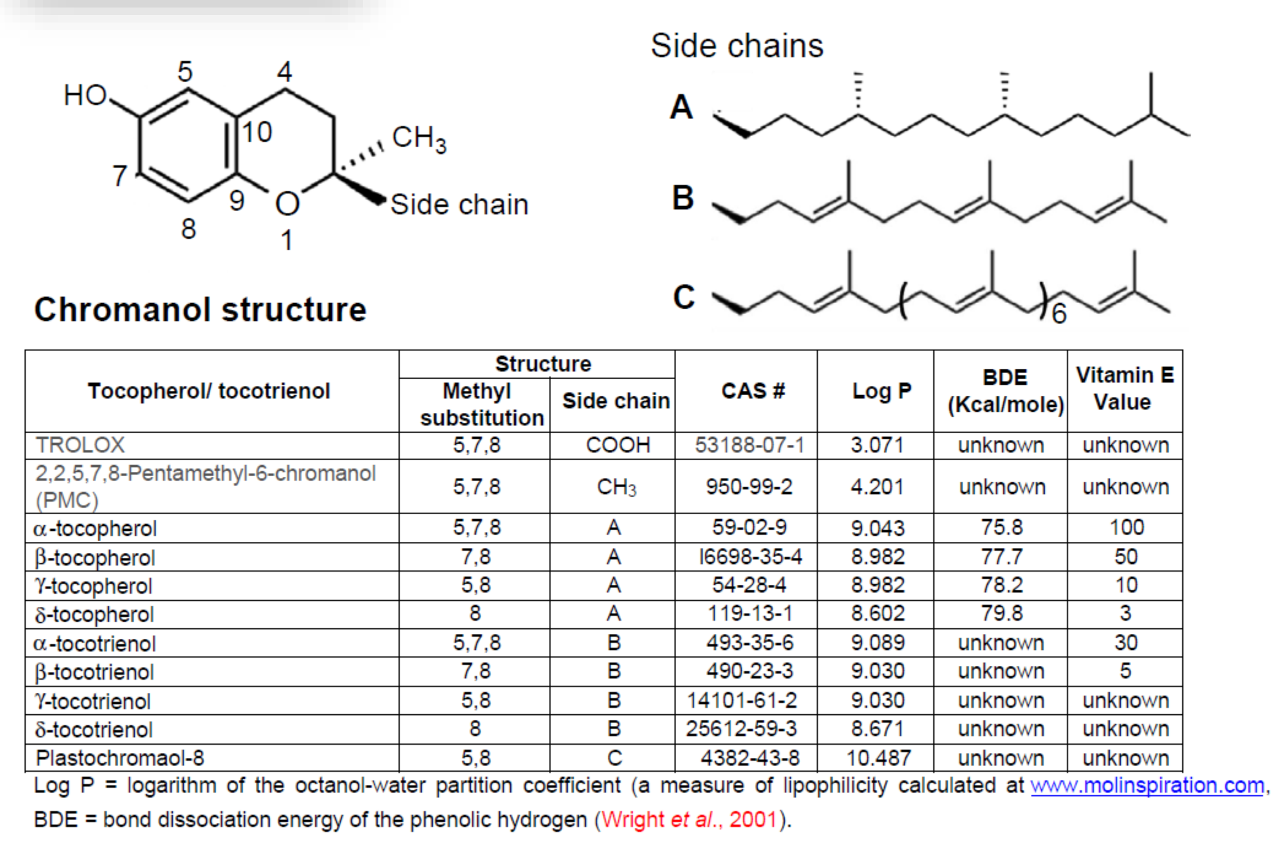

Chromanol structure

Tocopherol/ tocotrienol	Structure		CAS #	Log P	BDE (Kcal/mole)	Vitamin E Value
	Methyl substitution	Side chain				
TROLOX	5,7,8	COOH	53188-07-1	3.071	unknown	unknown
2,2,5,7,8-Pentamethyl-6-chromanol (PMC)	5,7,8	CH_3	950-99-2	4.201	unknown	unknown
α-tocopherol	5,7,8	A	59-02-9	9.043	75.8	100
β-tocopherol	7,8	A	l6698-35-4	8.982	77.7	50
ϒ-tocopherol	5,8	A	54-28-4	8.982	78.2	10
δ-tocopherol	8	A	119-13-1	8.602	79.8	3
α-tocotrienol	5,7,8	B	493-35-6	9.089	unknown	30
β-tocotrienol	7,8	B	490-23-3	9.030	unknown	5
ϒ-tocotrienol	5,8	B	14101-61-2	9.030	unknown	unknown
δ-tocotrienol	8	B	25612-59-3	8.671	unknown	unknown
Plastochromaol-8	5,8	C	4382-43-8	10.487	unknown	unknown

Log P = logarithm of the octanol-water partition coefficient (a measure of lipophilicity calculated at www.molinspiration.com,

BDE = bond dissociation energy of the phenolic hydrogen (Wright *et al*., 2001).

Tocopherols and tocotrienols are derivatives of 6-chromanol, differing in the number and position of methyl substituents in the phenolic ring and the chains at C-2.

The radical-scavenging properties of tocopherols and related compounds is determined by the ease of donation of the phenolic hydrogen, or its bond dissociation energy (BDE), which is enhanced by methyl substituents in the two ortho positions, in addition to
the alkoxy substitution in the para position.

α-tocopherol (with two ortho methyl substituents) is a stronger hydrogen donor than either β- or γ-tocopherols (with only one ortho methyl substituent), which are more potent than δ-tocopherol with no ortho methyl substituent. An antioxidant potency in the order of *α* > *β* > *γ* > *δ* would be expected, although it is much more affected inter alias by the tocopherols concentration.

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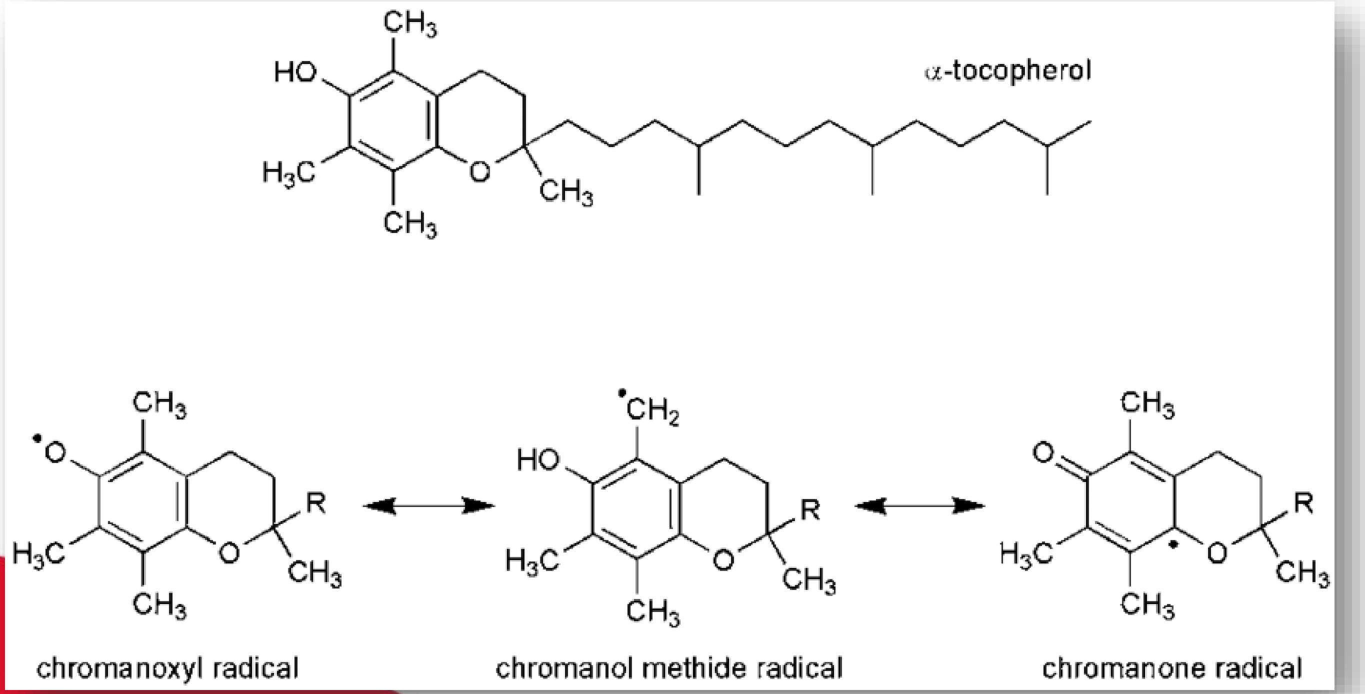
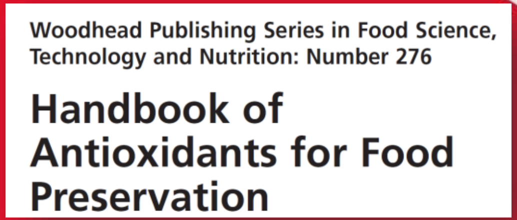
Antioxidants: tocopherols



When present, phenolic antioxidants, typically tocopherols, act as peroxyl radical scavengers and inhibit fatty acid oxidation chain reactions.

Nagaoka et al. (1992) proposed that initially, the tocopherol molecule and the peroxyl radical approach each other, and their electron clouds begin to overlap, reaching a transition state having the property of the charge transfer species (LOOδ−----TOHδ+).

Proton tunneling from the chromanol molecule to the lipid peroxyl radical will take place, via this complex, to form lipid hydroperoxides (LOOH) and a chromanoxyl radical, which is stabilized by electron delocalization.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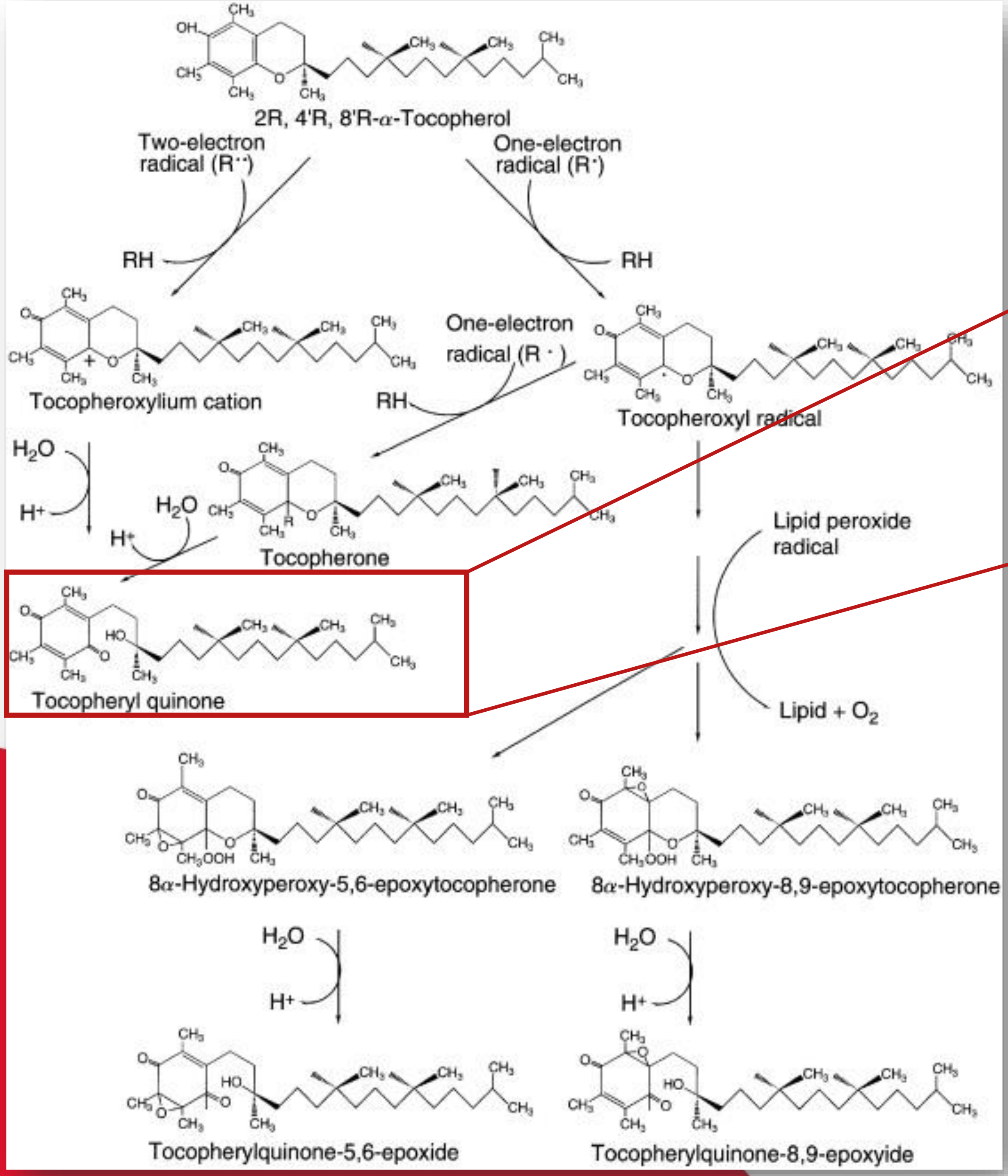
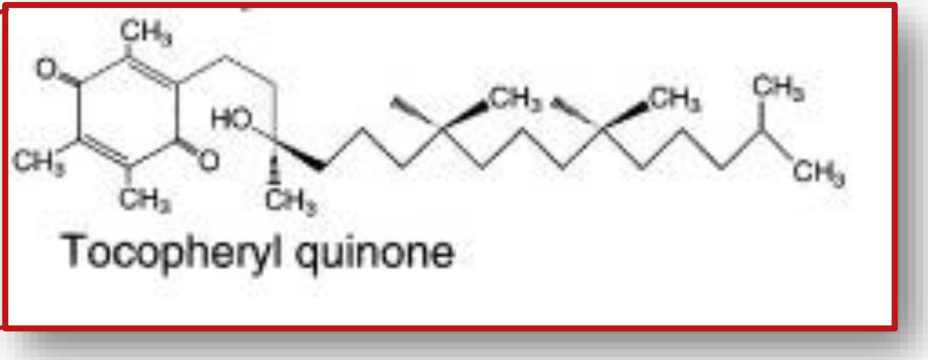
Antioxidants: tocopherols





Antioxidants: tocopherols

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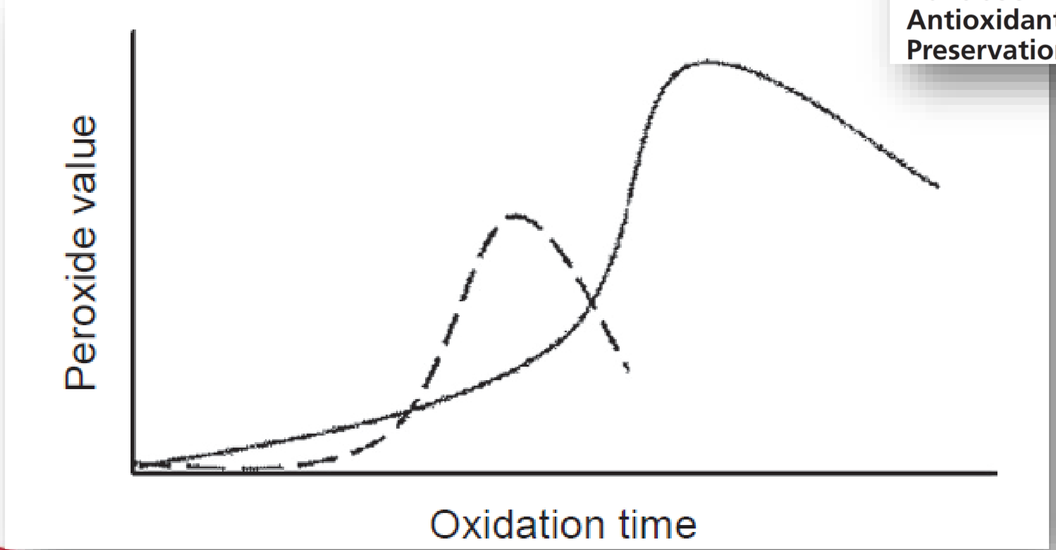
Handbook of Antioxidants for Food Preservation



Schematic representation of the antioxidant protection of α-tocopherol at low concentration (typically 100–200 ppm, dashed line) and at high concentration (>500 ppm, solid line). Although high antioxidant concentration prolongs the induction period for the oxidation, the rate of oxidation during the induction period is relatively higher, which is described as "loss of antioxidant activity."

The tocopherooxyl radical (TO•) may undergo radical–radical coupling with peroxyl radicals to form adducts.

$$TO^{\bullet} + LOO^{\bullet} \rightarrow \text{non-radical TO-OOL products}$$

Thus, each tocopherol molecule can neutralize two peroxyl radicals and the theoretical stoichiometric factor (n) for the tocopherols is considered to be equal to 2.0

The TO• is quite stable, and it reacts quickly with LOO• and slowly with LH.

Besides the interception of hydroperoxide formation, it was shown that tocopherols stabilize the formed hydroperoxides and prevent their decomposition to secondary oxidation products.

