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Chemical Reactions and Stability of Riboflavin in Foods

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ABSTRACT: Riboflavin is relatively stable during thermal and nonthermal food processing and storage but is very sensitive to light. It can accept or donate a pair of hydrogen atoms. It can act as a photosensitizer (through either Type I or Type II mechanism) or a prooxidant for food components under light. Photosensitization of riboflavin causes production of reactive oxygen species such as superoxide anion, singlet oxygen, hydroxy radical, and hydrogen peroxide. Radicals and reactive oxygen species accelerate the decomposition of proteins, lipids, carbohydrates, and vitamins, and could cause significant nutrient loss in foods. Carbohydrates are less sensitive to riboflavin-photosensitized oxidation than proteins, lipids, or vitamins. Riboflavin is an excellent photosensitizer for singlet oxygen formation and a superb reactant for singlet oxygen, with the reaction rate of 1.01×10^{10}/M/s.

Keywords: riboflavin, stability, photosensitized oxidation, reactive oxygen species

Introduction

Riboflavin, vitamin B_2, is a yellowish compound present in most living systems. Riboflavin was isolated from whey more than 100 y ago, and riboflavin and/or flavin adenine dinucleotide were isolated from brewers' yeast in 1932 (Warburg and Christian 1932). It was suggested at that time that riboflavin played an important role in cell respiration. The first pure riboflavin was synthesized in 1934 (Kuhn and others 1935). Riboflavin is produced commercially by chemical synthesis or microbial fermentation (Bretzel and others 1999; Schwogler and others 2000). Of the annual riboflavin production of 3000 tons, 2500 tons are produced by microbial fermentation.

Riboflavin is an active part of the coenzymes of flavin mononucleotide and flavin adenine dinucleotide, which catalyze many oxidation-reduction reactions. These coenzymes have essential roles in several dehydrogenases and oxidases. Riboflavin can accept or donate a pair of hydrogen atoms. Riboflavin has complex photochemistry by light due to the ability of being easily reduced and oxidized by accepting and donating hydrogen or an electron.

When irradiated with visible or UV light, riboflavin can produce reactive oxygen species such as superoxide anion radicals, singlet oxygen, hydroxy radical, and hydrogen peroxide in the presence of atmospheric oxygen. The distribution of reactive oxygen species in a particular riboflavin-photosensitized system depends on the availability of oxygen, the concentration of riboflavin and other oxidizable substrates, and quenchers. Reactive oxygen species can cause not only the destruction of protein, carbohydrates, lipids, and vitamins but also the formation of off-flavor and loss of nutrients in foods (Huk and others 1998; Levine 2002; Min and Choe 2002; Lee and others 2003).

This review focuses on (1) the chemistry of riboflavin in foods, (2) the formation of reactive oxygen and riboflavin species under light, and (3) riboflavin-photosensitized oxidation of proteins, carbohydrates, lipids, and vitamins.

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Chemistry and Biological Functions of Riboflavin

Riboflavin has many conjugated double bonds and nitrogens in its ring structure, as shown in Figure 1. Riboflavin shows absorption maxima at 225, 275, 370, and 450 nm at pH 7 (Drossler and others 2003) and exists in cationic form (RFH_2^+) at low pH (<4.0), neutral form (RFH), and anionic form (RF^-) at high pH (>9.7).

Cationic riboflavin is non-fluorescent, the neutral form is fluorescent, and the anionic form is weakly fluorescent (Drossler and others 2002). The fluorescence quantum yield and lifetime of riboflavin depend on the solvent, pH, and presence of amino acids in the system (Drossler and others 2003). Riboflavin in organic protic solvent such as methanol gives a higher fluorescence quantum yield and longer lifetime than that in sulfur-containing organic solvent, such as dimethylsulfoxide, or in inorganic protic solvent such as water. The fluorescence of riboflavin is quenched by sulfur-containing amino acids such as methionine and cystein (Drossler and others 2003). The lifetime of riboflavin decreased as the concentration of methionine and cystein increased. Methionine quenches riboflavin fluorescence by formation of riboflavin anion-methionine cation pair in the ground state and excited state; this quenching is not pH-dependent in the range of about 5.25 to 9.0. Riboflavin fluorescence-quenching by cystein increases with pH increase. Cystein, present in thiolate form (RS^-) at high pH, reacts with neutral riboflavin; the riboflavin is deprotonated and in turn produces riboflavin anion and cystein in a thiol form (RSH; Drossler and others 2003).

Riboflavin is essential for normal growth and development of the body, production and regulation of certain hormones, and formation of red blood cells (Ajayi and others 1993). Riboflavin occupies an important position in metabolizing carbohydrates, lipids, and proteins and is crucial for production of biological energy in the electron-transport system. It is also necessary for the maintenance of good vision, skin, hair, and nails (Kirschmann 1996). It is involved in the use of neurotransmitters, which is associated with emotional well being and development of depression (Somer 1995). Deficiency of riboflavin is mainly manifested in the skin and mucous membranes, particularly through cracks and sores in the corners of the mouth, lesions of the lips, and a red and sore tongue. Visual disturbances such as a feeling of grit inside the eyelids, burning and fatigue of eyes, dilation of the pupil, changes

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in the cornea, and sensitivity to light may appear from riboflavin deficiency, and sometimes cataract results. Riboflavin should be consumed from the diet because it is not stored in the body. The recommended dietary reference intake of riboflavin is 1.1 to 1.6 mg/d depending on age, sex, pregnancy, and lactation (Institute of Medicine 1998). Milk, eggs, leafy vegetables, and soybeans are good source of riboflavin. Gliszczynska-Swiglo and Koziolowa (2000) reported that riboflavin contents were 1154 μg in 100 g egg powder, 310 μg, and 352 μg in raw egg white and raw egg yolk, respectively. Various milk products have riboflavin from 100 μg to 180 μg/100 g (USDA 2004).

Stabilities of Riboflavin

Processing effect

Riboflavin is relatively stable in dehydration, γ-irradiation, and various food-storage conditions (Farrell and Fellers 1942). Riboflavin in dehydrated fruits and vegetables was quite stable even after being stored for a year at 54 °C. Riboflavin was stable when carotene, ascorbic acid, and thiamin were not stable in dehydrated foods packed in metal containers with air, with N_2 or with CO_2, and in paper cartons for 1 y at 54 °C (Heberlein and Clifcorn 1944). Riboflavin in milk powder was relatively stable at 60 °C when folic acid, thiamin, vitamin B_6, and pantothenic acid were rapidly destroyed.

