Vitamins

9

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Introduction

Vitamins are minor components of foods that play an essential role in human nutrition. Many vitamins are unstable under certain conditions of processing and storage (Table 9.1), and their levels in processed foods, therefore, may be considerably reduced. Synthetic vitamins are used extensively to compensate for these losses and to restore vitamin levels in foods. The vitamins are usually divided into two main groups, the water-soluble and the fat-soluble vitamins. The occurrence of the vitamins in the various food groups is related to their water-or fat-solubility. The contribution of foods to vitamins in the diet is varies significantly between food groups and specific products within the food groups. Some vitamins function as part of a coenzyme, without which the enzyme would be ineffective as a biocatalyst. Frequently, such coenzymes are phosphorylated forms of vitamins and play a role in the metabolism of fats, proteins, and carbohydrates. Some vitamins occur in foods as provitamins—compounds that are not vitamins but can be changed by the body into vitamins. Vitamers are members of the same vitamin family.

The contribution of vitamins by foods varies greatly among food groups. Water soluble vitamins are found in fruits and vegetables. Vitamin D is found almost exclusively in animal sources. In Table 9.2 the vitamins found in a range of commonly consumed foods are reported. This data is from the USDA Nutrient data base and more data can be found on raw, and processed foods including various commercial preparations.

Healthy levels of vitamins in the diet refers to the absence of disease based on clinical signs and symptoms of deficiency or excess, and normal function of the individual. The concept of protective nutrient intake for some vitamins refers to an amount which may be protective against a specified health or nutritional risk, for example vitamin C intake of 25 mg with each meal to enhances iron absorption and prevent anemia) (Cook and Reddy 2001). Protective intake levels for a specific vitamin can be expressed either as a daily value or as an amount to be consumed with a meal.

In Fig. 9.1 the acceptable range of intake in the shaded ranges correspond to approaches defining requirements to prevent deficit and excess. The estimated average requirement is the average daily intake required to prevent deficit in half of the population. The recommended nutrient intake is the amount necessary to meet the needs of most (97.5%) of the population, which is defined as the set as the estimated average requirement plus two standard deviations. The tolerable upper intake level is the level at which no evidence of toxicity is observed. In Fig. 9.1 the risk function of deficiency and excess for individuals in a population related to food intake, assuming a Gaussian distribution of requirements to prevent deficit and avoid excess. The upper tolerable nutrient intake

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Table 9.1 Stability of vitamins under different conditions

		Unstable to:						
Vitamin	Vitamer	*UV* Light	Heat[a]	O_2	Acid	Base	Metals[b]	Most stable
Vitamin A	Retinol	+		+	+		+	Dark, seal
	Retinal			+	+		+	Seal
	Retinoic acid							Good stability
	Dehydroret.			+				Seal
	Ret. esters							Good stability
	β-carotene			+				Seal
Vitamin D	D_2	+	+	+	+		+	Dark, cool, seal
	D_3	+	+	+	+		+	Dark, cool, seal
Vitamin E	Tocopherols		+	+	+	+	+	Cool, neutral pH
	Tocopherol esters				+	+		Good stability
Vitamin K	K	+		+		+	+	Avoid reductants
	MK	+		+		+	+	Avoid reductants
	Menadione	+				+	+	Avoid reductants
Vitamin C	Ascorbic acid			+[b]		+	+	Seal, neutral pH
Thiamine	Disulfide form		+	+	+	+	+	Neutral pH
	Hydrochloride[d]		+	+	+	+	+	Seal, neutral pH
Riboflavin	Riboflavin	+[e]	+			+	+	Dark, pH 1.5–4
Niacin	Nicotinic acid							Good stability
	Nicotinamide							Good stability
Vitamin B_6	Pyridoxal	+	+					Cool
	Pyridoxol (HCl)							Good stability
Biotin	Biotin			+		+		Seal, neutral pH
Pantothenic	Free acid[f]	+		+		+		Cool, neutral pH
Acid	Ca salty[d]		+					Seal, pH 6–7
Folate	FH_4	+	+	+	+[g]		+	Good stability
Vitamin B_{12}	Cn-b_{12}	+			+[h]		+[i]	Good stability