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Antioxidants: tocopherols

Paradoxes in the antioxidant efficacy of tocopherols

A number of repeating inconsistencies or seemingly illogical experimental findings relevant to the antioxidant potency of tocopherols were observed:

1) **loss of efficacy at high antioxidant concentrations**, using α-tocopherol as an example;
2) **change from the initial reaction rate (induction period)** to the exponential propagation phase;
3) unexplained synergistic interactions with phospholipids and amino acids.

1-2

It was shown that while α-tocopherol and other tocopherols act as preventive inhibitors against the oxidative deterioration of polyunsaturated fatty acid, this action becomes less effective as the antioxidant concentration increases beyond a certain threshold.

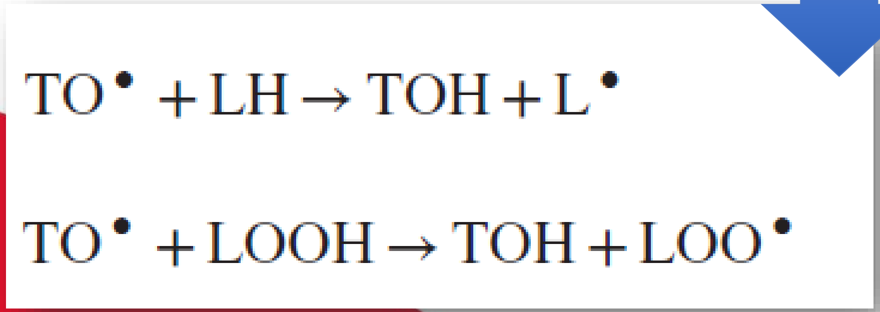
To note: lipids with added tocopherols are still far more stabilized than lipids devoid of tocopherols (purified triacylglycerols), and that is why the term *loss of antioxidant efficacy* is more appropriate than *prooxidant effect*, commonly used to describe this phenomenon.

Antioxidants: tocopherols

1-2

At very low concentrations, the induction period increases with the increasing initial tocopherol concentration. Three types of reaction make the greatest and most significant contribution in the manifestation of prooxidant properties of α-tocopherol involving the tocopheroxyl radical, the tocopherol molecule, and tocopherol oxidation products. The three types are as follows:

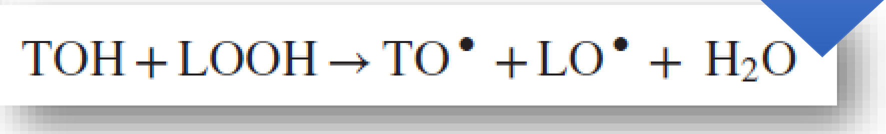
a) Chain transfer reaction of the abstraction of hydrogen atom from methyl linoleate molecule and from the methyl linoleate hydroperoxides by tocopheroxyl radical. The reaction was described as the α-tocopherol-mediated peroxidation (TMP) responsible for prooxidation of low-density lipoproteins.



$$TO^{\bullet} + LH \rightarrow TOH + L^{\bullet}$$

$$TO^{\bullet} + LOOH \rightarrow TOH + LOO^{\bullet}$$

b) The autoinitiation reaction in the reaction of α-tocopherol with hydroperoxides



$$TOH + LOOH \rightarrow TO^{\bullet} + LO^{\bullet} + H_2O$$

Antioxidants: tocopherols

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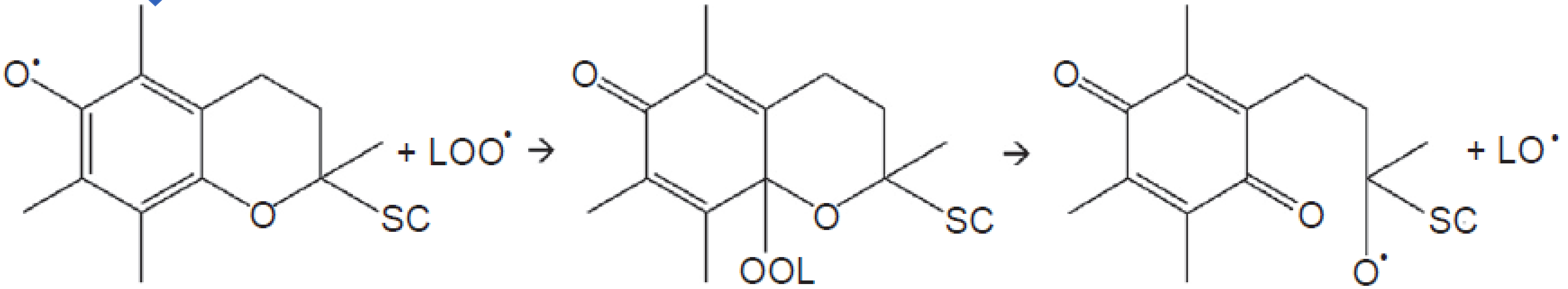
1-2

c) The reactions of homolytic decomposition of quinolide peroxides, which are the combination products of tocopheroxyl radicals and lipid peroxyl radicals (TO-OOL) formed in reaction:

$$TO^{\bullet} + LOO^{\bullet} \rightarrow \text{non-radical TO-OOL products}$$



Tocopheroxyl radical (LO•)

It was also known that the antioxidant activity of tocopherols decreases with increasing temperature, which can be explained by the acceleration of the initiation reactions, especially those caused by hydroperoxide decomposition.

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Paradoxes in the antioxidant efficacy of tocopherols

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2) change from the initial reaction rate (induction period) to the exponential propagation phase;
3) unexplained synergistic interactions with phospholipids and amino acids.

The polar paradox

3

Porter in 1993 published his treatise on the polar paradox, by distinguishing between the effectiveness and behavior of antioxidants in bulk lipids and in emulsions and describing the anomalous effect of antioxidants when they are in different physical systems.
Polar (hydrophilic) antioxidants (Trolox C, ascorbic acid, propyl gallate, and TBHQ) are more effective in bulk lipids with a low surface/volume ratio, whereas nonpolar (lipophilic) antioxidants (α-tocopherol, ascorbyl palmitate, BHA, and BHT) are more effective in oil-in-water emulsions having a high surface/volume ratio.

Antioxidants: tocopherols

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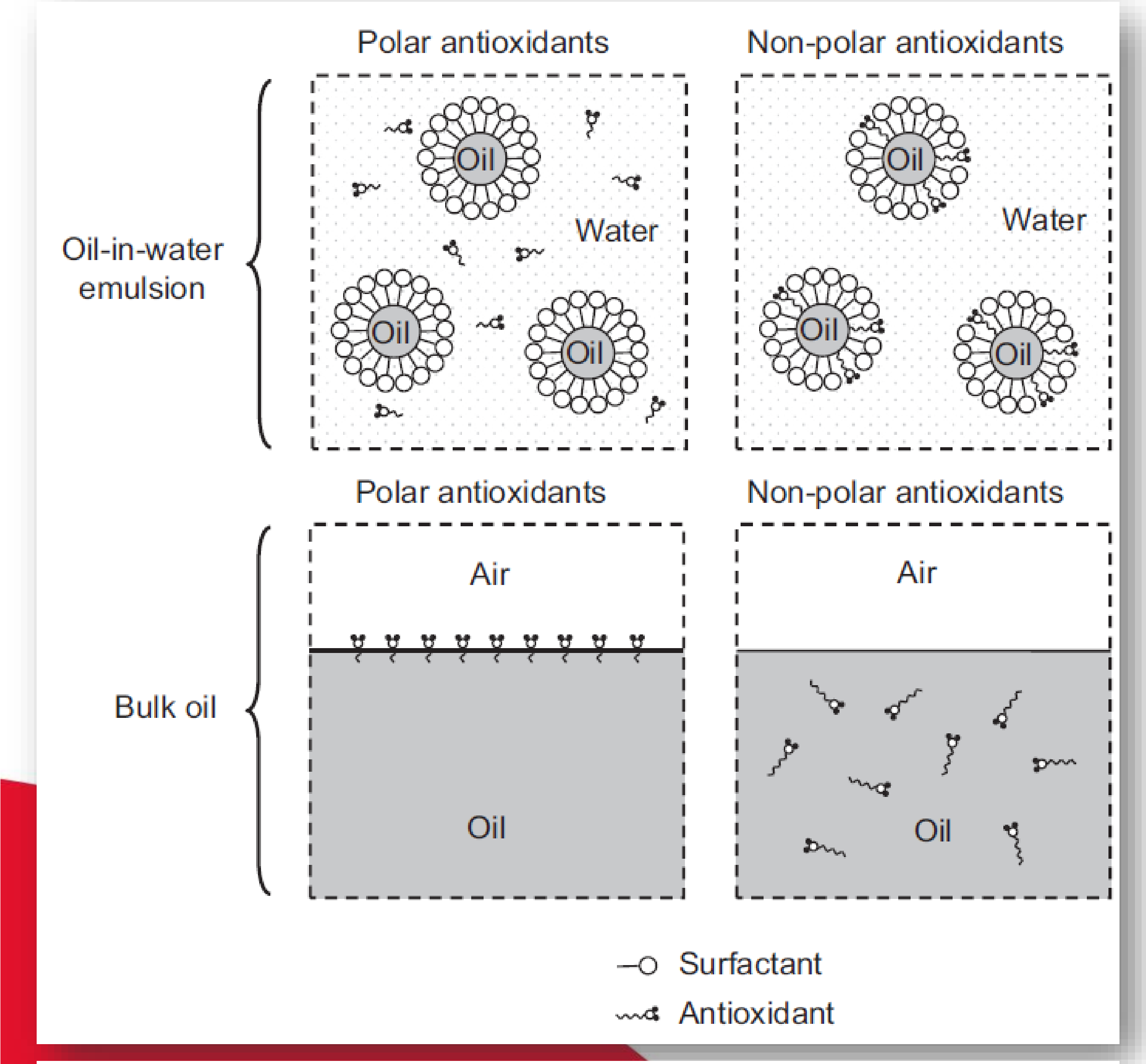
The polar paradox

Later Frankel, Huang, Kanner, and German in 1994, proposed the “interfacial phenomenon” as a framework to explain the reciprocal effect of antioxidants in bulk oil versus multiphase/colloidal systems.

According to this proposal, the partitioning of the antioxidants at the interface(s) between the aqueous and nonaqueous phases, which is dependent on the solvent properties and the surfactants, exert an important effect on the antioxidant lipid interactions and the antioxidant protection. These two works opened up the way to the understanding that lipid oxidation in emulsions is affected by several properties of emulsion droplets and interface properties including droplet size, and interfacial area, charge, thickness, and permeability.

Water and other polar compounds and amphiphiles present in lipids form *association colloids* (e.g., reversed micelles) providing reaction site(s) for oxidation to take place. The effects of the surface active agents are influenced by their hydrophilic–lipophilic balance (HLB) and quantities.



Interfacial phenomena as a possible mechanism of action of the polar paradox in oil-in-water emulsion and in bulk oil.

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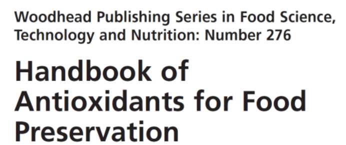
The polar paradox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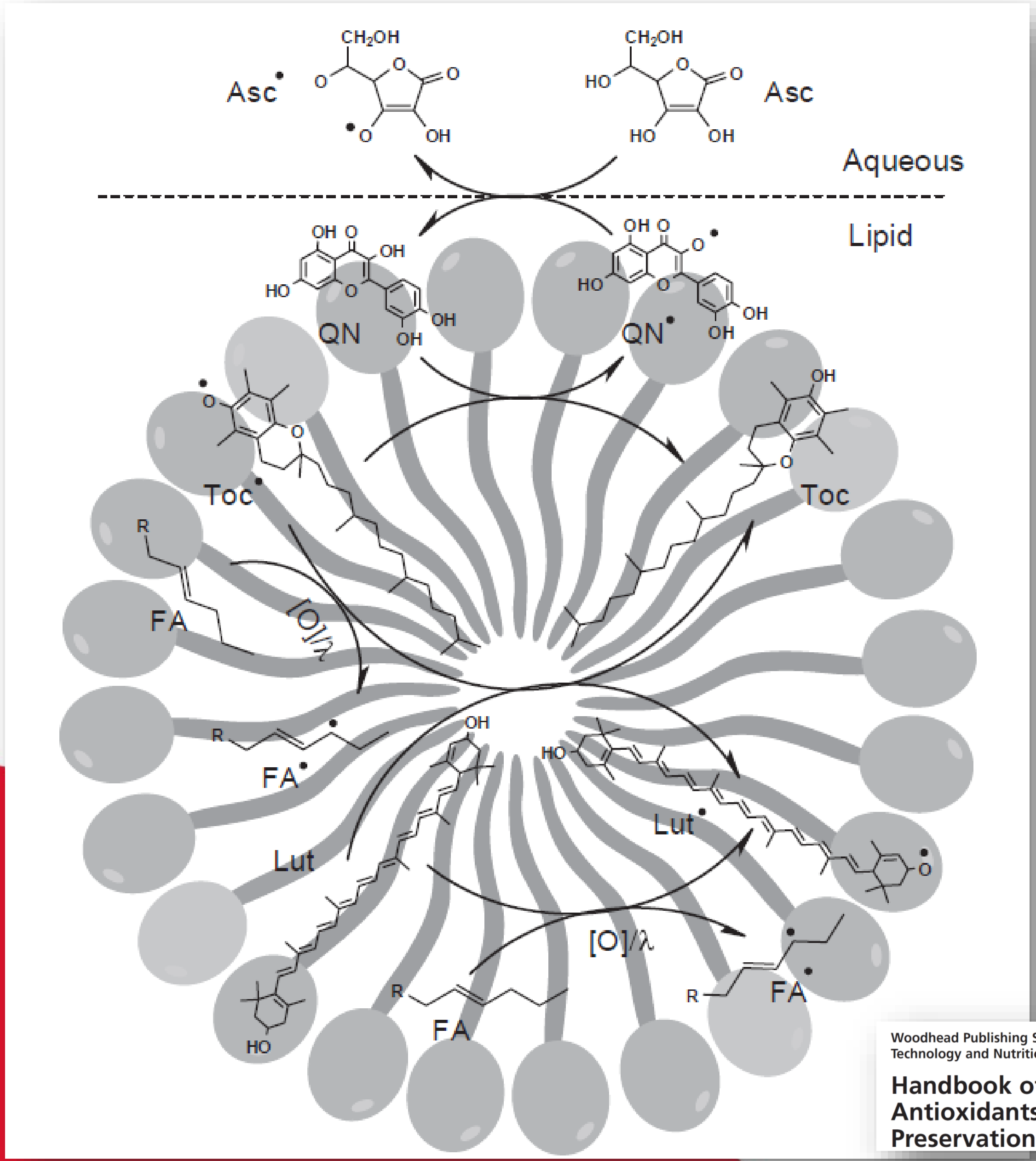
Simplified model

In oil-in-water emulsion, nonpolar antioxidants would concentrate in the oil-water interface (which is assumed to be the site where oxidation occurs) and inhibit oxidation more efficiently than polar antioxidants that partition into the water phase, where they would be less effective.

In contrast, in bulk oils, the increased effectiveness of hydrophilic antioxidants might be due to their ability to migrate and concentrate at the air-oil interface where oxidation is prevalent, whereas lipophilic antioxidants were solubilized in the oily phase, where they would be less effective.

Antioxidants: tocopherols

Synergisms with other antioxidants



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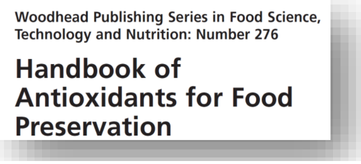
A schematic depiction of the synergistic antioxidant network across the aqueous–lipid interface.
Asc, ascorbic acid; QN, quercetin; Toc, alpha-tocopherol; Lut, lutein; FA, fatty acids; [O]/λ, oxygen/light.