Riboflavin in cod fish fillets was reduced 6% by irradiation and 9% by cooking (Kennedy and Ley 1971). Riboflavin in prawn did not significantly change after γ-irradiation up to 7 kGy and even after post-irradiation heating at 100 °C for 10 min (Lee and Hau 1996). Riboflavin is normally bound to proteins, which protects the prosthetic groups from being attacked directly or indirectly by γ-irradiation. The level of riboflavin remained largely unchanged in most foods during 18 mo at 37 °C (Brenner and others 1948).

Riboflavin stability is affected by oxygen, other components such as metal sulfates or amino acid chelates, and water activity. When oxygen was present during storage, the destruction rate of riboflavin increased dramatically (Dennison and others 1977). When riboflavin was mixed with metal sulphates, riboflavin was significantly ($P < 0.01$) deteriorated at 37 °C during 90 to 180 d of storage (Marchetti and others 2000). However, riboflavin stability was not affected by metal chelates. Water activity (A_w) plays an important role in riboflavin stability in a low-moisture dehydrated model food system. Riboflavin retention at A_w 0.1 to 0.65 at 20 °C and A_w 0.1 to 0.40 at 30 °C was almost 100% after 8 mo. Riboflavin loss increased with increasing A_w (Dennison and others 1977; Furuya and others 1984). Other components in food may also affect the riboflavin degradation rates. For example, the rate of riboflavin loss was lower in whole milk than in skim milk. Addition of 1% nonfat dry milk to skim milk seems to slow down the riboflavin degradation (Gaylord and others 1986).

Agitation and sample location had significant impact on riboflavin loss under light storage condition. After 5 d of light exposure, riboflavin retention at the top of the unagitated milk containers averaged 58%. On the other hand, 92% of the riboflavin retention was found for milk located at the bottom of the containers (Palanuk and others 1988).

The effect of soaking and soaking plus cooking on riboflavin retention seemed to be raw material–specific (Prodanov and others 2004). Riboflavin content in legumes after different pH soaking and soaking plus cooking treatment did not have significant effect on the riboflavin retention in Faba beans. Although the different pH soaking did not show any effect on the riboflavin retention, the treatment of soaking plus cooking did cause a significant amount of riboflavin loss in chickpeas. In lentils, on the other hand, soaking treatment significantly increased the content of riboflavin, which was believed to be caused by microbial activity. After soaking plus cooking, the riboflavin content in lentils remained high (Prodanov and others 2004).

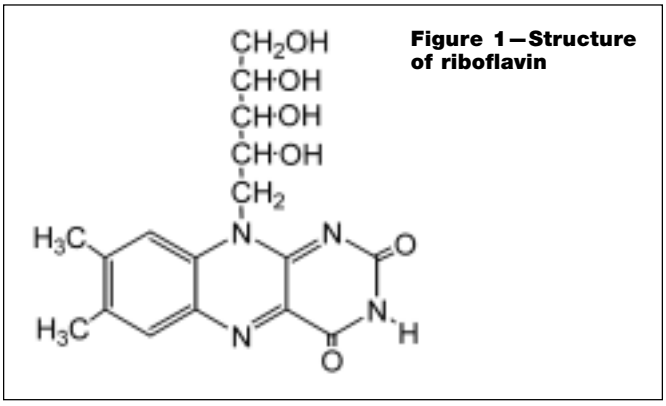

Figure 1—Structure of riboflavin

Heat effect

Heating processes barely affect the riboflavin in foods. A high amount of riboflavin in roasted pork was retained after a heating process that significantly destroyed other vitamins (Lassen and others 2002). Ang and others (1975) reported that riboflavin retention was independent of heating methods such as hot air convection, infrared, high-pressure steam, or microwave. The rate constants for riboflavin degradation in open pan cooking, pressure cooking, and a fuel-efficient "Eco-cooker" cooking for green gram whole (*Vigna radiata L.*) were very similar, which were 7.1×10^{-3}, 6.6×10^{-3}, and 7.0×10^{-3}, respectively (Nisha and others 2005). Riboflavin is more heat-stable and less temperature-sensitive than thiamin (Kwok and others 1998). Thermal degradation of riboflavin in soymilk followed the 1st order and the rates were 7.05×10^{-4}, 4.26×10^{-3}, and 2.12×10^{-2}/ min at 90 °C, 120 °C, and 140 °C, respectively. The D values of riboflavin at 90 °C, 120 °C, and 140 °C were 3268, 540, and 109 min, respectively, and the Z value was 36 °C (Kwok and others 1998).

Light effect

Although it is heat-stable, riboflavin is very sensitive to light. Under dark condition, riboflavin in enriched pasta was extremely stable (Kamman and others 1981). In the presence of light, however, the degradation of riboflavin was much more significant. Milk lost 30% of its riboflavin to sunlight exposure and only 12% to boiling for 30 min (Wishner 1964). In macaroni, >50% of the riboflavin content was lost within 1 d. Light intensity was the rate-determining factor for the riboflavin loss (Woodcock and others 1982). When pasta samples were exposed to light, it only took 2 d to lose 57.8% to 64.3% of riboflavin (Furuya and Warthesen 1984). Furuya and others (1984) reported that the riboflavin photodegradation in dried macaroni and nonfat dried milk was a 2-phase mechanism that includes an initial rapid degradation followed by slow loss of riboflavin under light. Both phases showed 1st-order degradation. Riboflavin photodegradation followed the 1st-order degradation mechanism in liquid systems such as skim milk and a buffered solution of riboflavin. Riboflavin loss by light was dependent on light intensity, exposure time, and wavelength; packaging materials; and food processing. Sunlight was more detrimental to riboflavin than fluorescent light. Light at 450 nm, the absorption maximum of riboflavin, was the most destructive to riboflavin. Riboflavin in milk in a clear bottle or white sachet was lost faster than riboflavin in milk packed in a brown bottle or car-

ton (Satter and deMan 1975; Bekbolet 1990). Heat treatment and homogenization increased the photostability of riboflavin in milk by light absorption or scattering by changing some of the physicochemical properties of milk (Saidi and Warthesen 1995).

Wold and others (2002) reported that riboflavin in cheese decreased 25% after 100-d storage under light. However, our preliminary study showed that the riboflavin on the cheese surface was almost completely destroyed, whereas the riboflavin content inside the cheese did change only slightly during light storage for 1 mo.