[a] i.e., 100°C

[b] In solution with Fe^{+++} and Cu^{++}

[c] Unstable to reducing agents

[d] Slightly hygroscopic

[e] Especially in alkaline solution

[f] Very hygroscopic

[g] $pH < 5$

[h] $pH < 3$

[i] $pH > 9$

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have been set for some vitamins and other micronutrients and are defined as the maximum intake from food, water and supplements that is unlikely to pose risk of adverse health effects from excess in almost all (97.5%) of healthy individuals in specific age groups. ULs should be based on long-term exposure to all foods, including fortified food products. Most vitamins cause no adverse effects when they are consumed as foods because their absorption and/or excretion are regulated. The special situation of consumption of nutritional supplements which, when added to the nutrient intake from food, may result in a total intake in excess of the upper limit of the nutrient.

Lack of vitamins has long been recognized to result in serious deficiency diseases. It is now also recognized that overdoses of certain vitamins, especially some of the fat-soluble vitamins which can result in serious toxic effects. For this reason, the addition of vitamins to foods should be carefully controlled.

Our requirements for vitamins changes as a function of age. Table 9.3 illustrates the recommended daily allowance for the water and fat soluble vitamins. Vitamin requirements are listed either in mg/day or in International Units per day (IU). The international units are used in cases where the actual amounts per day are small and more accurately expressed in activity units.

Fat-Soluble Vitamins

Vitamin A (Retinol)

The structural formula of vitamin A is shown in Fig. 9.2. It is an alcohol that occurs in nature predominantly in the form of fatty acid esters. Highest levels of vitamin A are found in certain fish liver oils, such as cod and tuna. Other important sources are mammalian liver, egg yolk, and milk and milk products. The levels of vitamin A and its provitamin carotene in some foods are listed in Table 9.4. The structural formula of Fig. 9.2 shows the unsaturated character of vitamin A. The all-*trans* form is the most active biologically. The 13-*cis* isomer is known as neovitamin A; its biological activity is only about 75% of that of the all-*trans* form. The amount of neo-vitamin A in natural vitamin A preparations is about one-third of the total. The amount is usually much less in synthetic vitamin A. The synthetic vitamin A is made as acetate or palmitate and marketed commercially in the form of oil solutions, stabilized powders, or aqueous emulsions. The compounds are insoluble in water but soluble in fats, oils, and fat solvents.

There are several provitamins A; these belong to the carotenoid pigments. The most important one is β-carotene, and some of the pigments that can be derived from it are of practical importance. These are β-apo-8′-carotenal and β-apo-8′-carotenoic acid ethyl ester (Fig. 9.3). Other provitamins are α- and γ-carotene and cryptoxanthin.

Beta-carotene occurs widely in plant products and has a high vitamin A activity. In theory, one molecule of β-carotene could yield two molecules of vitamin A. The enzyme 15-15′-dioxygenase is able to cleave a β-carotene molecule symmetrically to produce two molecules of vitamin A (Fig. 9.4). This enzyme occurs in intestinal mucosa, but the actual conversion is much less efficient. As shown in Fig. 9.4, there are other reactions that may cause the yield of retinol to be less than two. After cleavage of the β-carotene, the first reaction product is retinal, which is reduced to retinol (Rouseff and Nagy 1994). A general requirement for the conversion of a carotenoid to vitamin A is an unsubstituted β-ionone ring. Citrus fruits are a good source of provitamin A, which results mostly from the presence of β-cryptoxanthin, β-carotene, and α-carotene. Gross (1987) reported a total of 16 carotenoids with provitamin A activity in citrus fruits.