Antioxidants: tocopherols

Synergisms with other antioxidants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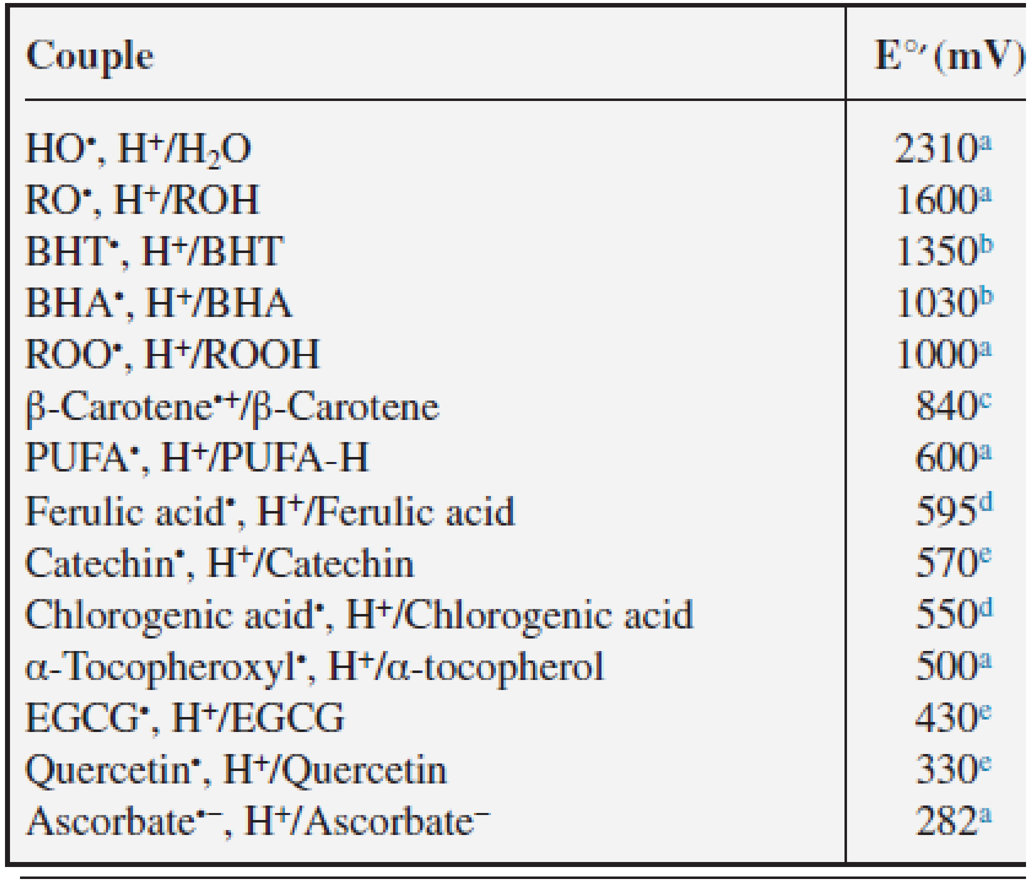

Couple	E°′ (mV)
$HO^{\bullet}, H^+/H_2O$	2310[a]
$RO^{\bullet}, H^+/ROH$	1600[a]
$BHT^{\bullet}, H^+/BHT$	1350[b]
$BHA^{\bullet}, H^+/BHA$	1030[b]
$ROO^{\bullet}, H^+/ROOH$	1000[a]
β-Carotene$^{\bullet+}$/β-Carotene	840[c]
$PUFA^{\bullet}, H^+/PUFA\text{-}H$	600[a]
Ferulic acid$^{\bullet}$, H^+/Ferulic acid	595[d]
Catechin$^{\bullet}$, H^+/Catechin	570[e]
Chlorogenic acid$^{\bullet}$, H^+/Chlorogenic acid	550[d]
α-Tocopheroxyl$^{\bullet}$, H^+/α-tocopherol	500[a]
$EGCG^{\bullet}, H^+/EGCG$	430[e]
Quercetin$^{\bullet}$, H^+/Quercetin	330[e]
Ascorbate$^{\bullet-}$, H^+/Ascorbate$^-$	282[a]

The synergistic effect is generally considered to occur because of the difference in the reduction potential of different antioxidants present in the same system.

The oxidation-reduction potential, or redox potential (E°′), is a key thermodynamic property of antioxidants. Theoretically speaking, any net one-electron transfer potential greater than zero ($\Delta E°' > 0$) for lipids such as polyunsaturated fatty acids (PUFA) is a potential oxidant, and any negative net potential ($\Delta E°' < 0$) is an antioxidant.

In a biological system, vitamin C functions as a water-soluble and vitamin E as a lipid-soluble chainbreaking antioxidant, respectively, in the aqueous phase and the lipid membranes, to protect lipids, proteins, and membranes from oxidative damage.

The lower redox potential of vitamin C (E°′ = 282 mV) enables its reducing power against vitamin E radicals formed, while vitamin E (E°′ = 500 mV) scavenges (reduces) the free radicals (E°′ = 600–2310 mV) of the chain reaction of lipid oxidation.

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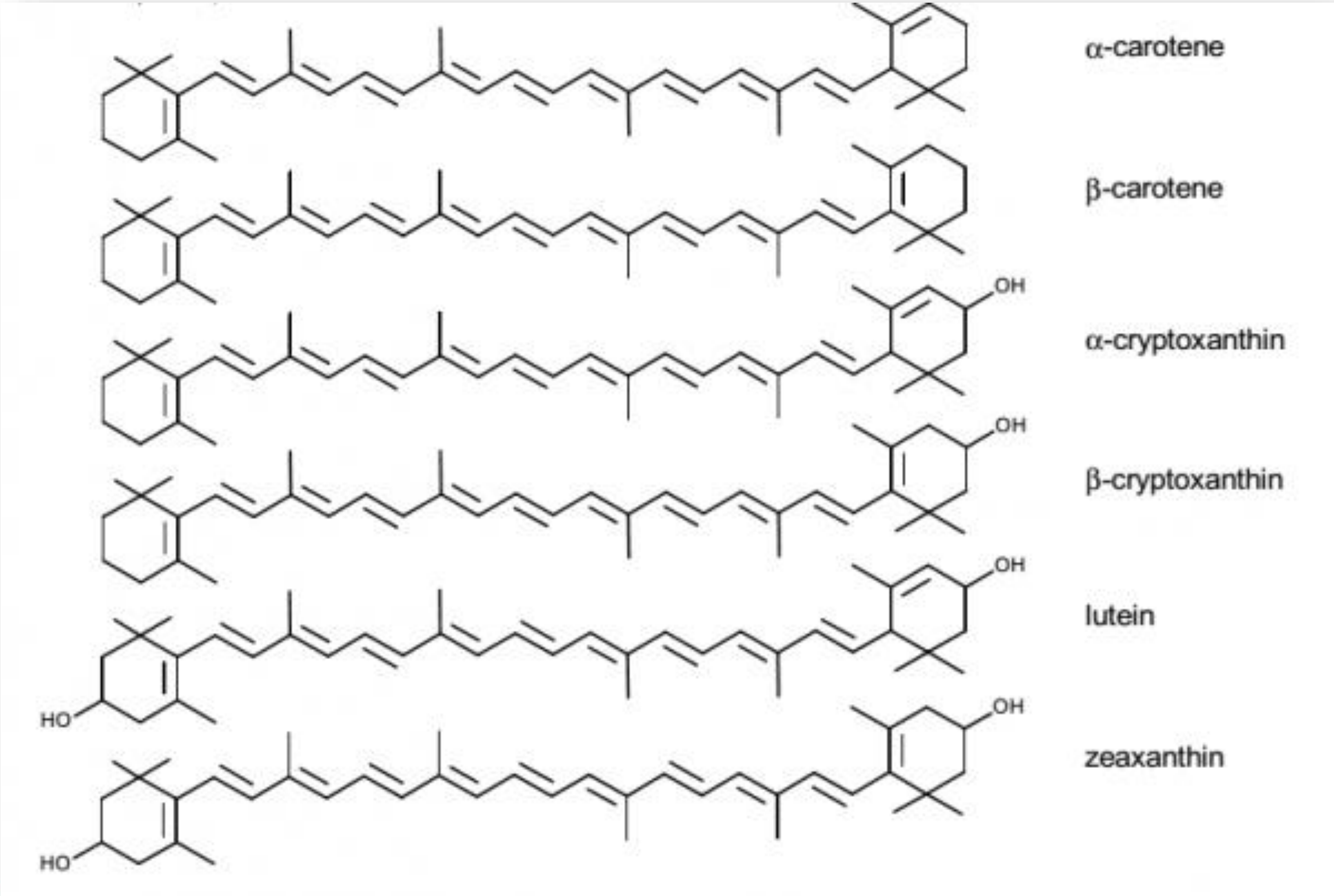
Antioxidants: carotenoids

Carotenoids in foods are usually C40 tetraterpenes/tetraterpenoids formed from eight C5 isoprenoid units joined head-to-tail, except at the center where a tail-to-tail linkage reverses the order.

The basic skeleton is linear and symmetrical with lateral methyl groups separated by six C atoms at the center and the others by five C atoms. The most distinctive feature is a centrally located, extended double-bond system.



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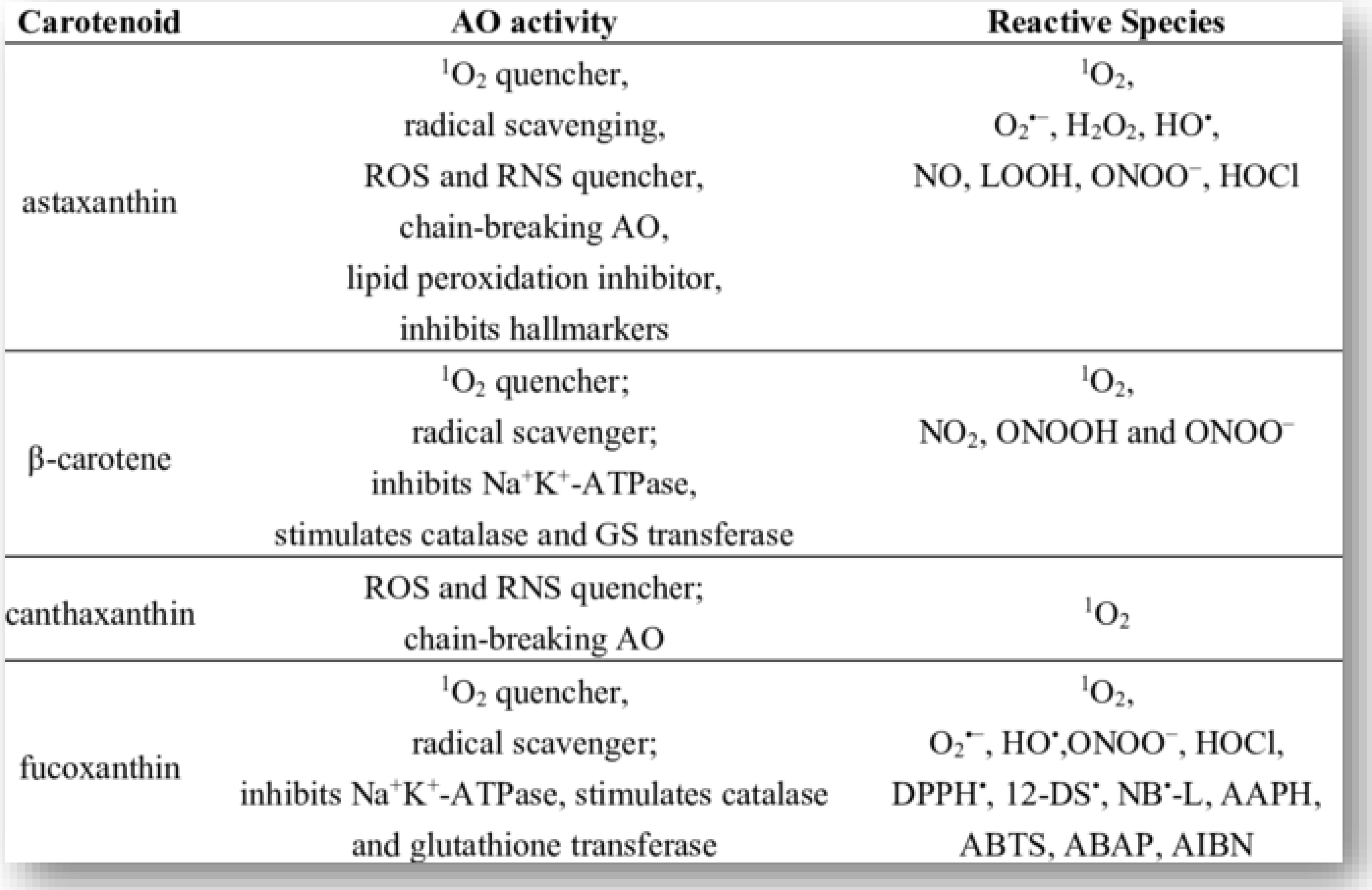
Antioxidants: carotenoids

Carotenoids act as antioxidants by quenching singlet oxygen ($^1O_2$) or reacting with free radicals.
In biological systems, a number of sensitizers (e.g., chlorophyll, riboflavin, myoglobin) can absorb energy from light and, in its excited triplet state, can promote the transformation of triplet oxygen ($^3O_2$) to $^1O_2$.
It is well documented that carotenoids have the ability to quench the highly reactive and destructive $^1O_2$ through physical or chemical quenching.



Carotenoid	AO activity	Reactive Species
astaxanthin	$^1O_2$ quencher, radical scavenging, ROS and RNS quencher, chain-breaking AO, lipid peroxidation inhibitor, inhibits hallmarkers	$^1O_2$, $O_2^{\bullet-}$, H_2O_2, $HO^\bullet$, NO, LOOH, $ONOO^-$, HOCl
β-carotene	$^1O_2$ quencher; radical scavenger; inhibits Na^+K^+-ATPase, stimulates catalase and GS transferase	$^1O_2$, NO_2, ONOOH and $ONOO^-$
canthaxanthin	ROS and RNS quencher; chain-breaking AO	$^1O_2$
fucoxanthin	$^1O_2$ quencher, radical scavenger; inhibits Na^+K^+-ATPase, stimulates catalase and glutathione transferase	$^1O_2$, $O_2^{\bullet-}$, $HO^\bullet$,$ONOO^-$, HOCl, $DPPH^\bullet$, 12-$DS^\bullet$, $NB^\bullet$-L, AAPH, ABTS, ABAP, AIBN

Antioxidants: carotenoids

With an efficacy greatly exceeding that of chemical quenching, physical quenching involves the transfer of excitation energy from $^1O_2$ to the carotenoid, resulting in ground-state oxygen and excited triplet-state carotenoid. The excitation energy is dissipated harmlessly through rotational and vibrational interactions between the excited carotenoid and the surrounding solvent, yielding groundstate carotenoid and thermal energy.

$$^1O_2 + CAR \rightarrow {}^3O_2 + {}^3CAR^*$$

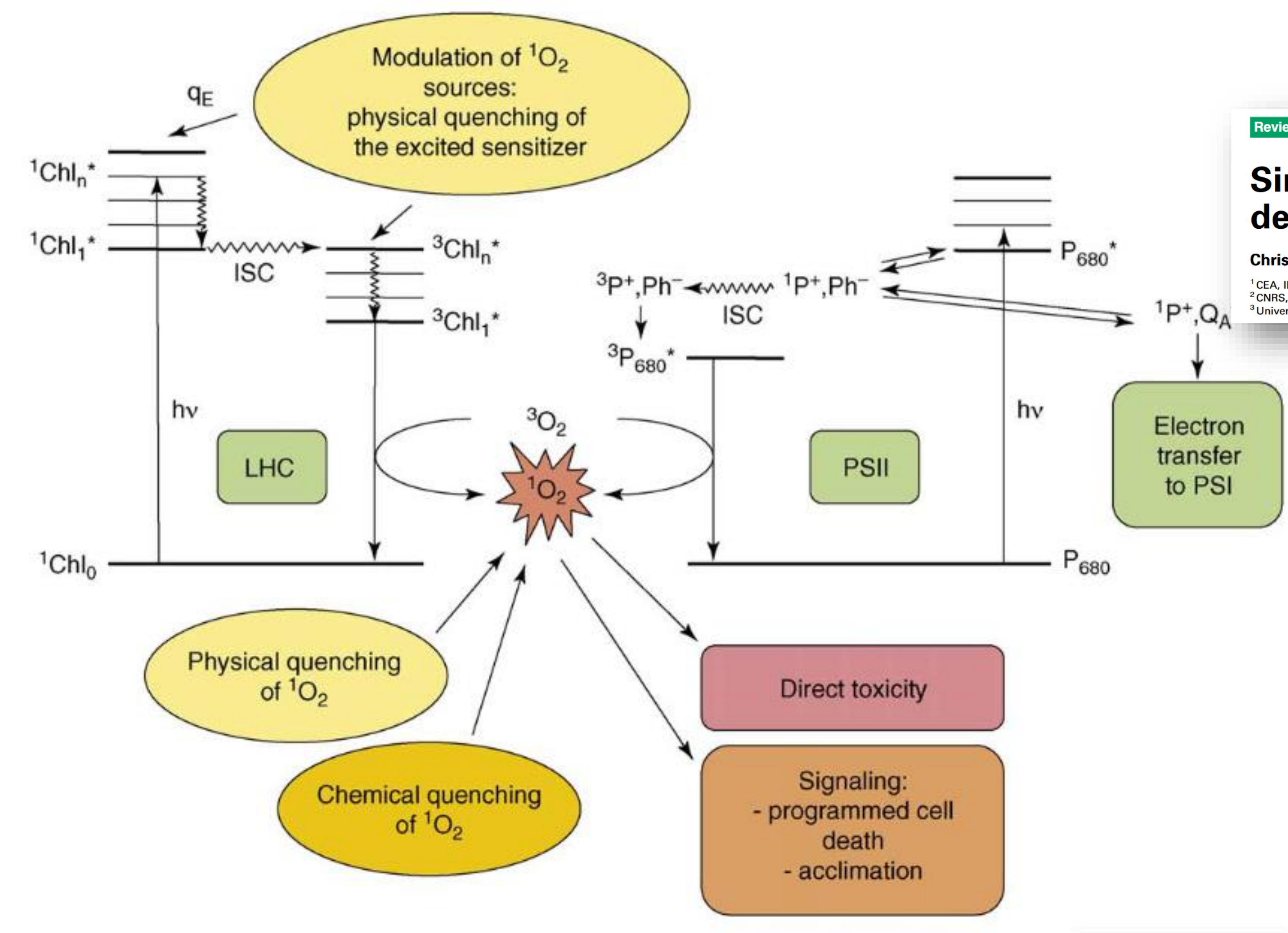
$$^3CAR^* \rightarrow CAR + heat$$

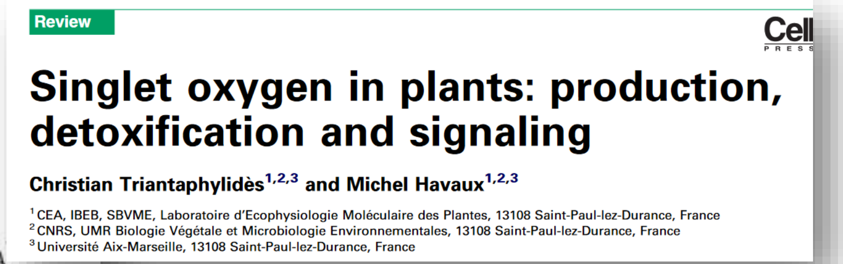
Carotenoids can also quench the excited triplet-state chlorophyll (CHL or other excited sensitizers), thereby preventing the formation of $^1O_2$.