Riboflavin as Photosensitizer: Reactive Oxygen and Riboflavin Species Formation

Riboflavin is a well-known photosensitizer. The excitation and deactivation of riboflavin under light is shown in Figure 2.

During Type II photosensitization (Figure 3), excited triplet riboflavin, which is diradical, reacts with triplet oxygen having unpaired electrons and produces superoxide anion by electron transfer or singlet oxygen by energy transfer (Min and Boff 2002). The reaction rate of triplet state riboflavin with triplet oxygen is 9×10^8 /M/s (Lu and others 2000). Formation of superoxide anion by interaction between triplet riboflavin and triplet oxygen is very low (Kepka and Grossweiner 1972). Bradley and others (2003) proved the formation of singlet oxygen by riboflavin under light by electron spin resonance spectroscopy. Singlet oxygen productions by lumiflavin and lumichrome at 320 to 400 nm were 15% higher and 60% lower, respectively, than riboflavin (Joshi 1989).

Triplet riboflavin is frequently reduced by abstraction of electrons or hydrogen atom from food components (R'H) and produces anionic riboflavin radical (RF•) and reduced riboflavin radical (RFH_2•). This is called the radical or Type I photosensitization mechanism.

Reactive oxygen species such as singlet oxygen and superoxide anion are formed from triplet oxygen in the presence of riboflavin under light (Jernigan 1985; Bradley and Min 1992; Naseem and others 1993). Superoxide anion can form hydrogen peroxide by dismutation. The reaction of superoxide anion and hydrogen peroxide produces hydroxy radical by Haber-Weiss reaction (Haseloff and Ebert 1989).

$$O_2^{\cdot-} + O_2^{\cdot-} \xrightarrow{\text{Dismutation}} H_2O_2 + {}^1O_2$$

$$H_2O_2 + O_2^{\cdot-} \xrightarrow{\text{Haber-Weiss reaction}} O_2 + OH^- + HO^{\cdot}$$

Mechanisms for the Light Sensitivity of Riboflavin

The light sensitivity of riboflavin has been extensively studied and well known for more than 60 y, but the detailed chemical mechanisms for light sensitivity of riboflavin have not been discussed. The hydroxy radical, superoxide anion, singlet oxygen, riboflavin cationic and anionic radicals that are formed by photosensitized riboflavin, can be involved in the destruction of riboflavin in foods.

Hydroxy radical, which has a reduction potential of 2300 mV, is one of the strongest oxidizing agents among reactive oxygen species in foods. Hydroxy radical is also a strong electrophilic molecule and can easily react with food compounds containing double bonds. Hydroxy radical can react with any food compounds, and the reaction rate is in the order of 10^9 or 10^{10}/M/s, which is the diffusion-controlled reaction rate (Hoffman and Hayon 1973; Solar and others 1984; Motohashi and Saito 1993; Zhao and others 1994). The reaction rate of riboflavin with hydroxy radical is 1.2×10^{10}/M/s (Kishore and others 1991).

Singlet oxygen formed by photosensitized riboflavin can contribute to riboflavin degradation in foods. Riboflavin can directly react with electrophilic singlet oxygen due to its many double bonds (Allen and Parks 1979). The reaction rate of riboflavin with singlet oxygen ranges from 6×10^7 /M/s (Chacon and others 1988) to 1.01×10^{10} /M/s (Huang and others 2004), depending on the solvent involved in the experiments. Sodium azide, a singlet oxygen quencher, reduced the riboflavin-sensitized oxidation of riboflavin (Lee and others 1998). Storage temperature did not affect riboflavin photodegradation, which suggests such degradation is due to singlet oxygen oxidation (Kristensen and others 2001). Long and Kearns (1975) reported that temperature dependence of singlet oxygen decay was very small. Riboflavin is photodegraded faster in D_2O than in H_2O, which indicates that singlet oxygen is involved in the degradation of riboflavin in the riboflavin photosensitization (Huang and others 2004). The lifetime of singlet oxygen in D_2O is about 13 times longer than in H_2O (Rodgers and Snowden 1982; Li 1997).

When excited triplet riboflavin reacts with other excited or ground state riboflavin molecules, riboflavin cationic ($RFH?^+$) and anionic radicals (RF•) are produced, as shown in Figure 4. This one electron oxidation of riboflavin occurs at the C-8 methyl group and at the extended π–electron system (Lu and others 1999). The radicals formed can react with triplet oxygen, and the electron transfer caused by riboflavin radicals may be important in the photochemistry and destruction of riboflavin.

$$RFH_2\bullet + O_2 \rightarrow \text{Oxidized riboflavin}$$

The excited diradical triplet state riboflavin can be converted to deuteroflavin by oxidation or form an N_1-N_{10} bridged leucodeuteroflavin by proton exchange as shown in Figure 5.

The polyhydroxy-containing ribityl group in riboflavin is easily cleaved under light (Shuping and others 2001). Fragmentation be-

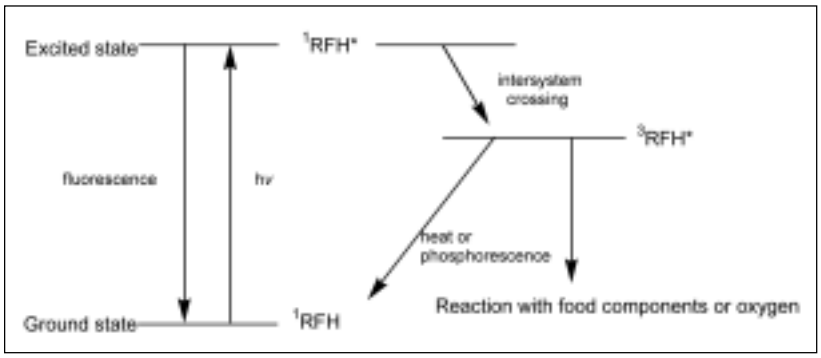

Figure 2—Excitation and deactivation of riboflavin under light

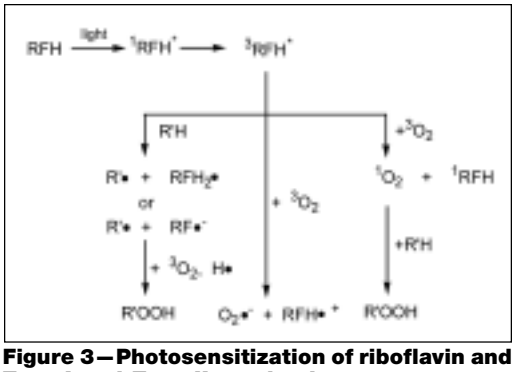

Figure 3—Photosensitization of riboflavin and Type I and Type II mechanisms

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tween N 10 and C 1' in excited triplet riboflavin produces lumichrome and lumiflavin upon exposure to sunlight and UV light, as shown in Figure 6 (Allen and Parks 1979; Joshi 1989; Cui and others 2001). Riboflavin transforms mainly to lumichrome through removal of the ribityl group and reconfiguration of a double bond in the ring structure in neutral and acid solutions. The triplet riboflavin transforms to lumiflavin in alkaline solution (Pan and others 2001). Lumichrome and lumiflavin are stable to UV irradiation (Shuping and others 2001). Photoreduction and photodealkylation occur predominantly through the excited triplet state of riboflavin.