Vitamin A levels are frequently expressed in International Units (IU). One IU equals 0.344 μg of crystalline vitamin A acetate, or 0.300 μg vitamin A alcohol, or 0.600 μg β-carotene. The recommended daily allowance (RDA) of vitamin A of the National Research Council Food and Nutrition Board as seen in Table 9.2. Other sources quote the human requirement at about 1 μg/day. Conditions of rapid growth, pregnancy, or lactation increase the need for vitamin A.

Vitamin A, or retinol, is also known as vitamin A_1. Another form, vitamin A_2, is found in fish liver oils and is 3-dehydroretinol.

The Food and Agriculture Organization and the World Health Organization of the United Nations (FAO/WHO) and the National Academy of Sciences of the United States (1974a) have recommended that vitamin A activity be reported as the equivalent weight of retinol. To calculate total retinol equivalents, it is proposed that food analyses list retinol, carotene, and other provitamin A carotenoids separately. It is also desirable to distinguish between the *cis*- and *trans*- forms of the provitamins in cooked vegetables. By definition, 1 retinol equivalent is equal to 1 μg of retinol, or 6 μg of β-carotene, or 12 μg of other provitamin A carotenoids. The National Academy of Sciences (1974a) states that 1 retinol equivalent is equal to 3.3 IU of retinol or 10 IU of β-carotene.

Table 9.2 Vitamin content of some commonly consumed foods Data from USDA Nutrient Data base

	Water soluble vitamins 100 g food							Fat soluble vitamins 100 g food			
Food	Ascorbic acid (mg)	Thiamin (mg)	Riboflavin (mg)	Niacin (mg)	B-6 (mg)	Folate (μg)	B-12 (μg)	A (IU)	E (mg)	D (IU)	K (μg)
Vegetables											
Asparagus	5.6	1.143	0.141	0.978	0.091	52	0.00	756	1.13	0	41.6
Pinto beans raw, sprouted	21.7	0.230	0.175	2.280	0.171	118	0.00	2	–	0	–
Green beans, snap raw	12.2	0.082	0.104	0.734	0.141	33	0.00	690	0.41	0	43
Beets, raw	4.9	0.031	0.040	0.334	0.067	109	0.00	33	0.04	0	0.20
Broccoli, raw	89.2	0.071	0.117	0.639	0.175	63	0.00	623	0.78	0	101.6
Carrots, raw	5.9	0.066	0.058	0.983	0.138	19	0.00	16,706	0.66	0	13.2
Corn, sweet yellow	6.8	0.155	0.055	1.770	0.093	42	0.00	187	0.07	0	0.30
Lettuce, iceberg	2.8	0.041	0.025	0.123	0.042	29	0.00	502	0.18	0	24.1
Onions, raw	7.4	0.046	0.027	0.116	0.120	19	0.00	2	0.02	0	0.4
Green peas, raw	40	0.266	0.132	2.090	0.169	65	0.00	765	0.13	0	24.8
Green peppers, raw	80.4	0.057	0.028	0.480	0.224	10	0.00	370	0.37	0	7.4
Potatoes, fresh with skin, raw	19.7	0.081	0.032	1.061	0.298	15	0	2	0.01	0	2.0
Spinach, raw	28.1	0.078	0.189	0.724	0.195	194	0	9377	2.03	0	482.9
Summer squash, all varieties, raw	17.0	0.48	0.142	0.487	0.218	29	0	200	0.12	0	3.0
Fruits											
Apples, raw with skin	4.6	0.017	0.026	0.091	0.041	3	0	54	0.18	0	2.2
Avocados, raw	10	0.067	0.130	1.738	0.277	81	0	146	2.07	0	21.0
Blueberries, raw	9.7	0.037	0.041	0.418	0.052	6	0	3	0.57	0	19.30