$$^3CHL^* + CAR \rightarrow CHL + {}^3CAR^*$$

Unit 2 Anti-oxidants

Antioxidants: carotenoids





Singlet oxygen in plants: production, detoxification and signaling

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Antioxidants: carotenoids

Carotenoids can also scavenge free radicals, thereby breaking chain propagation.
Carotenoids may interact with free radicals in three main ways.
Potential influencing factors affecting the rates and mechanisms of free radical reactions include the nature of the free radical and its environment (aqueous or lipid regions) and structural features of the carotenoid (cyclic or acyclic, polar or apolar end groups, redox properties).

$$CAR + ROO^{\bullet} \rightarrow CAR^{\bullet +} + ROO^{-} \text{ (electron transfer)}$$

$$CAR + ROO^{\bullet} \rightarrow CAR^{\bullet} + ROOH \text{ (hydrogen abstraction)}$$

$$CAR + ROO^{\bullet} \rightarrow (ROO - CAR)^{\bullet} \text{ (addition)}$$

Truscott in 1996 proposed a plausible mechanism for the interaction of vitamins A and E with β-carotene whereby the carotenoid molecule repairs the vitamin E radical and the resulting carotenoid cation radical is, in turn, repaired by vitamin C.

$$CAR + TOH^{\bullet +} \rightarrow CAR^{\bullet +} + TOH$$

$$CAR^{\bullet +} + ASCH_2 \rightarrow CAR + ASCH^{\bullet} + H^{+}$$

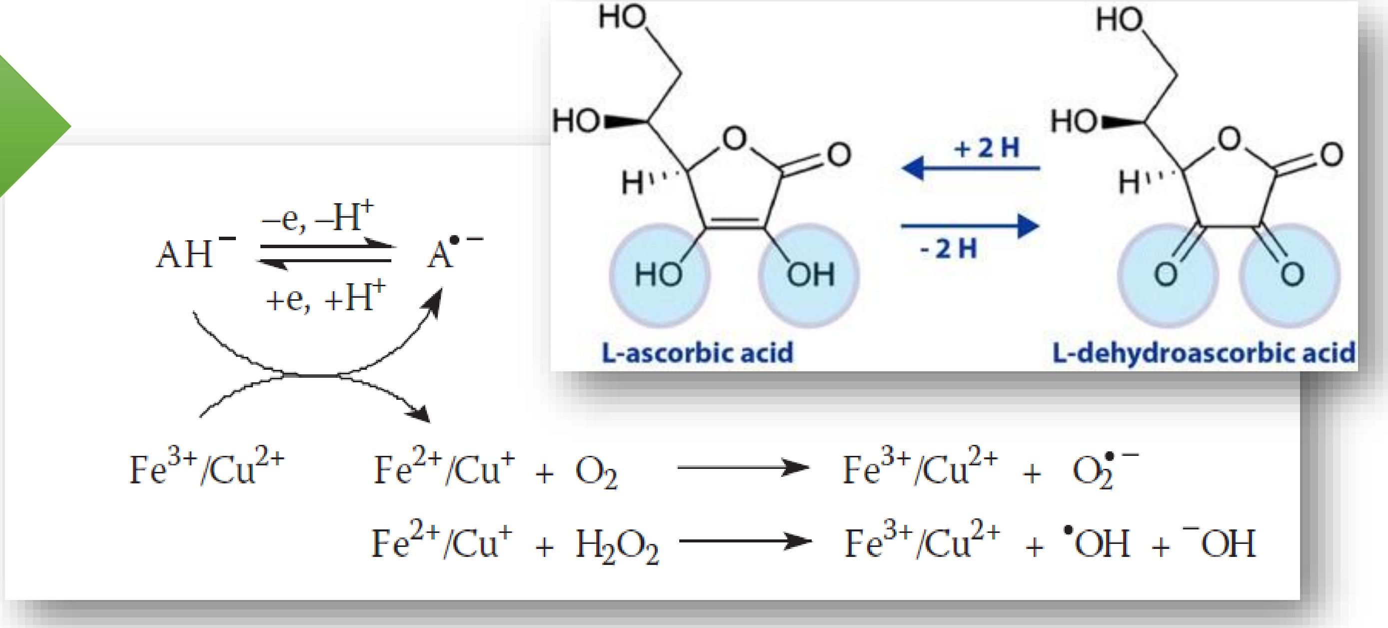
$$CAR^{\bullet +} + ASCH^{-} \rightarrow CAR + ASCH^{\bullet -} + H^{+}$$

Antioxidants: ascorbic acid

Vitamin C (L-ascorbic acid) is a water-soluble vitamin with high reductive potential.

It is considered to be a most important water-soluble antioxidant. It can directly scavenge superoxide anion radicals, singlet oxygen, hydrogen peroxide, and hydroxyl radicals.

The antioxidant chemistry of vitamin C in the human body and in most foods is the chemistry of the ascorbate anion because, at physiological pH, 99.9% of ascorbic acid (pKa1 = 4.17) is present as ascorbate anion (AH–) and only very small proportions as ascorbic acid (AH2; 0.05%) and A2– (0.004%).



$$AH^{-} \underset{+e,\ +H^{+}}{\overset{-e,\ -H^{+}}{\rightleftharpoons}} A^{\bullet -}$$

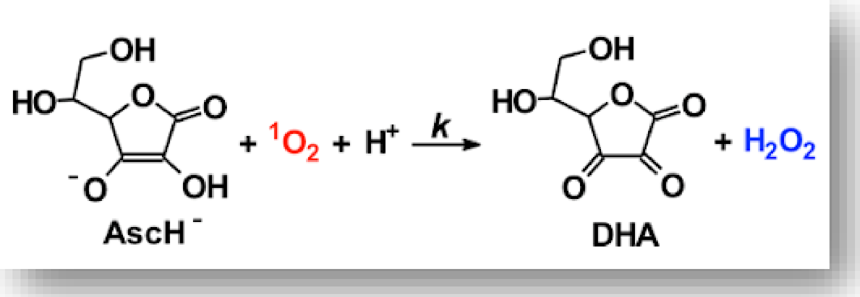
$$Fe^{2+}/Cu^{+} + O_2 \longrightarrow Fe^{3+}/Cu^{2+} + O_2^{\bullet -}$$

$$Fe^{2+}/Cu^{+} + H_2O_2 \longrightarrow Fe^{3+}/Cu^{2+} + {}^{\bullet}OH + {}^{-}OH$$

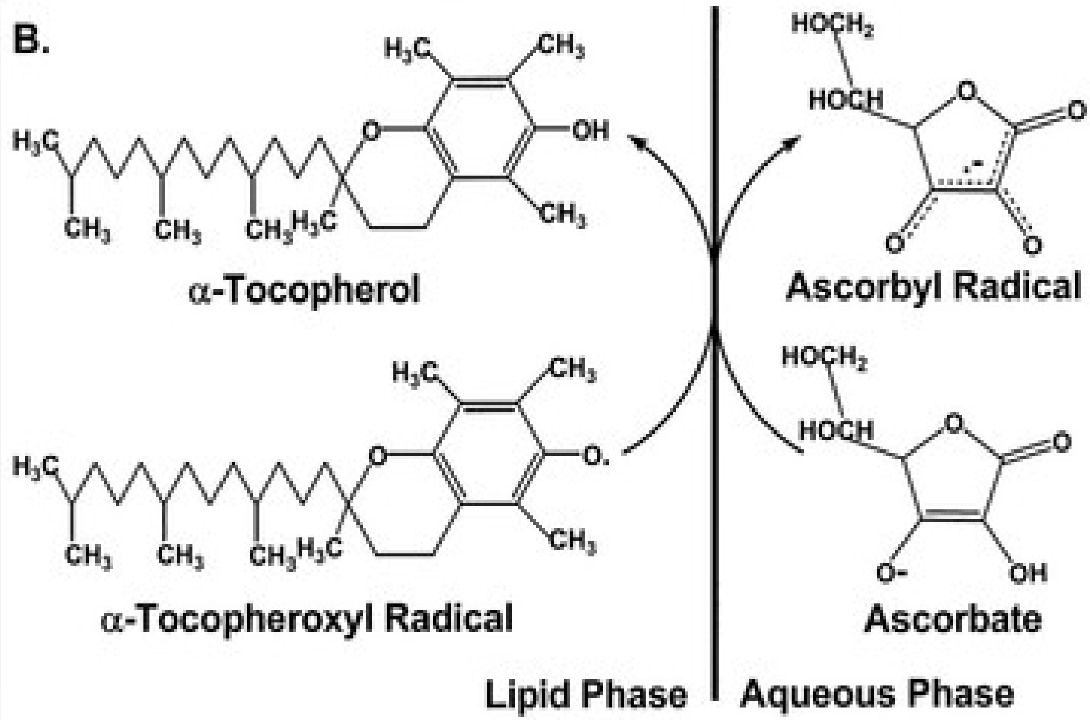
AH– reacts with radicals to produce an ascorbate free radical (AH•), which is not protonated (pKa = –0.86) but is present in the form of a poorly reactive emidehydroascorbate radical (ascorbyl radical; A•–)). Both ascorbate and the ascorbyl radical have a low reduction potential and can react with most other biologically relevant radicals and oxidants. Moreover, the ascorbyl radical reactivity is low as a result of the resonance stabilization of the unpaired electron; it dismutates to ascorbate and dehydroascorbic acid. In addition, ascorbate can be regenerated from both the ascorbyl radical and dehydroascorbic acid by enzyme-dependent and independent pathways.

Antioxidants: ascorbic acid

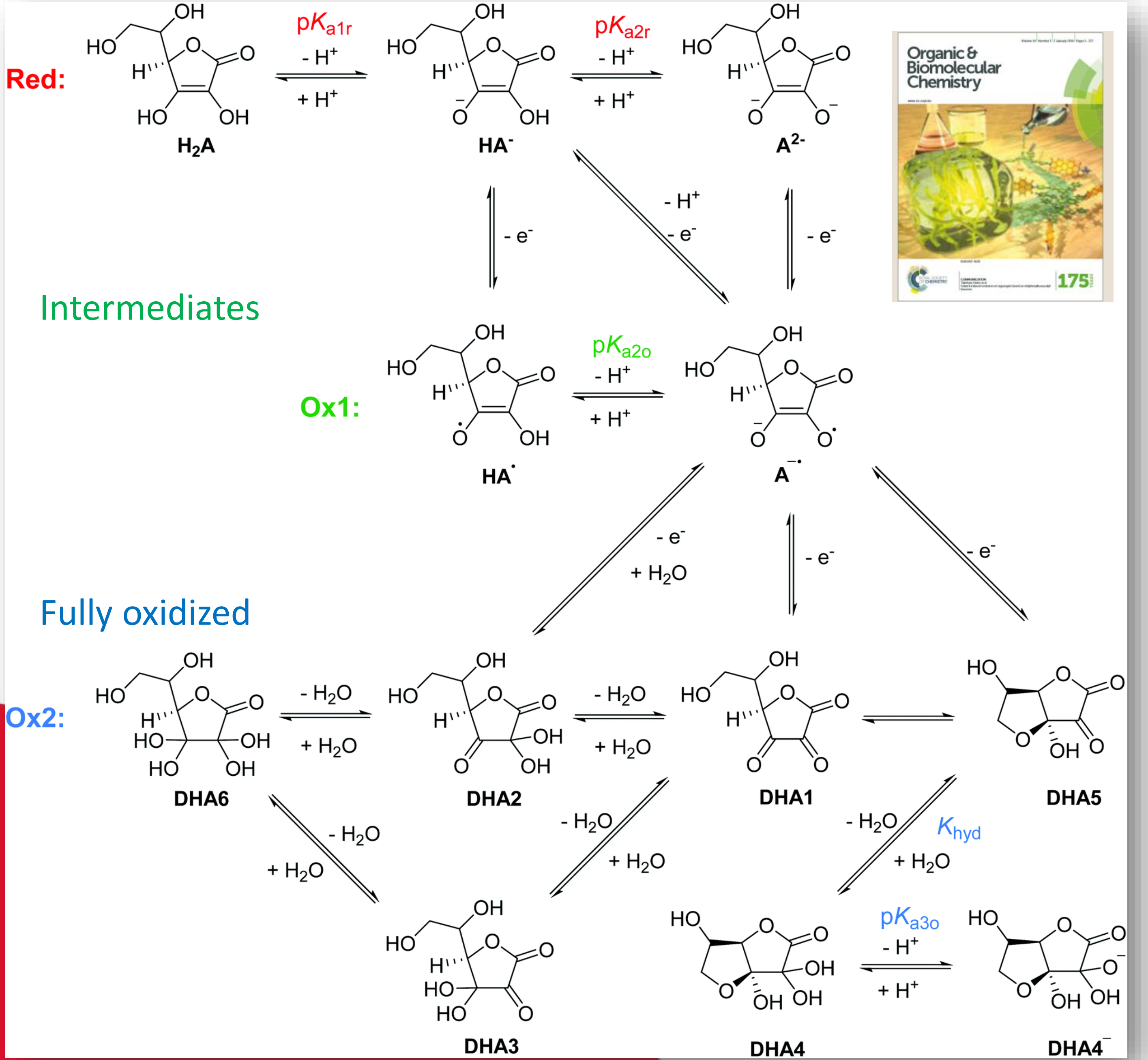
Singlet oxigen chemical quenching



Tocopherol/Ascorbate synergism



Antioxidants: ascorbic acid



Electrochemical equilibria and structures of ascorbic acid and its derivatives in water

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Antioxidants formation during food processing

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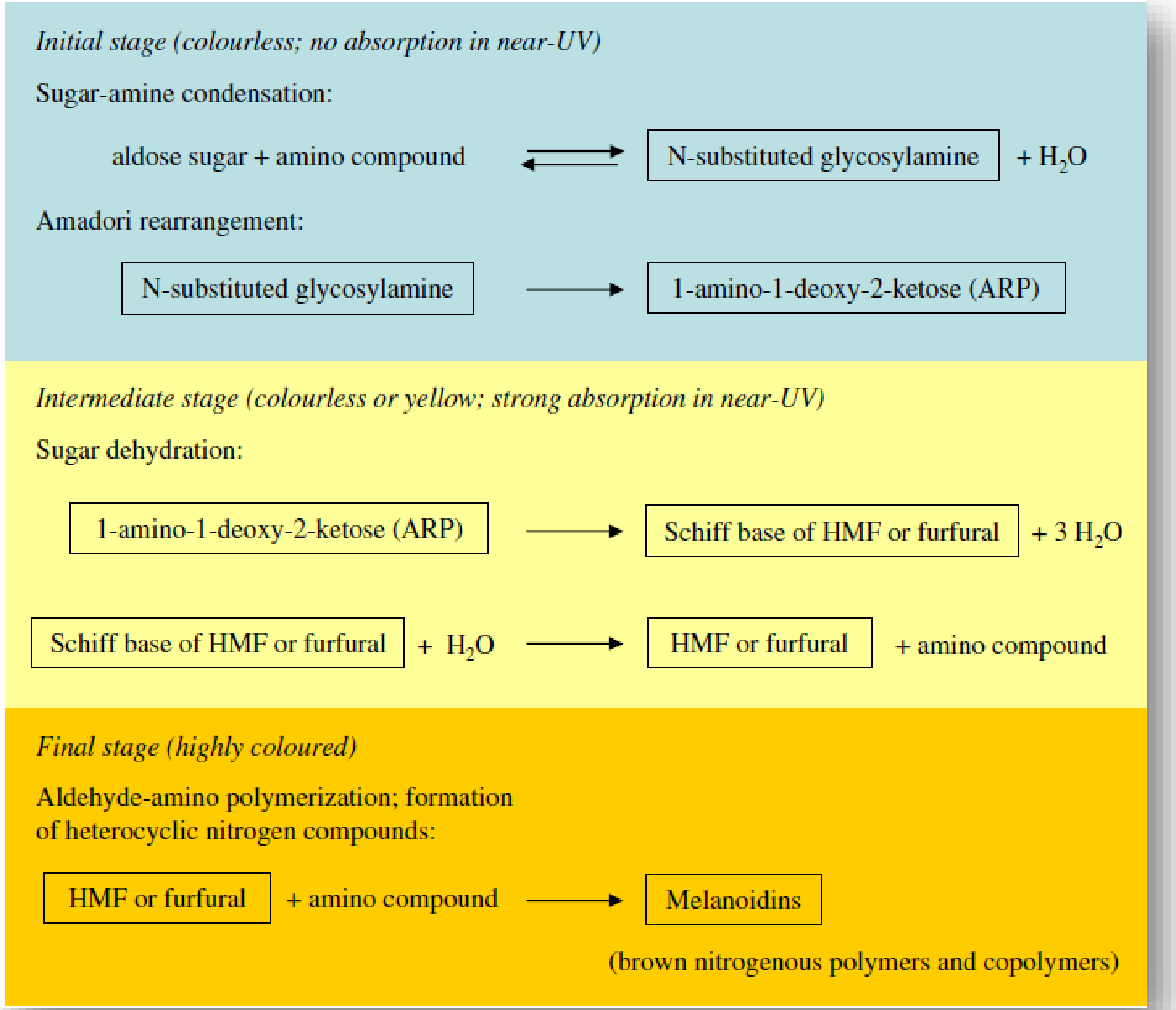
***Maillard* reaction**, or nonenzymatic browning, includes the formation of N-glycosides and their successive reactions (e.g., oxidation, dehydration, hydrolysis etc..). N-Glycosides are widely distributed in nature (nucleic acids, NAD, coenzyme A). They are formed in food whenever reducing sugars occur together with proteins, peptides, amino acids or amines.
They are obtained more readily at a higher temperature, low water activity and on longer storage.