Riboflavin Photosensitized Oxidation of Food Components

Triplet riboflavin has a higher reduction potential than amino acids, proteins, lipids, and many vitamins, and can induce food components to photodegrade (Silva and others 1998; Lu and others 2000). The reduction potentials of triplet riboflavin and electron-deficient cation radical of riboflavin ($RFH^{\bullet+}$) are 1.7 V and 2.28 V, respectively (Lu and others 1999). These riboflavin radicals are very strong oxidizing species.

Amino acids and proteins

Aliphatic amino acids produce carbon dioxide and an aldehyde by riboflavin-photosensitized oxidation (Figure 7). This reaction is very similar to the Strecker degradation reaction of amino acid.

It was reported that tyrosine and tryptophane in distilled water were oxidized in the presence of riboflavin at 7.5×10^{-6} *M* under light. Reduction potentials of triplet riboflavin, tyrosine, and tryptophane are 1.70 V, 0.93 V, and 1.01 V, respectively (Lu and Liu 2002). At a low oxygen concentration of 5%, excited triplet riboflavin reacts with tyrosine (TyrOH) and produces riboflavin radicals ($RFH_2^{\bullet}$) and oxidized radicals of tyrosine (TyrO•) via electron transfer by Type I mechanism (Garcia and Silva 1997; Viteri and others 2003).

$$^3RFH^* + TyrOH \rightarrow RFH^{\bullet-} + TyrOH^{\bullet+}$$
$$RFH^{\bullet-} + TyrOH^{\bullet+} \rightarrow RFH_2^{\bullet} + TyrO^{\bullet}$$

Photooxidation of tryptophane in the presence of riboflavin followed both Type I and Type II pathways. Type II is favored in riboflavin-sensitized oxidation of tryptophane at high oxygen concentration under light. Hydroxy radical and singlet oxygen were responsible for tryptophan photooxidation by riboflavin. Tryptophane, tyrosine, and histidine have electron-rich double bonds and are excellent reactants for singlet oxygen oxidation.

The main photoproducts of tyrosine and tryptophane are bityrosine and a mixture of indole-, flavin-, and indole-flavin-type aggregates, respectively. The reaction rate of riboflavin-photosensitized tryptophane oxidation is $4.19 \pm 1.85 \times 10^{-16}$ mol/s/mm^2 (Rochette and others 2003). Tryptophane degradation by riboflavin photosensitization increased with oxygen concentration up to 40 μM oxygen, and then decreased (Rochette and others 2000). Tyrosine and tryptophane are also degraded in the presence of riboflavin during illumination under nitrogen. Ascorbic acid reduces the tryptophane photooxidation by interacting with excited triplet riboflavin (Garcia and Silva 1997).

Peptides containing tryptophane were oxidized rapidly at pH 7.5 in the presence of 21 μM riboflavin and fluorescent light, mostly by singlet oxygen. The oxidation rate was higher when tryptophane was bound on the carboxyl side in dipeptide than when it was bound to the amino side. In tripeptide containing tryptophane, the oxidation rate was highest when tryptophane is in the carboxyl side and lowest when tryptophane is in the middle of a tripeptide (Kanner and Fennema 1987).

Histidine and methionine in distilled water were photooxidized by visible light in the presence of riboflavin at 7.5×10^{-6} *M* by Type II mechanism (Paine and Francis 1980).

Aspartame, a sugar replacement and methyl ester of the dipeptide aspartyl phenylalanine, is destroyed by riboflavin and light