Cranberries, raw	14	0.012	0.020	0.101	0.057	1	0	63	1.32	0	5.0
Oranges, Florida, raw	45	0.100	0.040	0.400	0.051	17	0	225	0.18	0	0.0
Pomegranates, raw	10.2	0.067	0.053	0.293	0.075	38	0	0	0.60	0	16.4
Strawberries, raw	58.8	0.024	0.022	0.386	0.047	24	0	12	0.29	0	2.2
Cereals and grains											
Corn flour, whole grain-yellow	0	0.246	0.080	1.90	0.370	25	0	214	0.42	0	0.3
Pasta, dry enriched	0	0.90	0.060	1.70	18	18	0	0	0.11	0	0.1
Rice, brown long grain	0	0.541	0.095	6.494	0.477	23	0	0	0.60	0	0.6
Rice, long grain, unenriched	0	0.224	0.050	5.048	0.452	8	0	0	0.03	0	0.1
Wheat, bread flour unenriched	0	0.080	0.060	1.000	0.037	33	0	2	0.40	0	0.3
Meat, eggs and dairy											
Ground beef, 20% fat uncooked	0	0.43	0.151	4.227	0.323	7	2.14	14	0.17	3	1.8
Beef tenderloin steak	0	0.071	0.441	6.235	0.765	7	4.27	5	0.28	3	1.4
Lamb, whole leg	0	0.141	0.287	4.964	0.359	2.70	2.70	–	–	–	–
Pork, fresh, composite of trimmed retail cuts (leg, loin, shoulder, and spareribs), raw	0.5	0.841	0.254	4.504	0.445	5	–	7	–	–	–
Chicken, broilers or fryers, back, meat and skin, raw	1.6	0.051	0.116	4.935	0.190	6	0.25	251	0.37	–	2.4
Cheese, cheddar	0	0.29	4.28	0.059	0.066	27	1.10	1242	0.71	24	4.2
Milk, whole, 3.25% milkfat Not fortified	0	0.046	0.169	0.089	0.036	5	0.45	46	162	2	0.3
Egg, raw. fresh	0	0.004	0.4390	0.105	0.005	4	0.09	0	0	0	0

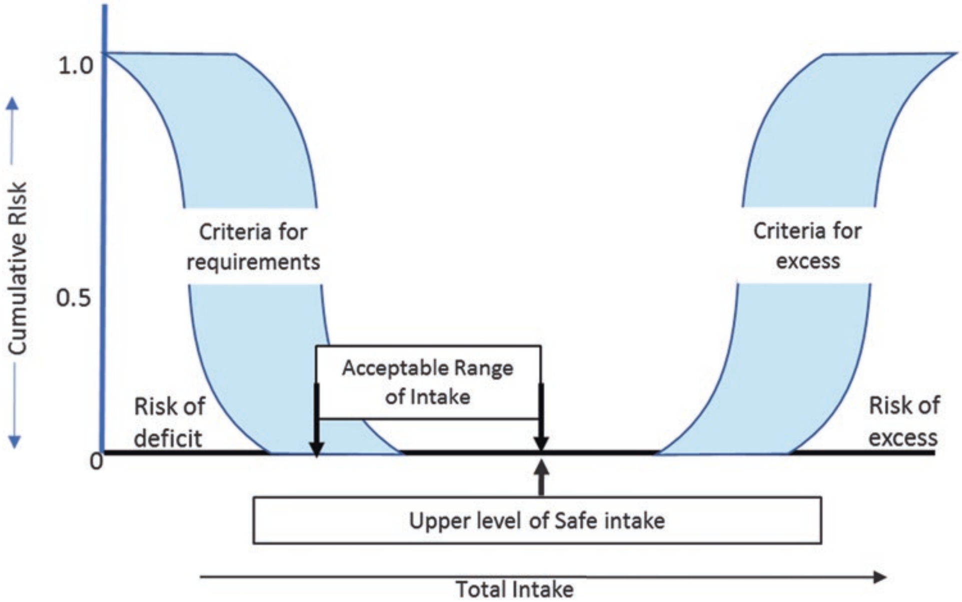


Fig. 9.1 Risk function of deficiency or excess for individuals in a population related to vitamin intake assuming a Gaussian distribution of requirements to prevent deficit and avoid excess