On the **sugar** side, the reactants are mainly **glucose, fructose, maltose, lactose** and, to a smaller extent, reducing **pentoses**, e. g., ribose.
On the side of the **amino component**, **amino acids** with a **primary amino group** are more important than those with a secondary because their concentration in foods is usually higher. Exceptions are, e. g., malt and corn products which have a high proline content. In the case of proteins, the **ε-amino groups of lysine** react predominantly.



Initial stage (colourless; no absorption in near-UV)

Sugar-amine condensation:

aldose sugar + amino compound $\rightleftarrows$ N-substituted glycosylamine + H_2O

Amadori rearrangement:

N-substituted glycosylamine $\longrightarrow$ 1-amino-1-deoxy-2-ketose (ARP)

Intermediate stage (colourless or yellow; strong absorption in near-UV)

Sugar dehydration:

1-amino-1-deoxy-2-ketose (ARP) $\longrightarrow$ Schiff base of HMF or furfural + 3 H_2O

Schiff base of HMF or furfural + H_2O $\longrightarrow$ HMF or furfural + amino compound

Final stage (highly coloured)

Aldehyde-amino polymerization; formation of heterocyclic nitrogen compounds:

HMF or furfural + amino compound $\longrightarrow$ Melanoidins

(brown nitrogenous polymers and copolymers)

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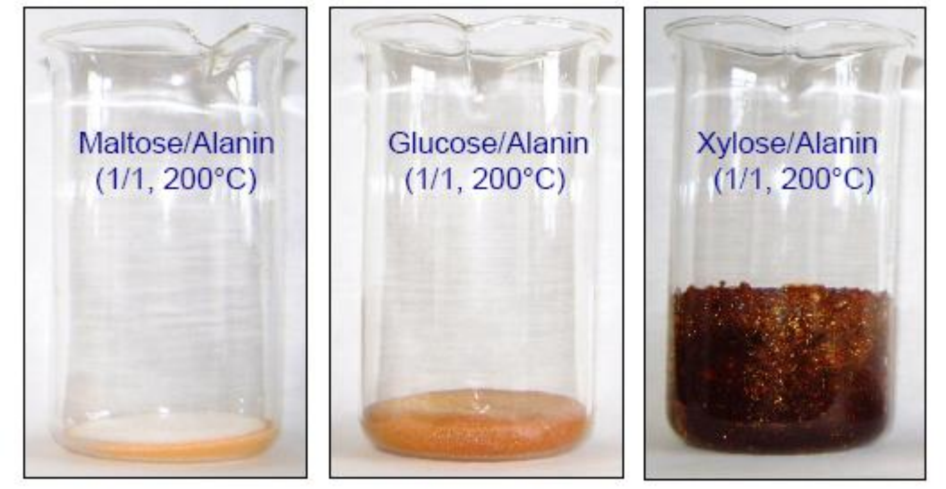
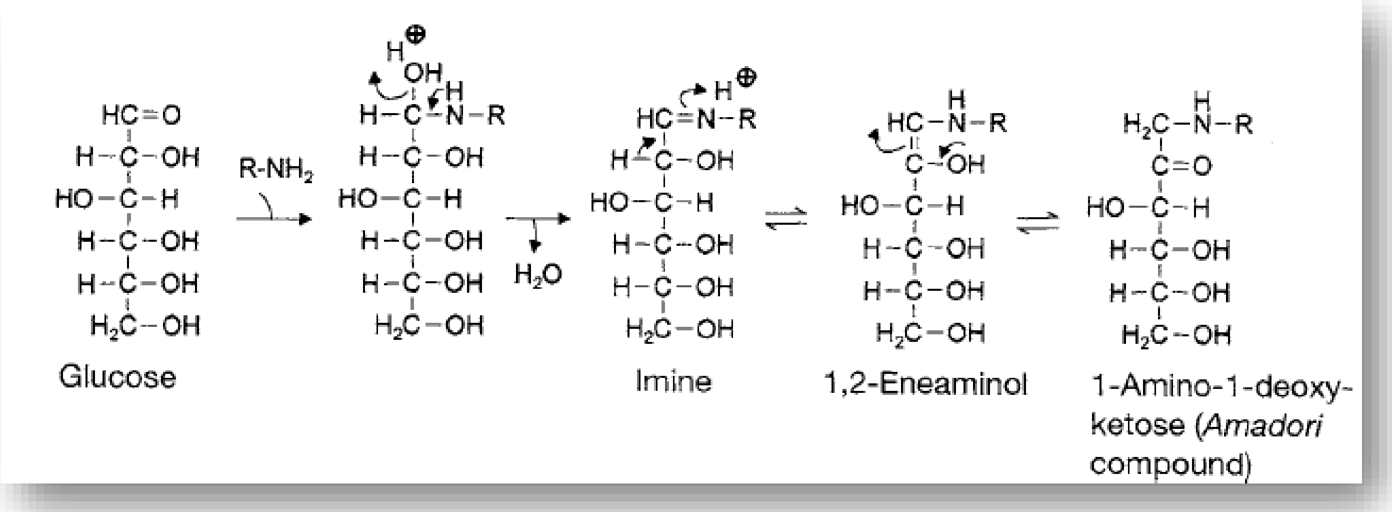
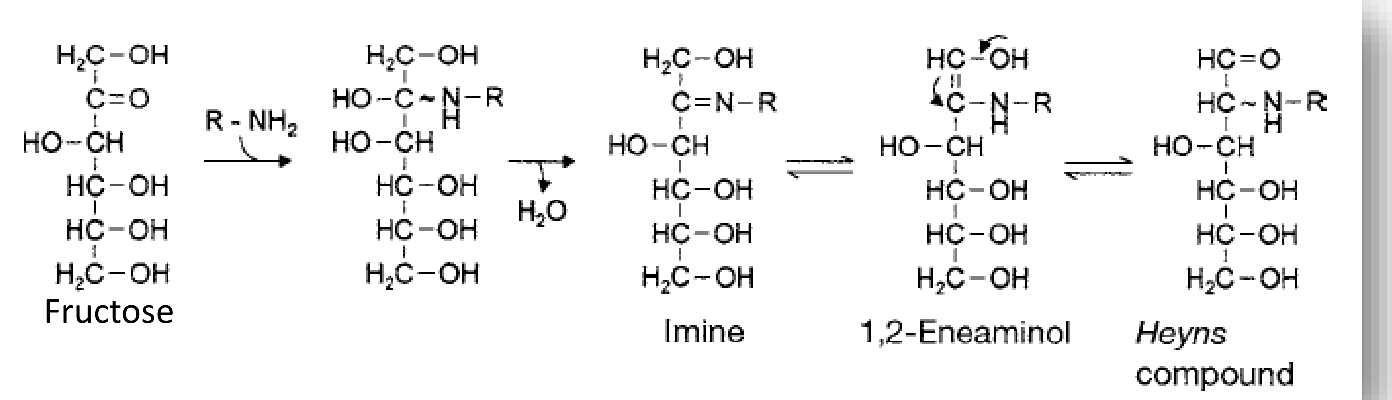
Triggering factors of Maillard reaction are:

✓Temperature;
✓Water activity(a_w);
✓pH (3-7);
✓Intrinsic reactivity of sugars involved:
(Pentoses > Fructose > hexoses > di-saccharides
Hexoses: galactose > mannose > glucose)







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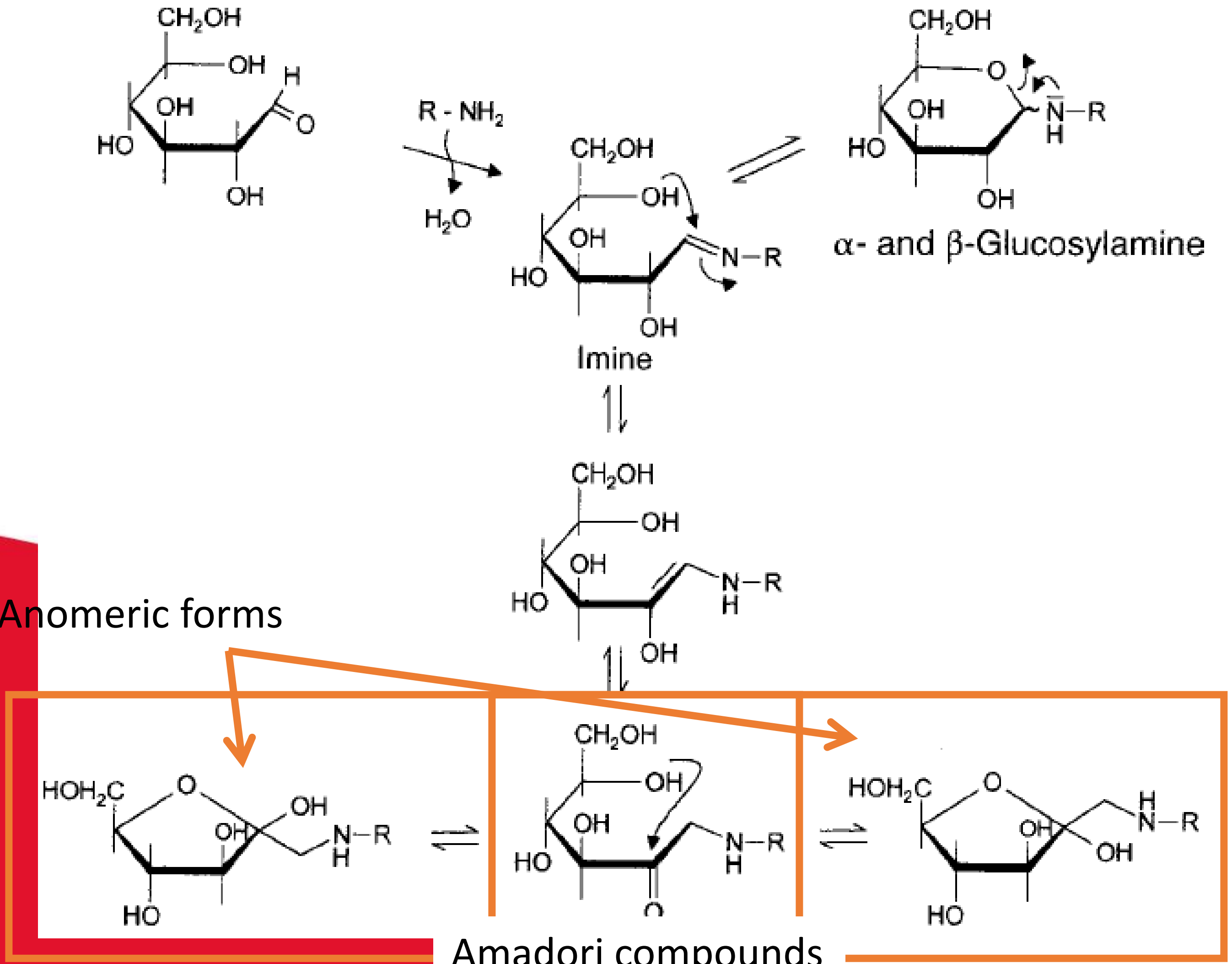

Anomeric forms

Amadori compounds

The imine formed by the reaction of glucose with the amine is easily converted to the cyclic hemiaminal, α- and β- glucosylamine.
However, N-glycosides of this type are relatively instable because they very easily mutarotate, i. e., they are easily hydrolyzed via the open-chain imine or are converted to the respective α- and β-anomer.

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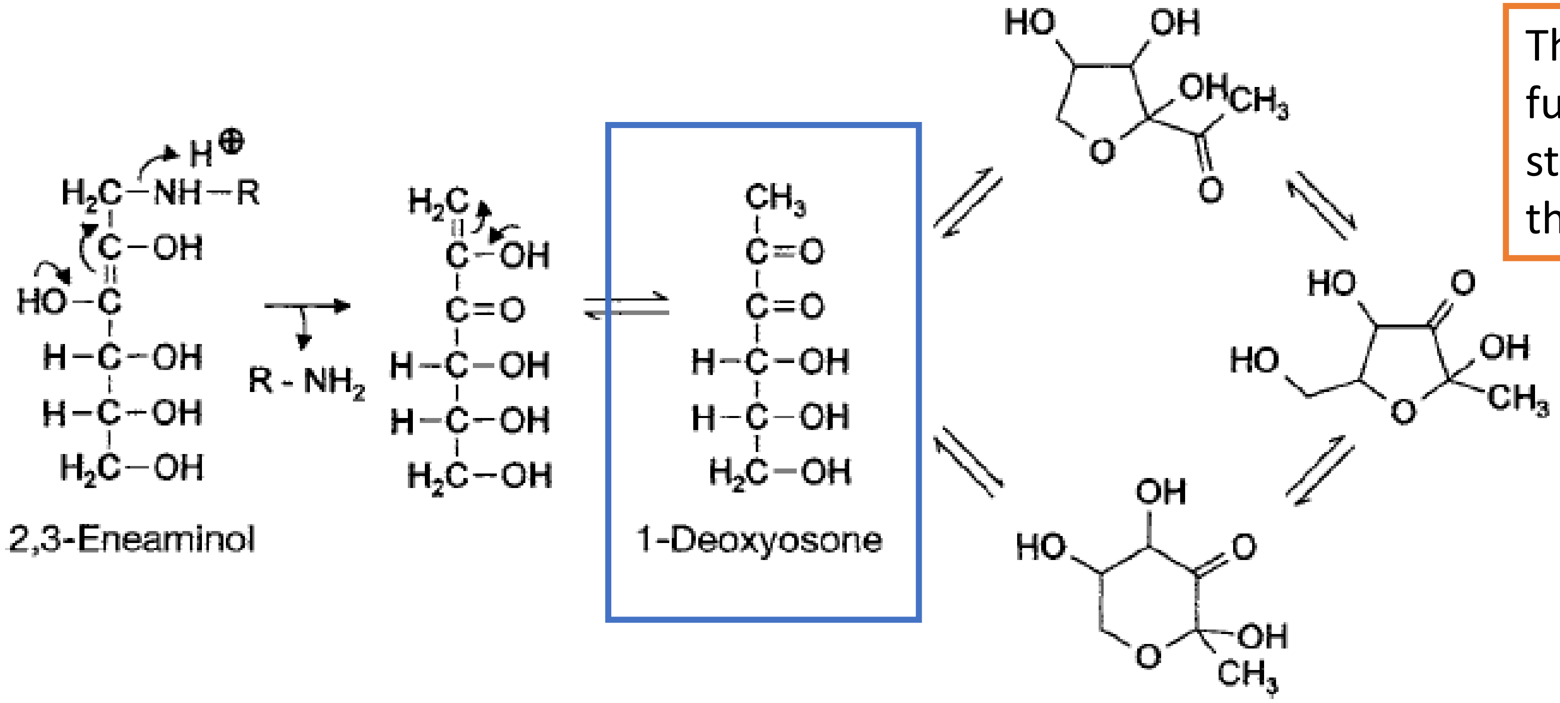

The *Amadori* rearrangement leads to furanose, which as a hemiacetal, has a stability to mutarotation comparable with that of carbohydrates.

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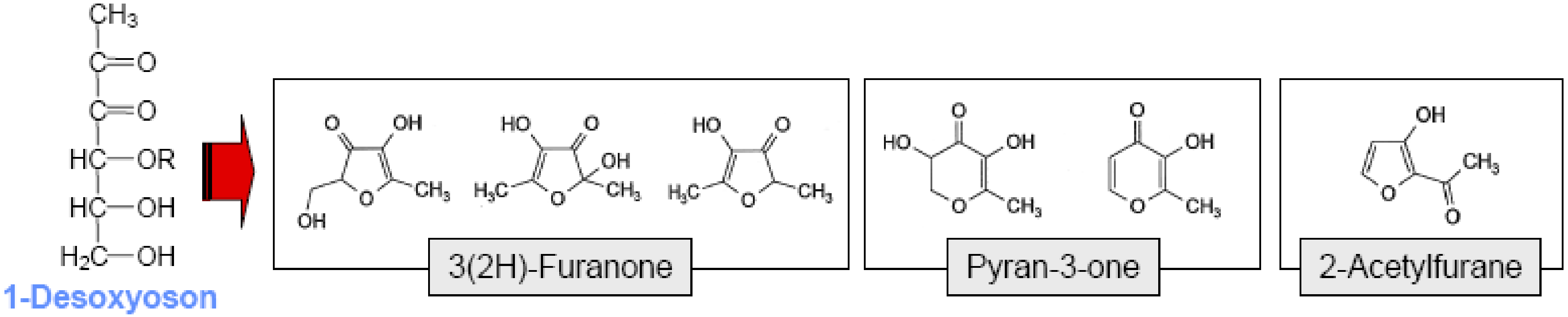

Unlike the acidic (pH <3) and alkaline (pH >8) sugar degradation reactions, the *Amadori* compounds are degraded to 1-, 3-, and 4-deoxydicarbonyl compounds (deoxyosones) in the pH range 4–7.