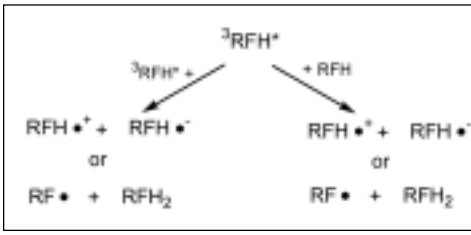

Figure 4—Formation of riboflavin cationic and anionic radicals

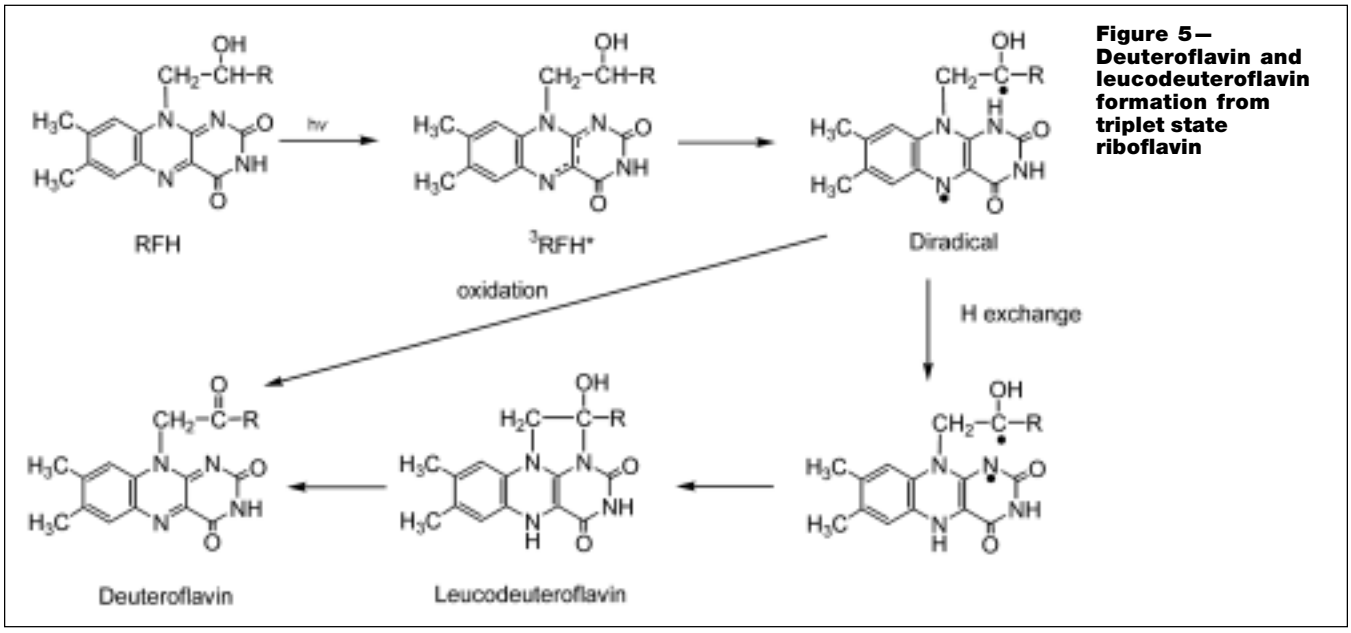

Figure 5—Deuteroflavin and leucodeuteroflavin formation from triplet state riboflavin

(Kim and others 1997). The photosensitizing activity of riboflavin for aspartame destruction was pH-dependent; aspartame destruction was high at pH 7, but no significant photosensitization by riboflavin at pH 4 and 6.

Collagen is cross-linked by riboflavin-photosensitized reactions (Kato and others 1994). The aggregation of collagen due to cross-linkage was accompanied by the loss of tyrosine and histidine residues in the collagen. Tyrosine (TyrOH) reacts with hydrogen peroxide formed by riboflavin and produces phenoxyl radicals (TyrO•) and finally bityrosine by radical-radical coupling (Pichorner and others 1995).

$$2\,\mathrm{TyrOH} + \mathrm{H_2O_2} \rightarrow 2\,\mathrm{TyrO\bullet} + 2\,\mathrm{H_2O}$$
$$\mathrm{TyrO\bullet} + \mathrm{TyrO\bullet} \rightarrow \mathrm{TyrO\text{-}OTyr\ (bityrosine)}$$

Enzymes

The photosensitized modification of proteins by riboflavin often inactivates enzymes. Reactive oxygen species formed by photosensitized riboflavin cause cross-links in enzymes, the protein denaturation and finally loss of enzymatic activities. Singlet oxygen quenchers such as α-tocopherol acetate, β-carotene, sodium azide, and ascorbic acid can prevent protein cross-linking and photoinactivation of enzymes (Dalle Carbonare and Pathak 1992). Catalase and lysozyme were inactivated by Type I and Type II mechanisms (Edwards and Silva 2001). Among 20 amino acids present in lysozyme, only tryptophane, tyrosine, and histidine were modified by riboflavin-induced photochemical damage (Edwards and Silva 2001). Visible light irradiation on horseradish peroxidase in the presence of riboflavin decreased the enzyme activity only when the enzyme was deglycosilated.

Lipids

Riboflavin can photosensitize the *cis-trans* isomerization of olefinic compounds. Lipid oxidation sensitized by riboflavin is another important factor in the development of light-induced flavor, although the rate of lipid degradation photosensitized by riboflavin is relatively low compared with protein (Aurand and others 1966; Dimick 1982). Unsaturated fatty acids or esters are efficiently photooxidized in the presence of riboflavin derivative, riboflavin-2', 3', 4', 5'-tetraacetate, by the Type II mechanism (Fukuzumi and others 1989). Polyunsaturated fatty acids such as linoleic acid in lipid foods containing riboflavin or in milk products can be easily oxidized under light by singlet oxygen produced by triplet riboflavin (Figure 8). The reaction rate of singlet oxygen with linoleic acid is about 1450 times faster than triplet oxygen free radical oxidation (Rawls and Van Santen 1970).

Vegetable oils do not contain riboflavin, and there is no practical problem from the photosensitized oxidation of vegetable oils by riboflavin. Oxygen uptake by fish oil under light was higher in the presence of riboflavin than in the absence of riboflavin. Riboflavin had no effect on the oxygen uptake of fish oil stored in the dark. Fish oil is oxidized in the presence of riboflavin under light via Type II mechanism (Davis and others 1995).

Riboflavin and lumiflavin can undergo a facile photooxygenation of cholesterol derivatives in acetonitrile and pyridine and produce 6-en-5a'- hydroperoxide and 5-en-7- hydroperoxide. Singlet oxygen formed by riboflavin or lumiflavin is added to the double bond of cholesterol and adjacent double bond is migrated as shown in Figure 9 (Shuping and others 2001).

The yields of 6-en-5a'- hydroperoxide and 5-en-7- hydroperoxide varied depending on the experimental conditions (Shuping and others 2001). More 6-en-5a'- hydroperoxide (90%) was produced when cholesterol was reacted in acetonitrile in the presence of riboflavin and oxygen under light. However, when lumiflavin is used as a photosensitizer, cholesterol in pyridine and acetonitrile produced more 6-en-5a'- hydroperoxide (86%) and 5-en-7- hydroperoxide (80%), respectively.