Vitamin A occurs only in animals and not in plants. The A_1 form occurs in all animals and fish, the A_2 form in freshwater fish and not in land animals. The biological value of the A_2 form is only about 40% of that of A_1. Good sources of provitamin A in vegetable products are carrots, sweet potatoes, tomatoes, and broccoli. In milk and milk products, vitamin A and carotene levels are subject to seasonal variations. Hartman and Dryden (1978) report the levels of vitamin A in fluid whole milk in winter at 1083 IU/L and in summer at 1786 IU/L. Butter contains an average of 2.7 μg of carotene and 5.0 μg of vitamin A per g during winter and 6.1 μg of carotene and 7.6 μg of vitamin A per g during summer.

Vitamin A is used to fortify margarine and skim milk. It is added to margarine at a level of 3525 IU per 100 g. Some of the carotenoids (provitamin A) are used as food colors.

Vitamin A is relatively stable to heat in the absence of oxygen (Table 9.5). Because of the highly unsaturated character of the molecule, it is quite susceptible to oxidation—especially under the influence of light, whether sunlight or artificial light. Vitamin A is unstable in the presence of mineral acids but stable in alkali. Vitamin A and the carotenoids have good stability during various food processing operations. Losses may occur at high temperatures in the presence of oxygen. These compounds are also susceptible to oxidation by lipid peroxides, and conditions favoring lipid oxidation also result in vitamin A breakdown. The prooxidant copper is especially harmful, as is iron to a lesser extent. Pasteurization of milk does not result in vitamin A loss, but exposure to light does. It is essential, therefore, that sterilized milk be packaged in light-impervious containers. Possible losses during storage of foods are more affected by duration of storage than by storage temperature. Blanching of fruits and vegetables helps prevent losses during frozen storage.

Vitamin A added to milk is more easily destroyed by light than the native vitamin A. This is not because natural and synthetic vitamin A are different, but because these two types of vitamin A are dispersed differently in the milk (deMan 1981). The form in which vitamin A is added to food products may influence its stability. Vitamin A in beadlet form is more stable than that added as a solution in oil. The beadlets are stabilized by a protective coating. If this coating is damaged by water, the stability of the vitamin is greatly reduced (deMan 1986).

Table 9.3 Relative daily requirements of water and fat soluble vitamins as a function of age (https://ods.od.nih.gov/Health_Information/Dietary_Reference_Intakes.aspx)

	Water soluble vitamins							Fat soluble vitamins			
Age	Vitamin C (mg)	Folate (mcg)	Niacin (mg)	Pantothenic acid (mg)	Riboflavin (mg)	B-6 (mg)	B-12 (mcg)	A (IU)	D (IU)	E (IU)	K (mcg)
1–3	15	150	6	2	0.5	0.5	0.9	1000	600	13 (S) 9 (N)	30
4–8	25	200	8	3	0.6	0.6	1.2	1300	600	16 (S) 10(N)	55
9–13	45	300	12	4	0.9	1.0	1.8	2000	600	24 (S) 16(N)	60
14–18	75(m) 65 (f)	400	16 (m) 14 (f)	5	1.3 (m) 1 (f)	1.3 (m) 1.2 (f)	2.4	1000	600	33 (S) 22(N)	75
Adult	90 (m) 75 (f)	400	16 (m) 14 (f)	5	1.3 (m) 1.1 (f)	1.3 (19–50) 1.5 (50+)	2.4	3000 (m) 2300 (f)	600 800 (51+)	33 (S) 22(N)	120 (m) 90 (f)

m male, *f* female, *S* synthetic, *N* natural

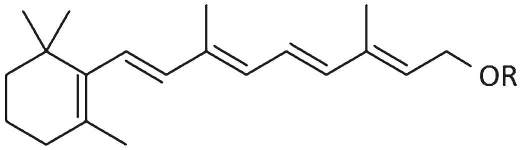


Fig. 9.2 Structural formula of vitamin A. Acetate: R=CO CH_3. Palmitate: R=CO $(CH_2)_{14}$ CH_3