As reactive α-dicarbonyl compounds, they yield many secondary products.

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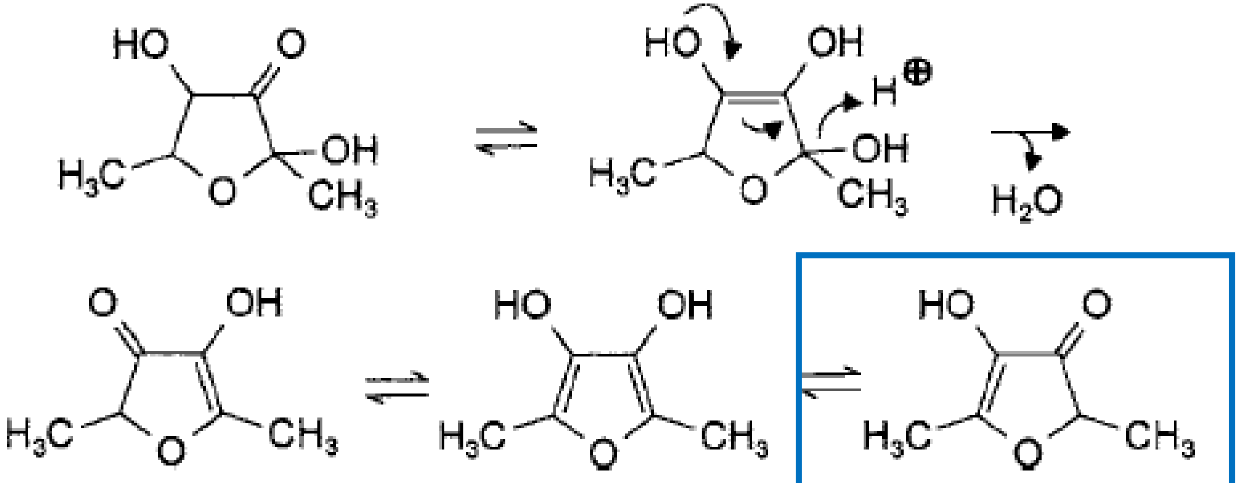

Furaneol®

The compound 4-hydroxy-2,5-dimethyl-3(2H)-furanone (furaneol®) is the degradation product from the 6-deoxy-L-mannose (rhamnose). Furaneol can also be formed from hexose phosphates under reducing conditions and from C-3 fragments. With a relatively low odor threshold value, furaneol has an intensive caramel-like odor. It is interesting that furaneol is also biosynthesized in plants, e. g., in strawberries and pineapples.

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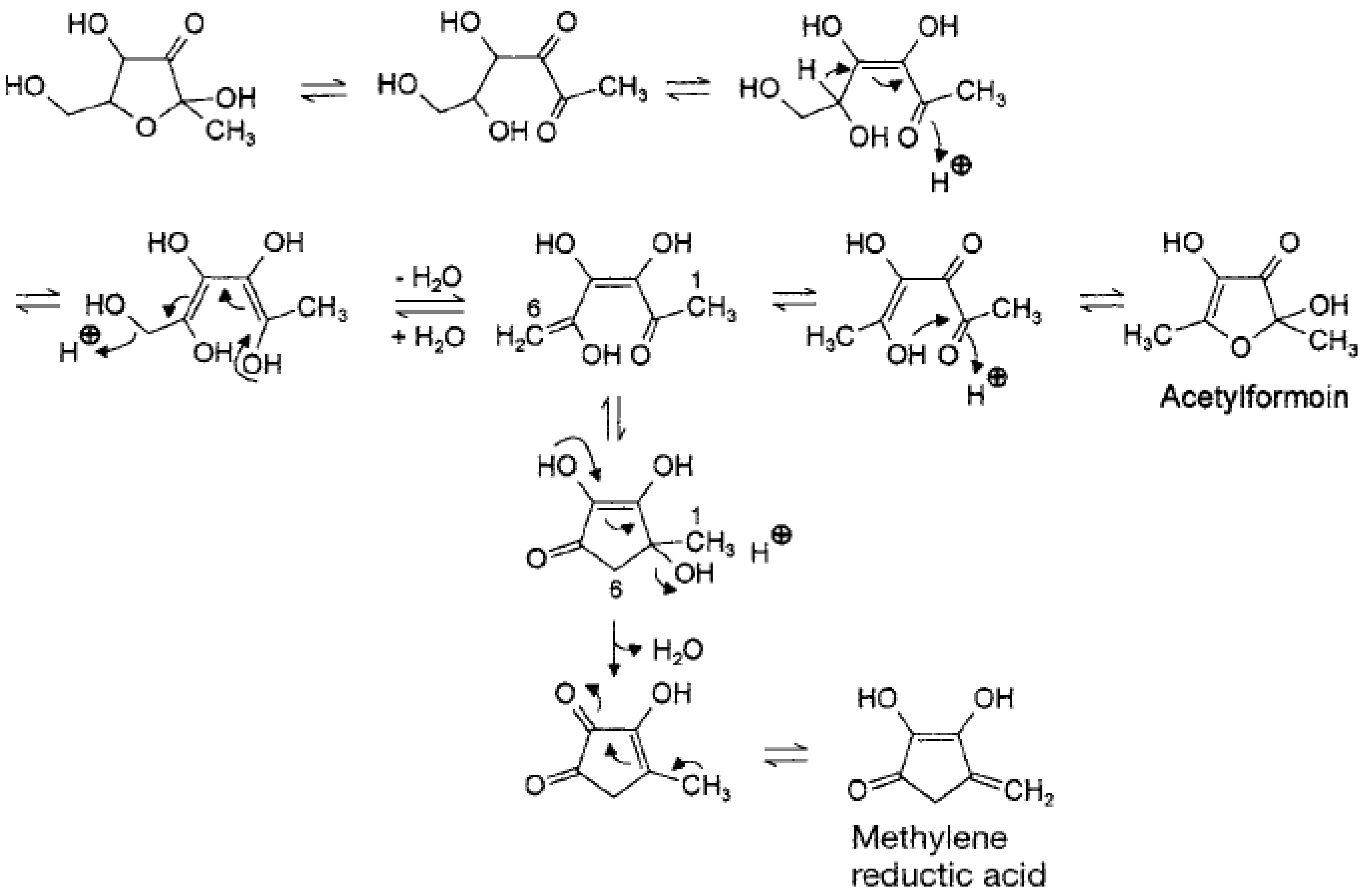
1-Desoxyoson



Water elimination at C-6 of the carbohydrate skeleton occurring *before* cyclization to the furan derivative. Although further water elimination is no longer easy, it is suggested to explain the formation of methylene reductic acid.

As a result of the presence of an enediol structure element in the α-position to the oxo function in the open-chain structures of acetylformoin, this compound belongs to the group of substances called reductones. Substances of this type, e. g., also vitamin C (ascorbic acid), are weakly acidic, reductive and exhibit antioxidative properties.

Antioxidants formation during food processing

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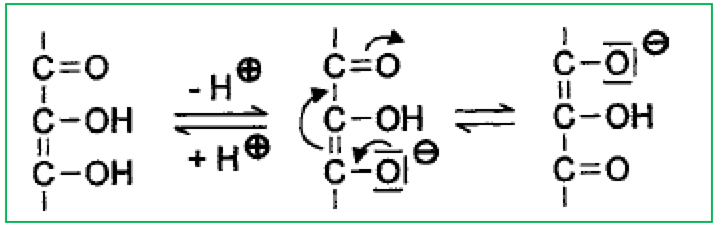
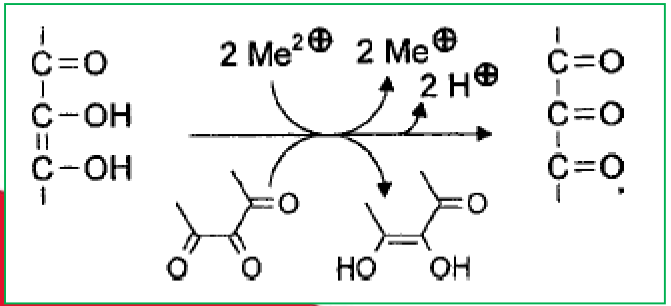
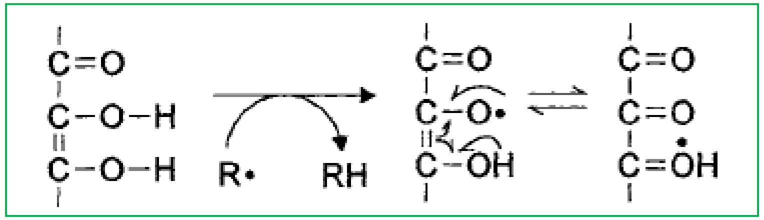
Acidic properties



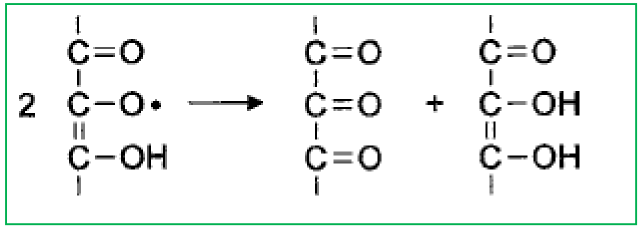
Reduction properties



Radical quenchers



Disproportion reactions



Antioxidant properties are attributed to the possible formation of resonance stabilized radicals and also to the disproportionation of two radicals with re-formation of the reductone structure.
Reductones reduce Ag^+, Au^{3+}, Pt^{4+} to the metals, $Cu2^+$ to Cu^+, Fe^{3+} to Fe^{2+} and Br_2 or I_2 to Br^- or I^- respectively.
Reductones are present as mono-anions at pH values <6. The di-anion occurring under alkaline conditions is easily oxidized in the presence of O_2.

Syntetic phenolics as antioxidants

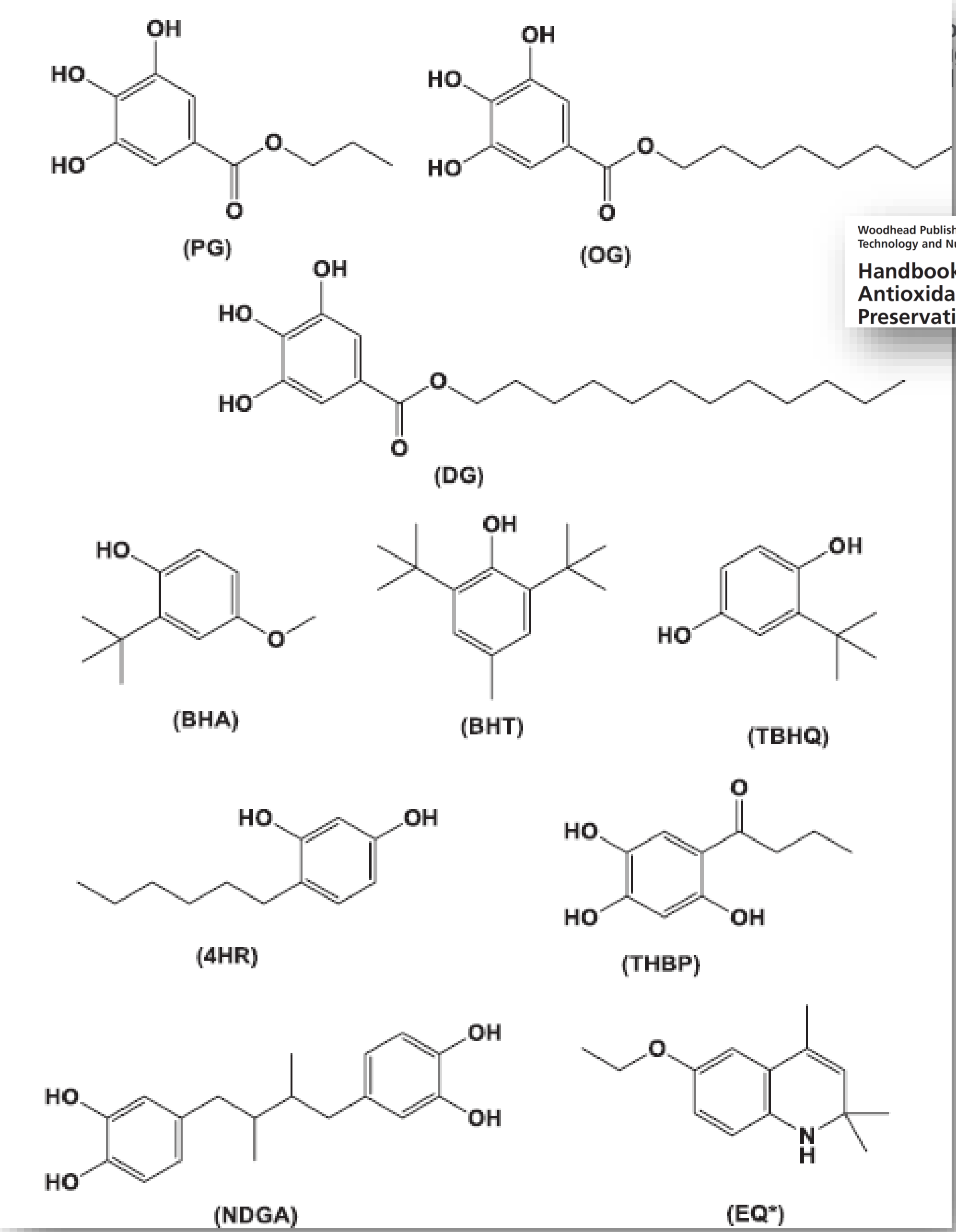
Chiara Emilia Irma Cordero <chiara.cordero@unito.it>

There are many synthetic compounds that exhibit better antioxidant activity than natural antioxidants, and these are more easily available.

They have been used in a wide variety of food products and these are mainly phenolic compounds, the common ones being *tertiary*-butylhydroquinone (TBHQ), butylated hydroxylanisole (BHA), butylated hydroxyltoluene (BHT), propyl gallate (PG), octyl gallate (OG), and dodecyl gallate (DG).
Phenolic antioxidants are effective in inhibiting the oxidation process by trapping the peroxyl radicals.

$$\mathrm{ArOH} + \mathrm{ROO}^{\bullet} \rightarrow \mathrm{ArO}^{\bullet} + \mathrm{ROOH}$$

$$\mathrm{ArO}^{\bullet} + \mathrm{ROO}^{\bullet} \rightarrow \text{Nonradical products}$$



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Handbook of Antioxidants for Food Preservation

Case study

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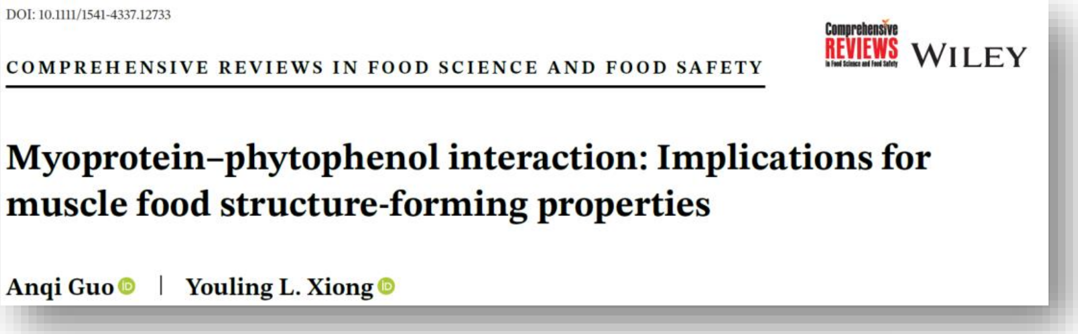
Phenolic compounds are commonly incorporated into muscle foods to inhibit lipid oxidation and modify product flavor. Those from plant sources (seeds, leaves, and stems) known as “phytophenols” are of particular importance in the current meat industry due to natural origins, diversity, and safety record.

In processed muscle foods, where the structure-forming ability is critical to a product’s texture-related quality attributes and palatability, the functional properties of proteins, especially gelation and emulsification, play an essential role. A vast amount of recent studies has been devoted to protein–phenol interactions to investigate the impact on meat product texture and flavor. Considerable efforts have been made to elucidate the specific roles of phytophenol interaction with “myoproteins” (i.e., muscle-derived proteins) probing the structure-forming process in cooked meat products.



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Myoprotein–phytophenol interaction: Implications for muscle food structure-forming properties

Anqi Guo | Youling L. Xiong

Case study

Similar to the process of lipid oxidation, meat proteins (MP) can be oxidized via free radical chain reactions leading to structural changes and the formation of protein carbonyls and disulfide bonds. As a result of oxidative modification, MP, particularly myofibrillar proteins, will exhibit altered functionality that is often manifested as increased toughness and cooking loss in whole-muscle meat.