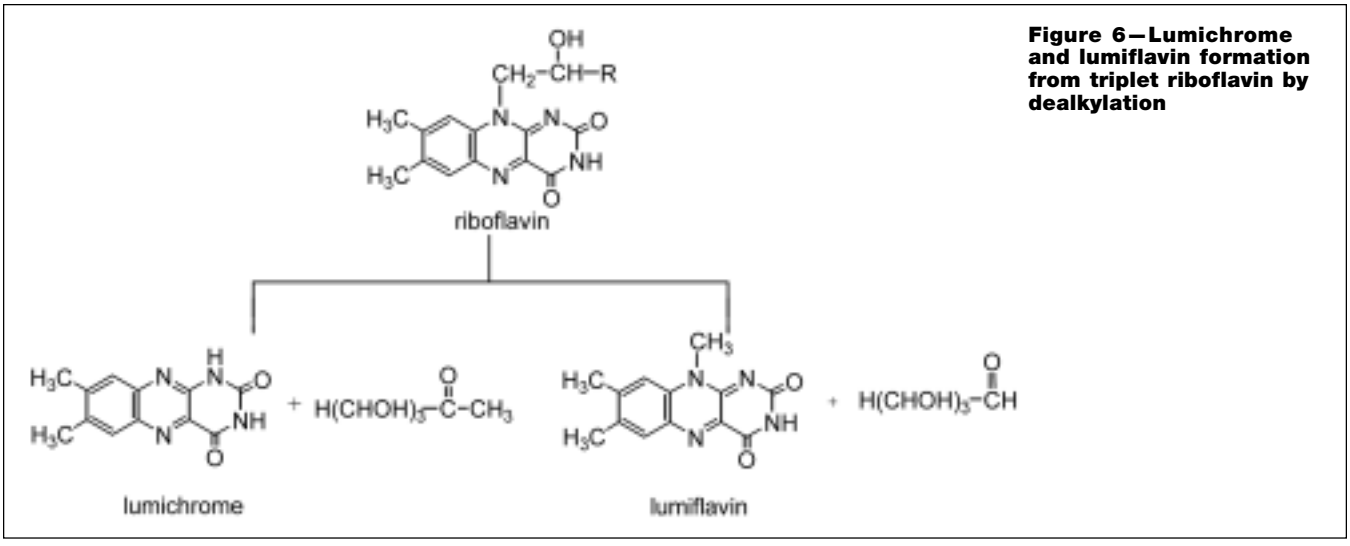

Figure 6—Lumichrome and lumiflavin formation from triplet riboflavin by dealkylation

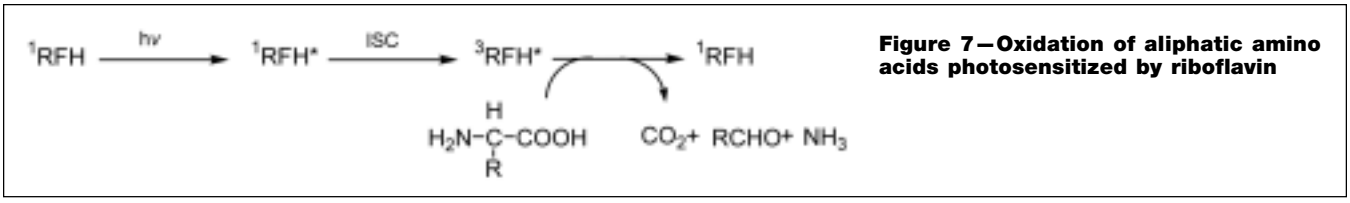

Figure 7—Oxidation of aliphatic amino acids photosensitized by riboflavin

Carbohydrates

Carbohydrates are relatively insensitive to photooxidation compared with lipids and proteins (Silva and others 1999; Min and Boff 2002). Riboflavin stimulates the oxidation of glucose under visible light via reactive oxygen species such as singlet oxygen, superoxide anion, hydrogen peroxide, and hydroxy radical (Goodman and Hochstein 1981; Silva and others 1999). The light dependency of glucose oxidation was not affected by catalase or superoxide dismutase, but was inhibited by a singlet oxygen scavenger (Goodman and Hochstein 1981). Photooxidation of glucose depends on riboflavin concentration, pH of the reaction medium, and glucose concentration (Silva and others 1999). Photooxidation of glucose is directly proportional to the concentration of excited riboflavin. At riboflavin concentrations of 10^{-6} *M*, glucose oxidation was stimulated by approximately 30%. When riboflavin concentration was higher than 10^{-5} *M*, light greatly enhanced the oxidation of glucose by 2- to 3-fold. Higher pH favors the glucose photooxidation by riboflavin under oxygen. Oxidation rate of glucose photosensitized by riboflavin at pH of 4.0, 7.0, and 10.0 were 3.79×10^{-3}, 8.30×10^{-3}, and 5.50×10^{-2} m*M* oxygen/min, respectively. Riboflavin acts preferentially as Type I sensitizer at a high glucose concentration of 20% (Silva and others 1999).

Vitamins

Riboflavin-photosensitized oxidation causes destruction of vitamin A, vitamin C, vitamin D, and vitamin E. Vitamin A and its esters in milk are destroyed by sunlight exposure with ring opening (DeMan 1981). Vitamin A loss increased with the length and intensity of light exposure, but decreased with the fat content of milk (Whited and others 2002). The oxidation products of vitamin A in the presence of riboflavin and oxygen under light were ethyl-(2, 6, 6-trimethylcyclohex-1-ene) carboxylate, retinal, 5, 8-peroxide of β-ionone, 5, 6-peroxide of vitamin A, and retinoic acid, as shown in Figure 10. Photooxidation of the palmitate ester of vitamin A sensitized by riboflavin causes cleavage of its side chain double bonds and produces aldehyde compounds.

Ascorbic acid is an excellent antioxidant, which does not absorb visible light. However, it is rapidly photooxidized with a high consumption of oxygen in the presence of riboflavin. The photooxidation of ascorbic acid by riboflavin proceeds essentially via Type I process, and the oxidation products of ascorbic acid contain carbonyl group (Rocchette and others 2000). Photodecomposition of ascorbic acid by riboflavin under oxygen also involves singlet oxygen (Sahbaz and Somer 1993; Jung and others 1995). The reaction rate of singlet oxygen with ascorbic acid is higher than that with α-tocopherol (Jung and others 1991), but is lower than that with β-carotene (Jung and Min 1991). Photosensitizing activity of riboflavin on ascorbic acid oxidation is higher than that of methylene blue, rose bengal or protoporphyrin IX. The relative photosensitizing activity of riboflavin, methylene blue, and protoporphyrin IX in photooxidation of ascorbic acid was reported as 21:15:1 (Jung and others 1995).

Photodegradation of ascorbic acid by riboflavin sensitization under oxygen depends on the light intensity, concentration of riboflavin, oxygen, and ascorbic acid, temperature, pH of the reaction media, and presence of other components (Sahbaz and Somer 1993; Jung and others 1995; Sansal and Somer 1997; Rochette and others 2000). Riboflavin-sensitized oxidation of ascorbic acid increases with the light intensity and concentration of riboflavin (Jung and others 1995). As riboflavin concentration in 0.01 *M* potassium phosphate buffer (pH 7.5) increased from 0 to 1.2, 2.4, 3.6, and 6.0 ppm, 2.1%, 35.4%, 58.3%, 74.0%, and 89.6% ascorbic acid were lost after 6 min of illumination. In an anaerobic environment, ascorbic acid photooxidation is negligible; however, it sharply increased when increasing oxygen pressure and was maximal at 100% oxygen (Rochette and others 2000). Decomposition of ascorbic acid in the presence of riboflavin under light increased with ascorbic acid (H_2A) concentration, especially the concentration of ascorbate ion, and temperature (Sansal and Somer 1997). Singlet oxygen oxidation of ascorbic acid occurs slowly at lower pH. The rate constant for the reaction of ascorbic acid with singlet oxygen at pH 7.5, 6.0, and 4.5 were 6.63×10^8, 5.77×10^8, and 5.27×10^8 /M/s, respectively (Jung and others 1995). Yang and Min (1994) reported that the reaction rate for the ascorbic acid with singlet oxygen was 3.08×10^8 / M/s in an aqueous solution of pH 7 and 25 °C.