Table 9.4 Vitamin A and carotene content of some foods

Product	Vitamin A (IU/100 g)	Carotene (mg/100 g)
Beef (grilled sirloin)	37	0.04
Butter (May–November)	2363–3452	0.43–0.77
Cheddar cheese	553–1078	0.07–0.71
Eggs (boiled)	165–488	0.01–0.15
Herring (canned)	178	0.07
Milk	110–307	0.01–0.06
Tomato (canned)	0	0.5
Peach	0	0.34
Cabbage	0	0.3
Broccoli (boiled)	0	2.5
Spinach (boiled)	0	6.0

Vitamin D

This vitamin occurs in several forms; the two most important are vitamin D_2, or ergocalciferol, and vitamin D_3, or cholecalciferol. The structural formulas of these compounds are presented in Fig. 9.5. Vitamin D does not occur in plant products. Vitamin D_2 occurs in small amounts in fish liver oils; vitamin D_3 is widely distributed in animal products, but large amounts occur only in fish liver oils. Smaller quantities of vitamin D_3 occur in eggs, milk, butter, and cheese (Table 9.6).

The precursors of vitamins D_2 and D_3 are ergosterol and 7-dehydrocholesterol, respectively. These precursors or provitamins can be converted into the respective D vitamins by irradiation with ultraviolet light. In addition to the two major provitamins, there are several other sterols that can acquire vitamin D activity when irradiated. The provitamins can be converted to vitamin D in the human skin by exposure to sunlight. Because very few foods are good sources of vitamin D, humans have a greater likelihood of vitamin D deficiency than of any other vitamin deficiency. Enrichment of some foods with vitamin D has significantly helped to eradicate rickets, which is a vitamin D deficiency disease. Margarine and milk are the foods commonly used as carrier for added vitamin D.

The unit of activity of vitamin D is the IU, which is equivalent to the activity of 1 mg of a standard preparation issued by the WHO. One IU is also equivalent to the activity of 0.025 μg of pure crystalline vitamin D_2 or D_3. The human requirement amounts to 400–500 IU but increases to 1000 IU during pregnancy and lactation. Adults who are regularly exposed to sunlight are likely to have a sufficient supply of vitamin D. Excessive intakes are toxic.

Vitamin D is extremely stable, and little or no loss is experienced in processing and storage. Vitamin D in milk is not affected by pasteurization, boiling, or sterilization (Hartman and Dryden 1978). Frozen storage of milk or butter also has little or no effect on vitamin D levels, and the same result is obtained during storage of dry milk.

The vitamin D potency of milk can be increased in several ways: by feeding cows substances that are high in vitamin D activity, such as irradiated yeast; by irradiating milk; and by adding vitamin D concentrates. The latter method is now the only commonly used procedure. The practice of irradiating milk to increase the vitamin D potency has been discontinued, undoubtedly because of the deteriorative action of the radiation on other milk components. Vitamin D is added to milk to provide a concentration of 400 IU per quart. Addition of vitamin D to margarine is at a level of 550 IU per 100 g.

Tocopherols (Vitamin E)

The tocopherols are derivatives of tocol, and the occurrence of a number of related substances in animal and vegetable products has been demonstrated. Cottonseed oil was found to contain α-, β-, and γ-tocopherol, and a fourth, δ-tocopherol, was isolated from soybean oil. Several other tocopherols have been found in other products, and Morton (1967) suggests that there are

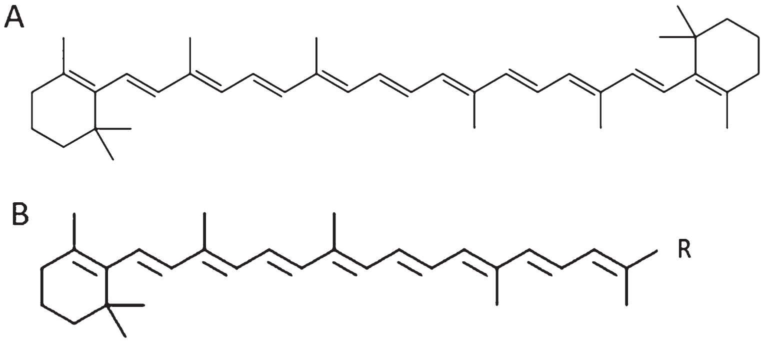


Fig. 9.3 Structural formulas of some provitamins A. (**a**) β-carotene, and (**b**) apocarotenal (R=CHO) and apocarotenoic acid ester (R=$COOC_2H_5$)