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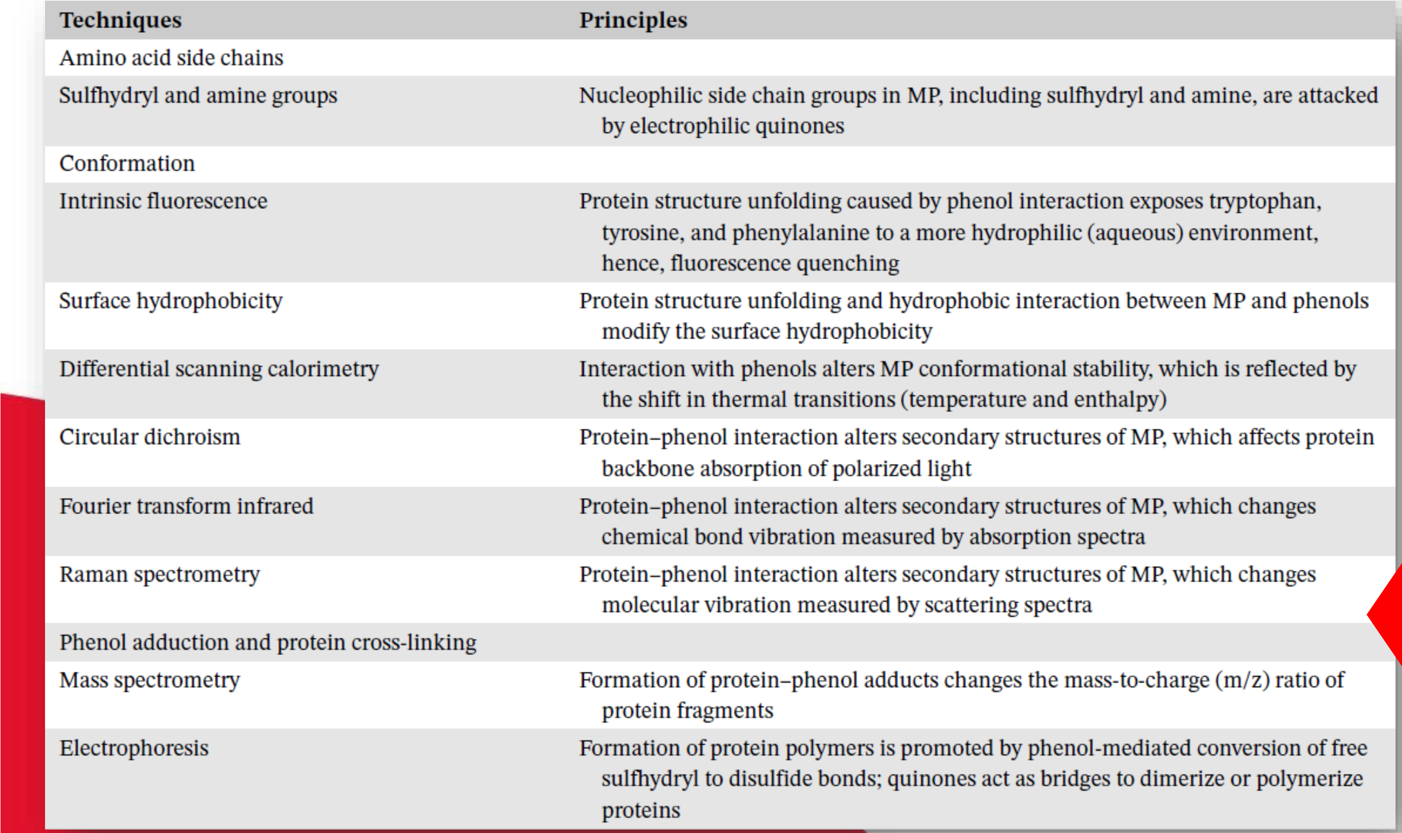


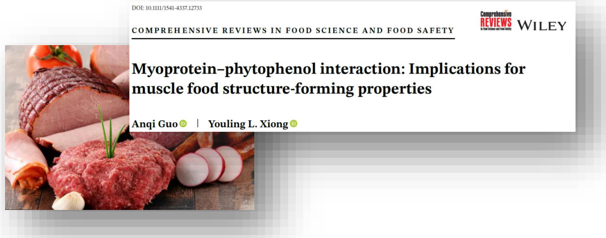
Techniques	Principles
Amino acid side chains	
Sulfhydryl and amine groups	Nucleophilic side chain groups in MP, including sulfhydryl and amine, are attacked by electrophilic quinones
Conformation	
Intrinsic fluorescence	Protein structure unfolding caused by phenol interaction exposes tryptophan, tyrosine, and phenylalanine to a more hydrophilic (aqueous) environment, hence, fluorescence quenching
Surface hydrophobicity	Protein structure unfolding and hydrophobic interaction between MP and phenols modify the surface hydrophobicity
Differential scanning calorimetry	Interaction with phenols alters MP conformational stability, which is reflected by the shift in thermal transitions (temperature and enthalpy)
Circular dichroism	Protein–phenol interaction alters secondary structures of MP, which affects protein backbone absorption of polarized light
Fourier transform infrared	Protein–phenol interaction alters secondary structures of MP, which changes chemical bond vibration measured by absorption spectra
Raman spectrometry	Protein–phenol interaction alters secondary structures of MP, which changes molecular vibration measured by scattering spectra
Phenol adduction and protein cross-linking	
Mass spectrometry	Formation of protein–phenol adducts changes the mass-to-charge (m/z) ratio of protein fragments
Electrophoresis	Formation of protein polymers is promoted by phenol-mediated conversion of free sulfhydryl to disulfide bonds; quinones act as bridges to dimerize or polymerize proteins

The interactions between MP and plant phenols are governed by multiple mechanisms.
Both reversible - noncovalent and irreversible - covalent bonds are involved, providing the driving force of such interactions in meat products and delivering measurable impact on muscle protein functionality and texture-related meat quality.

Analytical measurement of these interactions can be focused on changes in protein amino acid side chains (e.g., -SH and -NH groups), conformation (e.g., surface hydrophobicity and intrinsic fluorescence), and formation of protein–phenol adducts (e.g., electrophoresis and mass spectrometry [MS]).

Case study

Four different types of **noncovalent bonds** can be formed between MP and phenolic compounds:
hydrogen bonding, hydrophobic association, electrostatic attraction, and van der Waals forces.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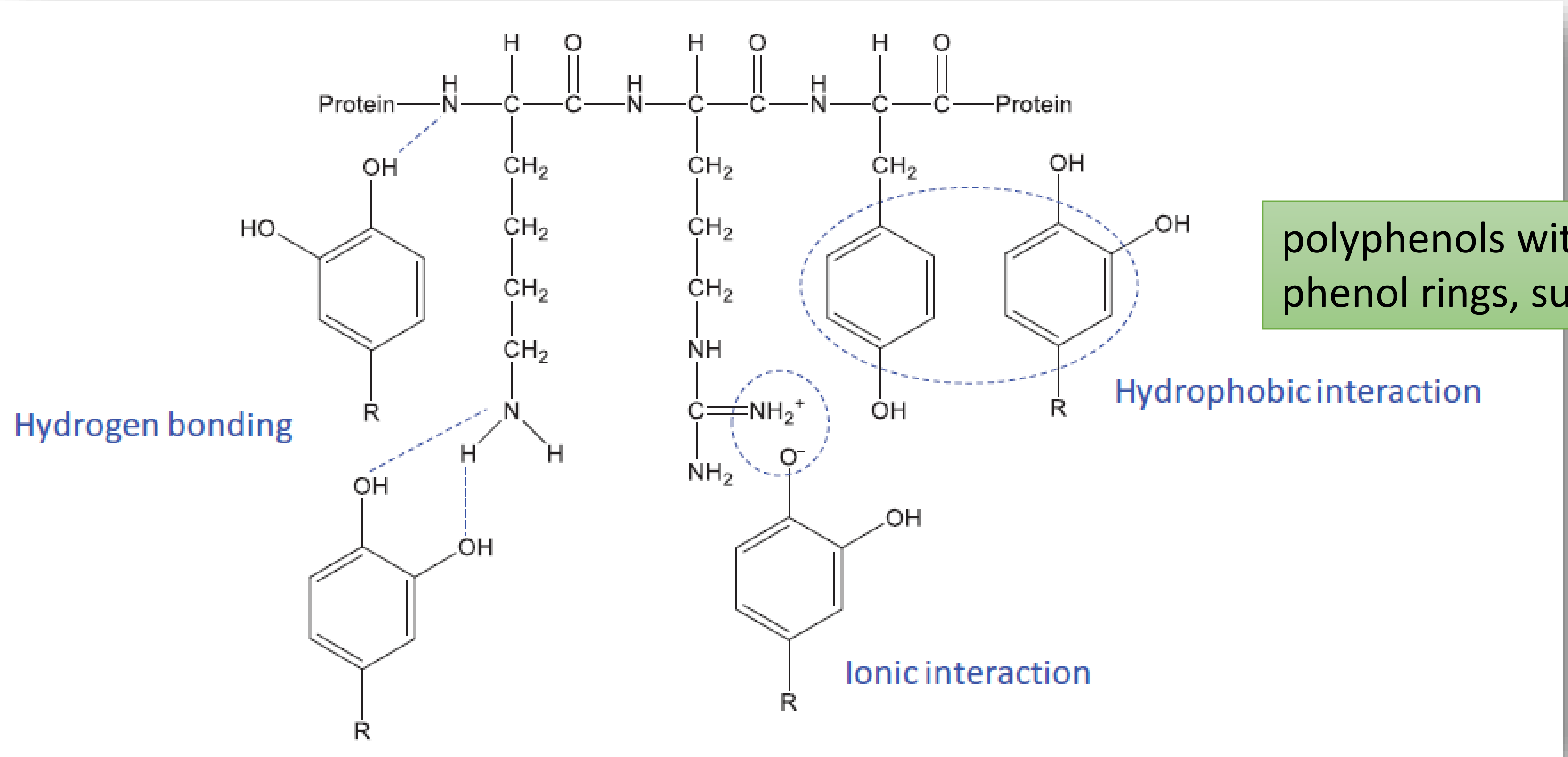
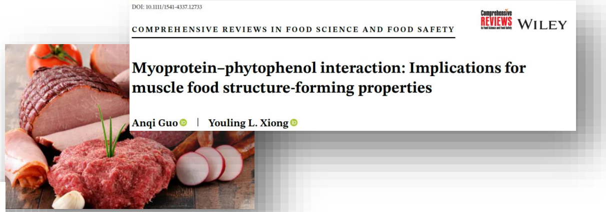


polyphenols with three or more phenol rings, such as tannins

Case study

Irreversible interactions occurring between phytophenols and MP can be characterized by the formation of **covalent linkages** that usually take place **in an oxidative environment**. At alkaline pH, phenols can be readily oxidized to quinone derivatives that are capable of forming covalent bonds with MP. The mechanisms involved in such irreversible interactions are depicted in Figure.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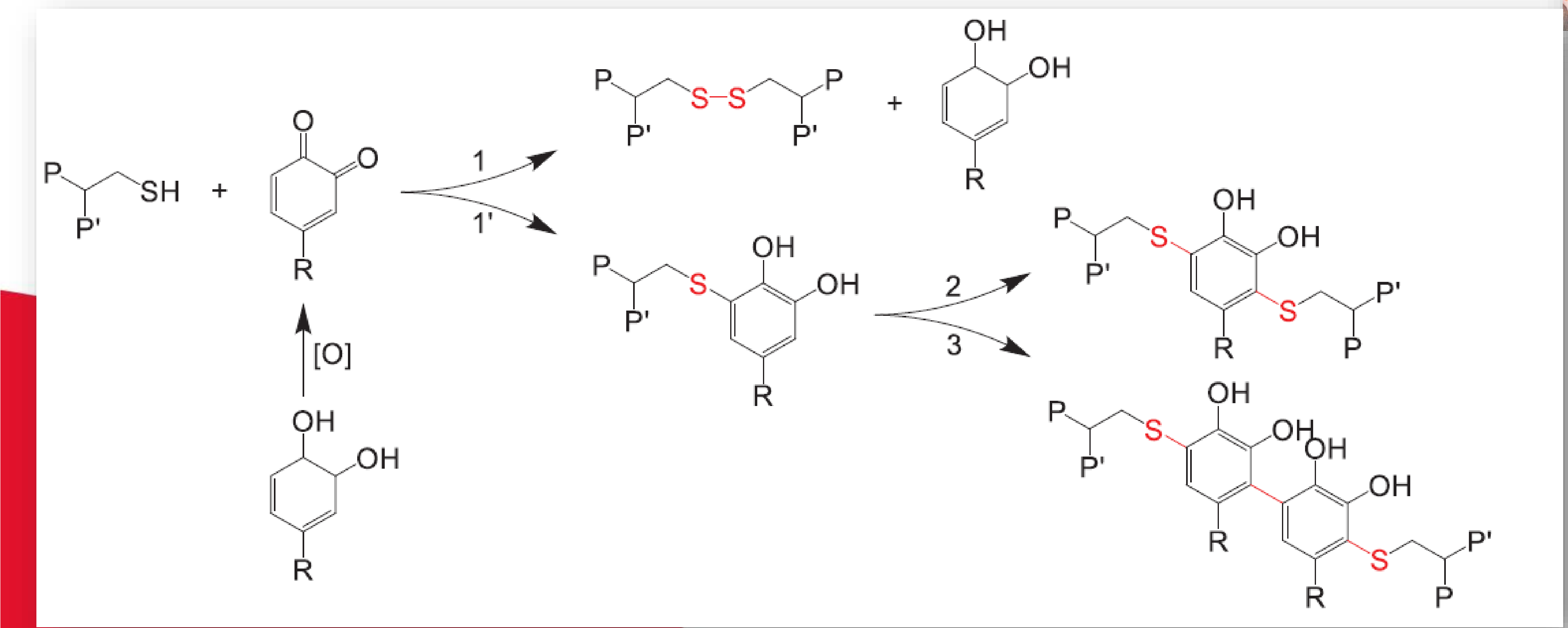
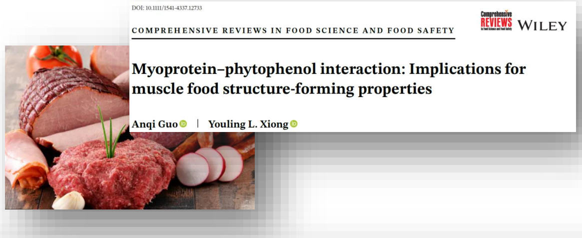


Proposed mechanism of covalent interactions between muscle proteins and phenolic compounds focusing on the role of protein thiol groups.
1: production of disulfide bond in redox reaction;
1′: adduction of quinone to -SH group in proteins;
2: formation of cross-linking by another protein binding to the phenol derivative;
3: formation of cross-linking through quinone–myoprotein adduct dimerization.

Case study

Several MP-dependent functional properties are the determinants of textural characteristics of muscle foods, of which gelation, emulsification, and water-binding are considered most important. In addition, film-forming properties are relevant to certain types of muscle-based foods. All these structure-related functional properties can be affected by their interaction with phytophenols.
Two principal fractions of MP with distinctive functionalities, MPf (fibrillary muscle) and gelatin, are the most studied for the interaction with phenolic compounds.