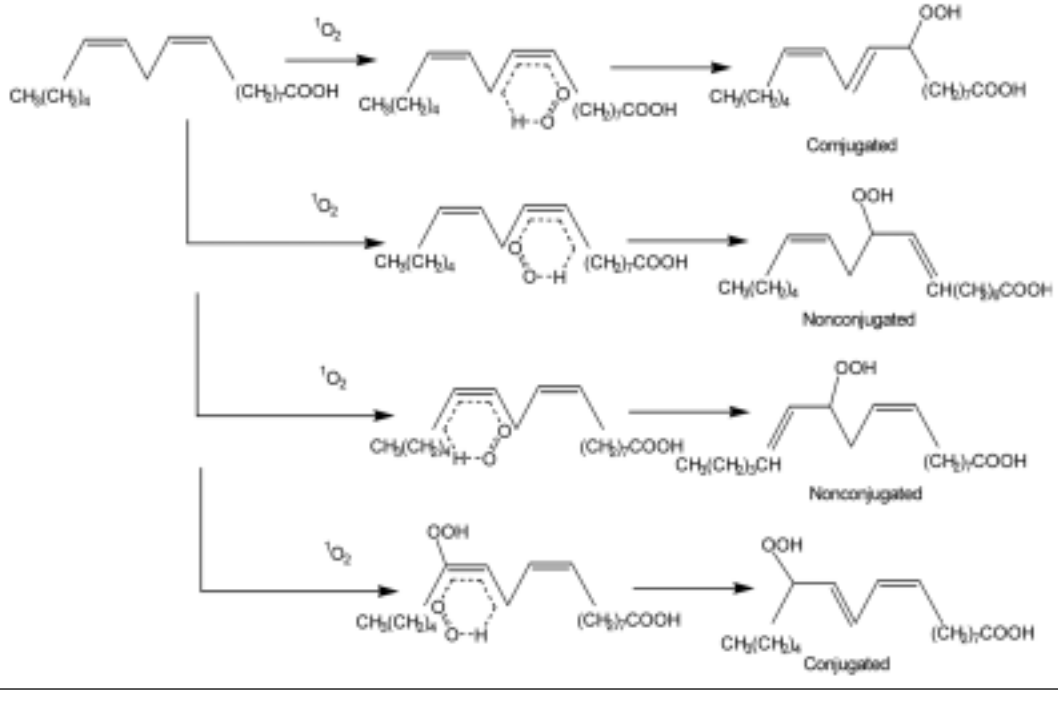

Figure 8—Singlet oxygen oxidation of linoleic acid

Sansal and Somer (1997) proposed that riboflavin associates with ascorbic acid. In the presence of riboflavin and light, ascorbic acid (H_2A), ionized to ascorbate ion (HA^-) in citrate buffer at pH 4.5, is decomposed via radical pathway (Sansal and Somer 1997) as shown in Figure 11. Complex of riboflavin and ascorbate can produce riboflavin radical and ascorbic acid radical upon irradiation. Two moles of ascorbic acid radical produce dehydroascorbic acid (A) or direct reaction between excited triplet riboflavin and ascorbic acid can produce dehydroascorbic acid.

Riboflavin accelerated the oxidation of vitamin D under light via singlet oxygen pathway (Li and Min 1998; Li and others 2000), and major oxidation product was 5, 6-epoxide of vitamin D (King and Min 2002). Riboflavin had no effect on the vitamin D oxidation in the dark (King and Min 1998). The reaction rate constant of vitamin D with singlet oxygen produced by riboflavin was 2.2×10^7 /M/s (Li and others 2000). Vitamin D degradation caused by singlet oxygen was independent of temperature. However, degradation of vitamin D caused by triplet oxygen under light and in the dark was temperature-dependent (Li and others 2000).

Effects of Riboflavin on Sunlight Flavor Milk

Sunlight flavor formation in milk has been recognized and extensively studied. The sunlight flavor is generally described as sulfur flavor. Methionine was proposed for the formation of sunlight flavor of milk in the presence of riboflavin (Patton and Josephson 1953). They reported that methional and dimethyl sulfide were the compounds responsible for sunlight flavor. The mechanisms for the formation of sunlight flavor have been very controversial. Singlet oxygen is formed from molecular triplet oxygen in the presence of riboflavin in milk under sunlight. Jung and others (1998) reported that singlet oxygen reacts with electron-rich sulfur in methionine to form hydroperoxide. The hydroperoxide on sulfur is decomposed to methional and thiomethyl radicals shown in Figure 12. Reaction between thiomethyl radicals produces dimethyl disulfide. Contents of dimethyl disulfide were highly correlated with the sunlight flavor sensory score (Jung and others 1998). The proportion of methional increases under the nonaqueous solvent (Foote 1976). Addition of ascorbic acid reduced dimethyl disulfide formation in milk and improved the sensory quality of milk (Jung and others 1998). The ascorbic acid is a good singlet oxygen quencher.

Conclusions

Riboflavin is relatively stable during food processing and storage except under light, where it absorbs light energy and produces excited triplet state riboflavin. The excited triplet riboflavin produces riboflavin radicals and reactive oxygen species such as superoxide anion by Type I and singlet oxygen by Type II pathway. Reactive oxygen species accelerate the oxidation of food components and cause