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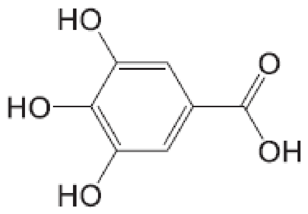
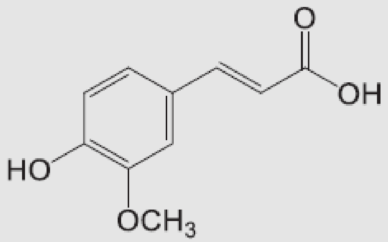
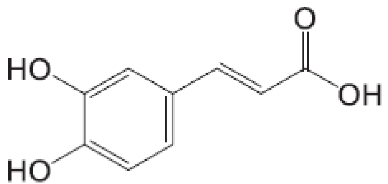
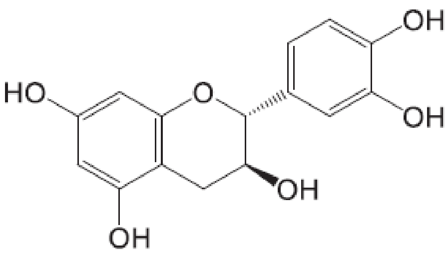
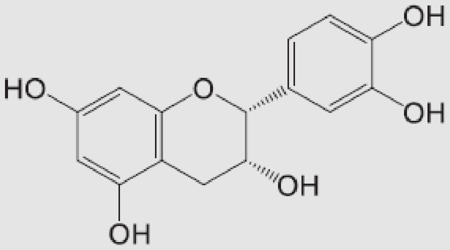
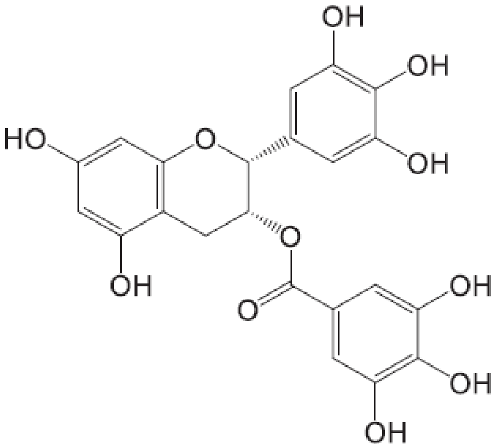
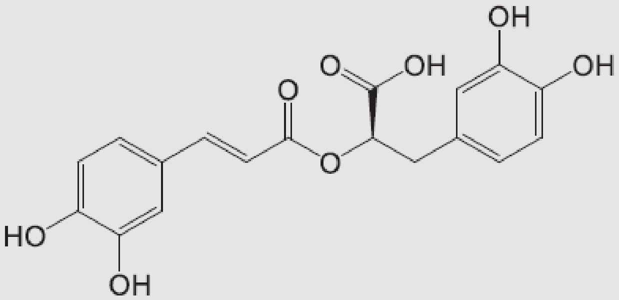
Phytophenol	Structure	Effect
Gallic acid		Improves porcine MP_f gelation and fish gelatin-based film formation
Ferulic acid		Improves fish MP_f and bovine gelatin-based film formation
Caffeic acid		Improves fish MP_f and fish gelatin-based film formation

Catechin		Improves fish MP$_f$-based film formation but impairs porcine MP$_f$ gelation
Epicatechin		Improves porcine MP$_f$ gelation
EGCG		Improves fish gelatin-based film formation but impairs porcine MP$_f$ gelation
Rosmarinic acid		Improves porcine MP$_f$ gelation but impairs emulsification

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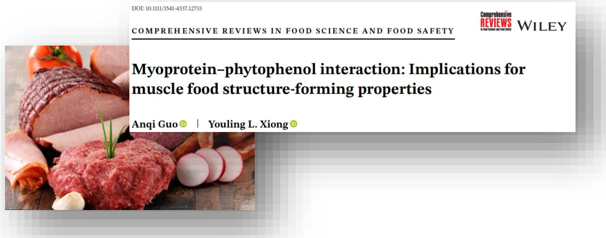

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Case study

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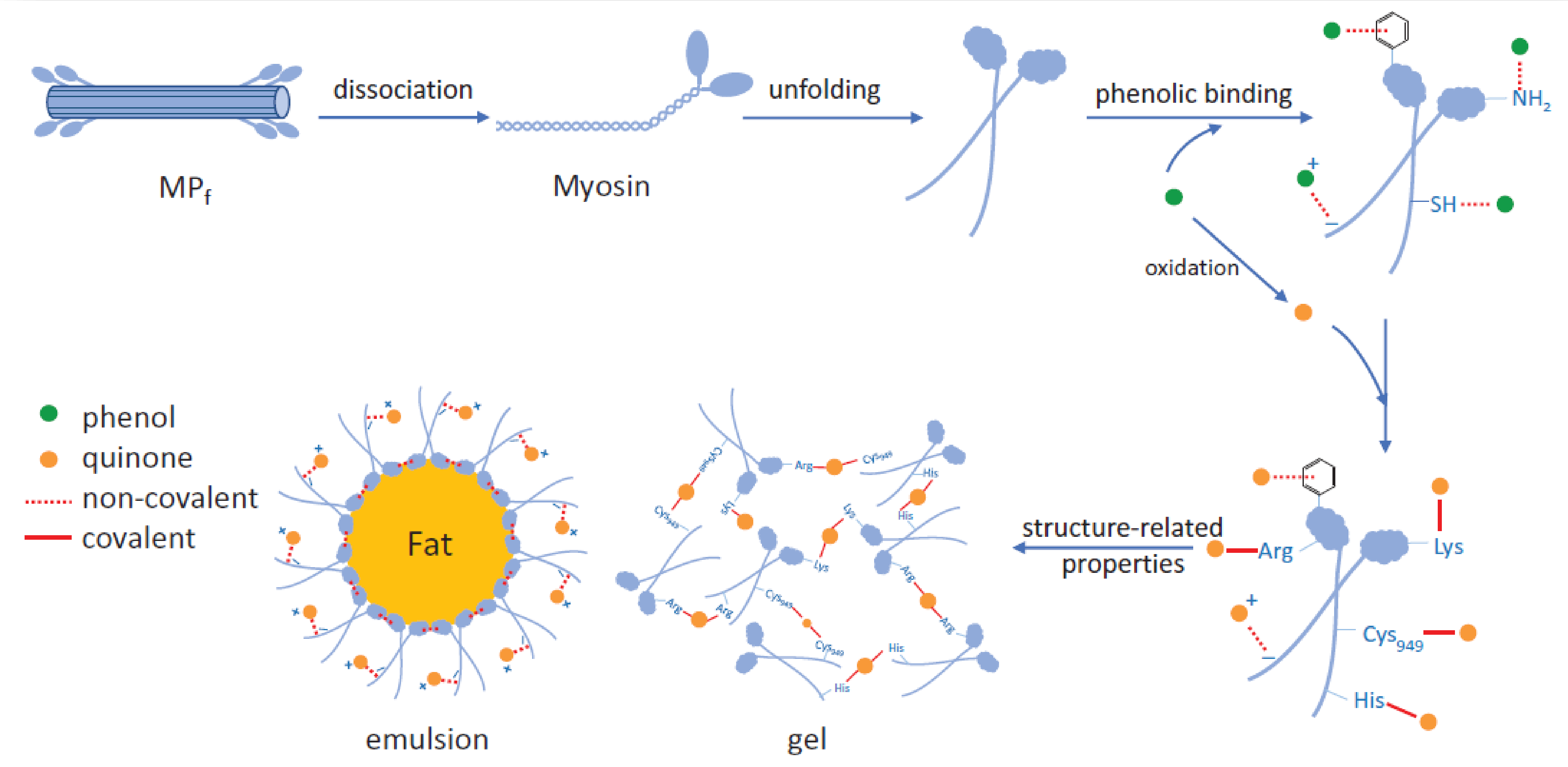


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Schematic presentation of myosin–phenol binding and the effect on structure-forming functionality in processed muscle food systems.

Case study

Gelation

MPf molecules undergo a series of structural changes during industrial transformation leading to denaturation, aggregation, cross-linking, and ultimately, the formation of a three-dimensional gel network. The interaction with phytophenols could modify MPf molecules physicochemical properties, affecting the association and cross-linking of protein molecules in the gelation process.

As shown in Figure during thermal gelation of MPf, the addition of gallic acid drastically increased the magnitude of the second G′ transition as well as the final G′ value on the plateau, indicating stronger myosin tail–tail interaction and formation of a more elastic gel network.

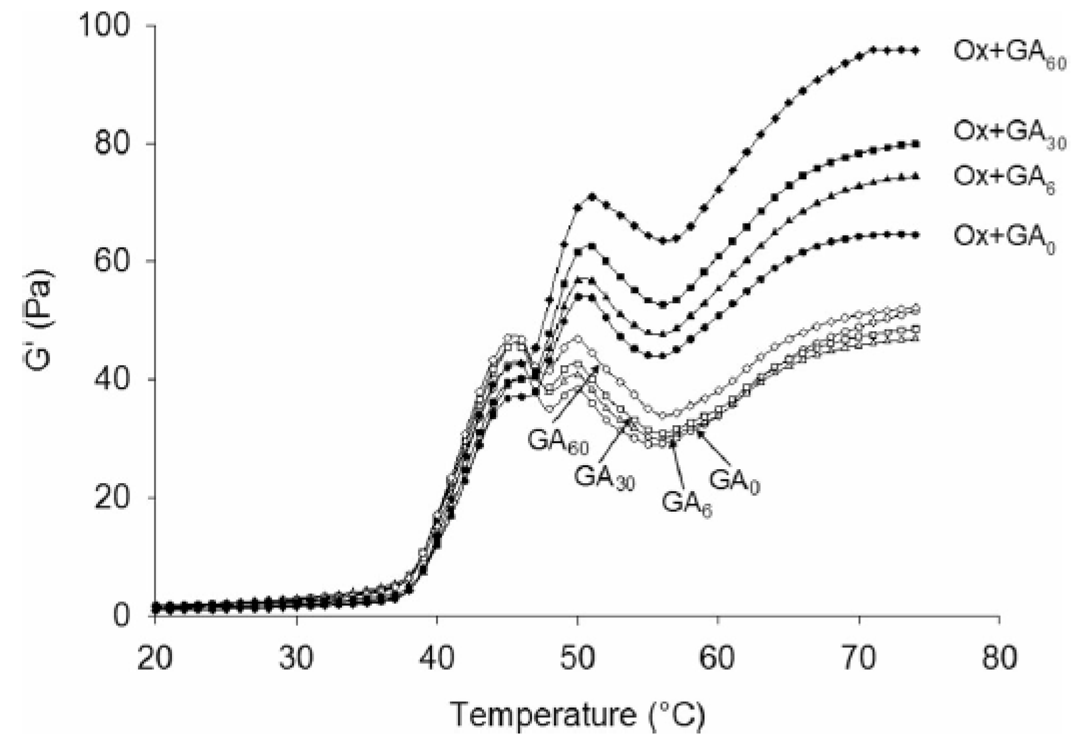

FIGURE 4 Storage modulus (G′) development during thermal gelation of myofibrillar proteins (MP_f) treated with various amounts of gallic acid (GA: 0, 6, 30, and 60 μmol/g MP_f) under nonoxidizing or oxidizing (Ox) conditions (Guo & Xiong, 2019)

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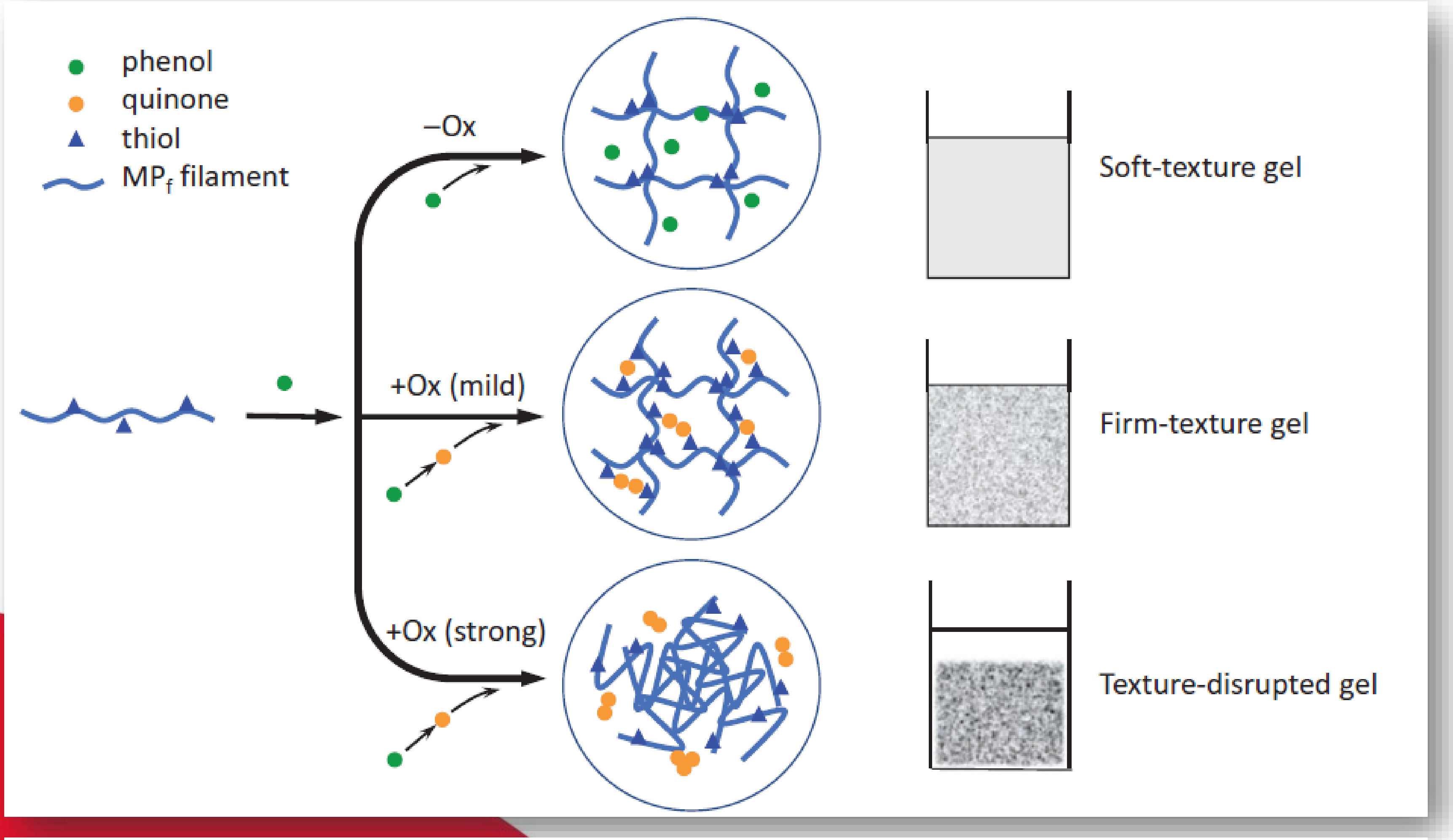
Case study



Proposed effects of quinones on thermal gelling properties of myofibrillar proteins (MPf) under different oxidative (Ox) conditions. Mild oxidation promotes gelation while strong oxidation disrupts the gel texture.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Case study

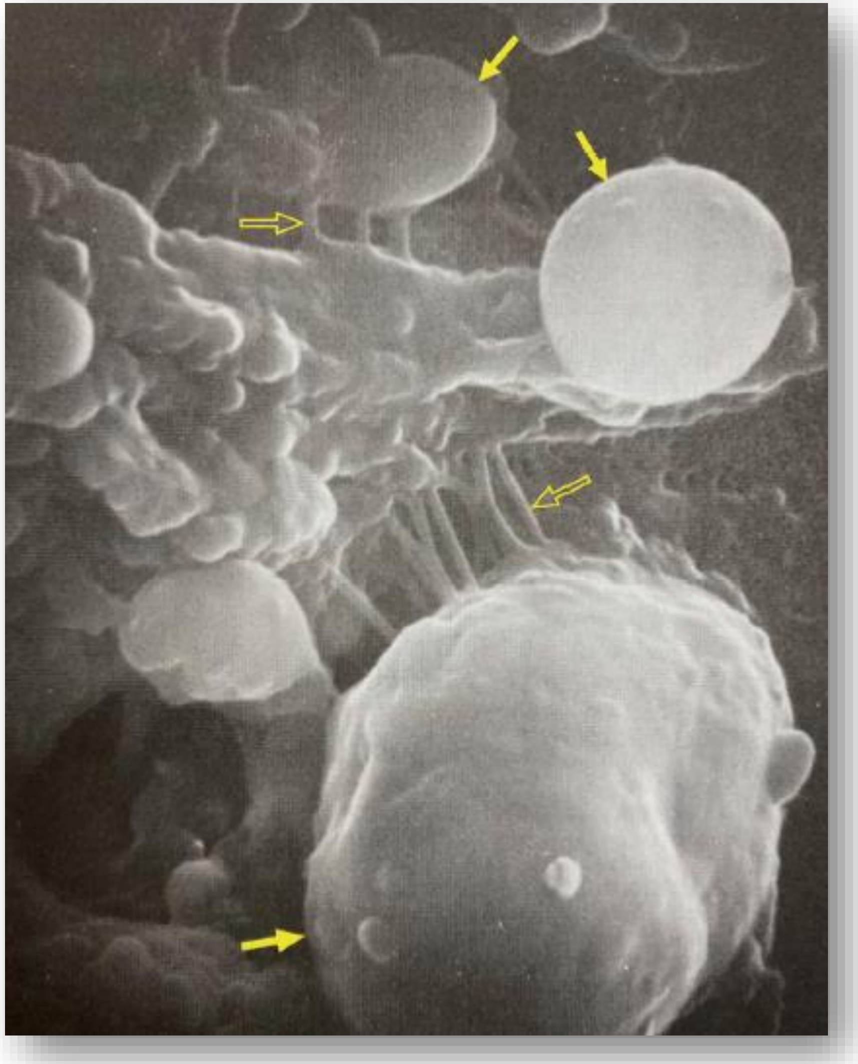
Emulsification

MPf are mostly amphiphilic macromolecules composed of hydrophilic and hydrophobic amino acid residues suitable for the formation of the interfacial membrane in emulsions.

In an oil-in-water (O/W) meat emulsion, fibrous myosin molecules are adsorbed as a monolayer at the interface where their nonpolar head anchors in the oil phase and the hydrophilic tail remains in the aqueous phase to thermodynamically stabilize the system.

Such structural orientations are applicable to other myofibrillar components.

The membrane formed in a typical meat emulsion (also referred to as batter, Figure) is unique in that the monolayer of myosin is overlaid with a relatively thick layer of additional MPf.



A scanning electron microscope micrograph of a frankfurter. The open arrows point to strands in the protein gel network and the solid arrows point to lipid droplets wrapped in a protein membrane.

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Case study

Emulsification

Compared to control protein, a MPf–phenol complex tends to be more easily adsorbed onto the oil/water interface and increases the surface charge of the protein membrane. This often leads to stronger electrostatic repulsions between particles hence a more stable emulsion with smaller oil droplets dispersed in the aqueous phase.


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