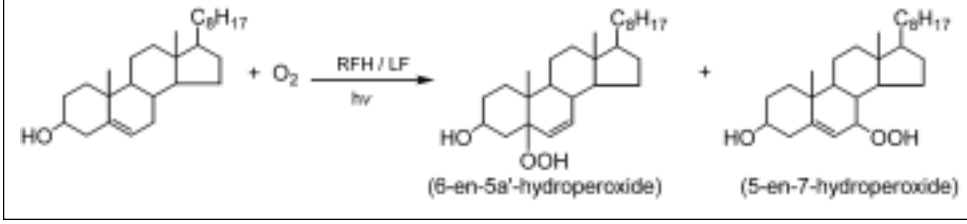

Figure 9—Cholesterol oxidation photosensitized by riboflavin

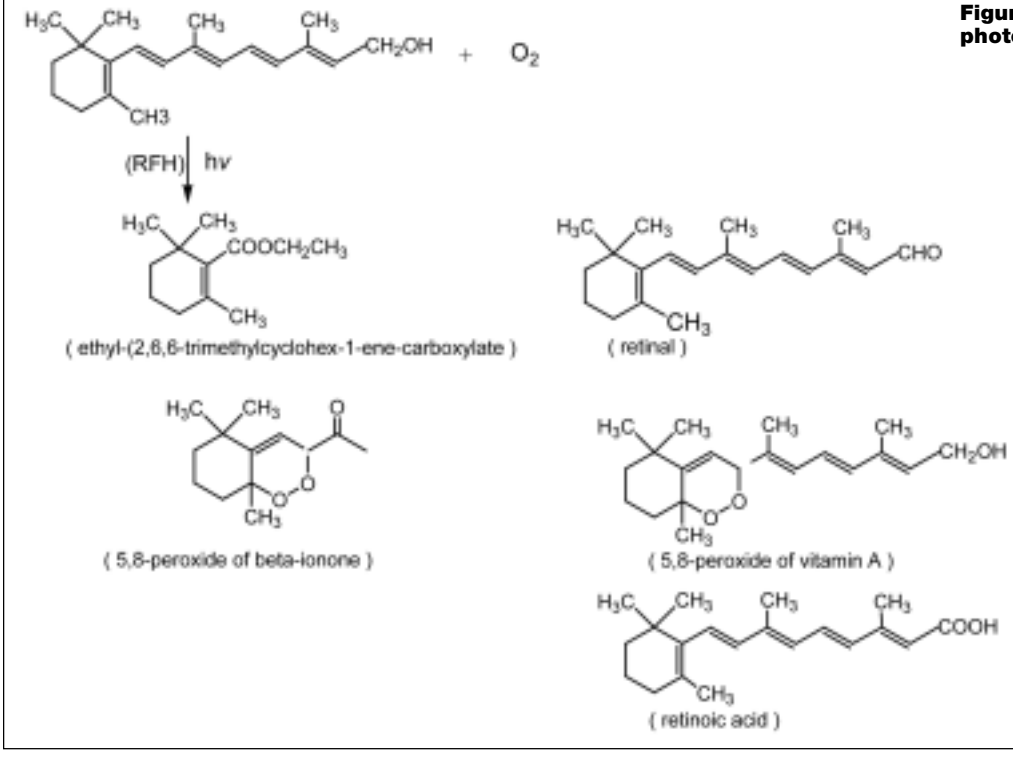

Figure 10—Vitamin A oxidation photosensitized by riboflavin

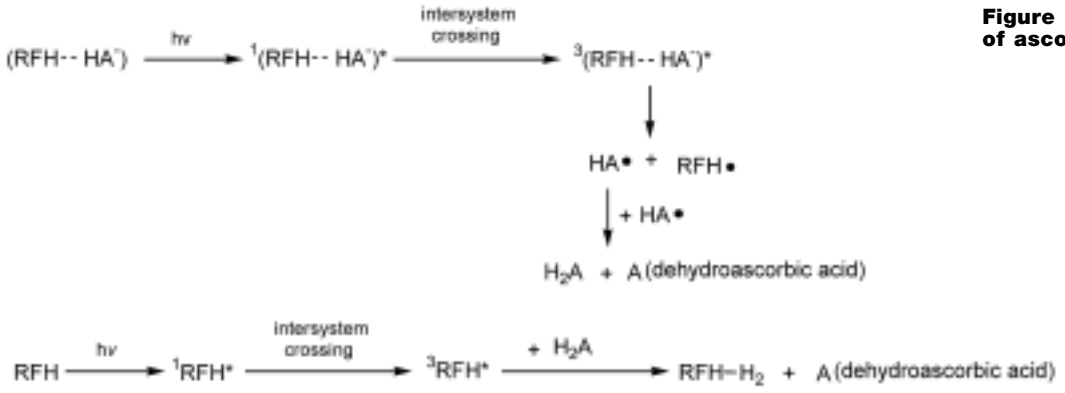

Figure 11—Decomposition of ascorbic acid

nutrient loss. Decomposition of the nutrients depends on the light, concentration of oxygen and riboflavin, and the presence of other components. Protein degradation sensitized by riboflavin under light is mainly by Type I pathway at low oxygen concentration and Type II pathway is favored at high oxygen concentration. Reaction of methionine and singlet oxygen formed by riboflavin photosensitization produces dimethyl disulfide, which is responsible for sunlight flavor of milk. Singlet oxygen is involved in lipids and cholesterol oxidation in the presence of riboflavin under light. Carbohydrates are less sensitive to riboflavin photosensitized oxidation than proteins and lipids. At high glucose concentration Type I pathway is favored. Vitamin A, C, and D are decomposed by Type I or by singlet oxygen which is Type II in the presence of riboflavin under light. Riboflavin is an excellent photosensitizer for singlet oxygen formation and a super reactant for singlet oxygen with the reaction rate of 1.01×10^{10} /M/s for the rapid decomposition of riboflavin itself under light.

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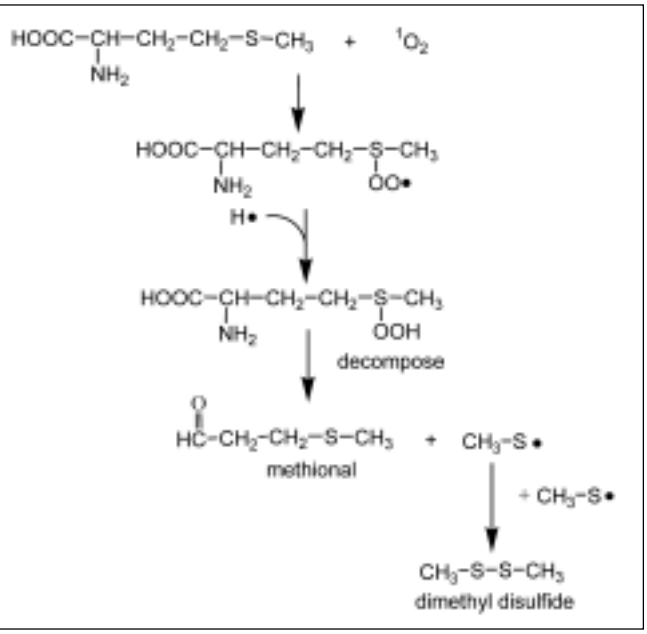

Figure 12—Oxidation of methionine by singlet oxygen

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