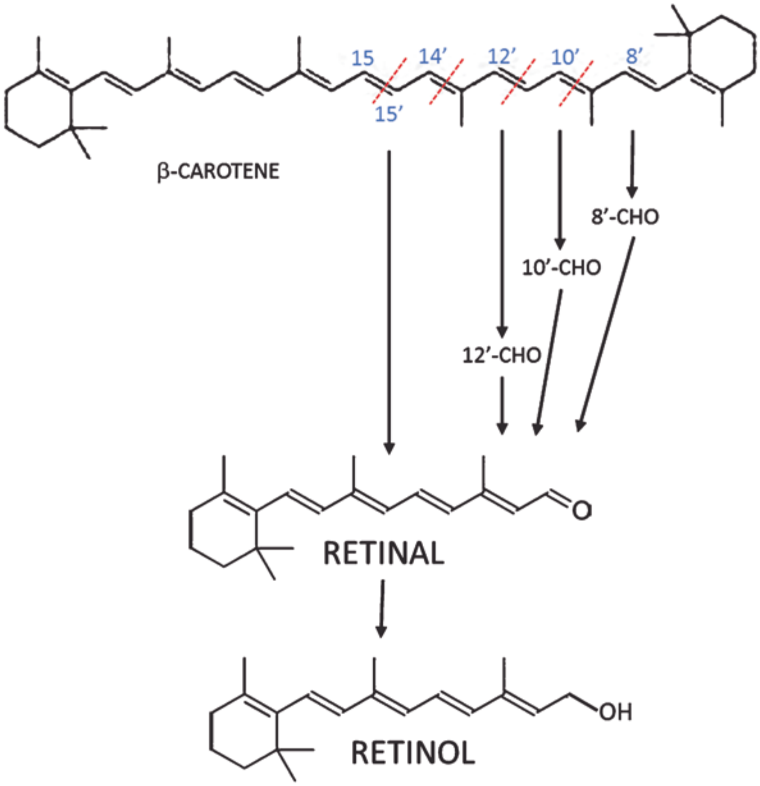


Fig. 9.4 Conversion of beta-carotene to vitamin A

four tocopherols and four tocotrienols. The tocotrienols have three unsaturated isoprenoid groups in the side chain. The structure of tocol is given in Fig. 9.6 and the structures of the tocopherols and tocotrienols in Fig. 9.7. The four tocopherols are characterized by a saturated side chain consisting of three isoprenoid units. The tocotrienols have three double bonds at the 3′, 7′, and 11′ carbons of the isoprenoid side chain (Fig. 9.7). The carbons at locations 4′ and 8′ in the side chains of the tocopherols are asymmetric, as is the number 2 carbon in the chroman ring. The resulting possible isomers are described as having R or S rotation. The natural tocopherols and tocotrienols are predominantly RRR isomers. Stocker and Kearney (2004) have summarized the chemistry of the oxidation of tocopherols as shown in Fig. 9.8.

Table 9.5 Vitamin A and carotene stability in foods

Product	Nutrient content	Storage conditions	Retention (%)
Vitamin A			
Butter	17,000–30,000 IU/Ib	12 months @ 5 °C	66–98
		5 months @ 28 °C	64–68
Margarine	15,000 IU/Ib	6 months @ 5 °C	89–100
		6 months @ 23 °C	83–100
Nonfat dry milk	10,000 IU/Ib	3 months @ 37 °C	94–100
		12 months @ 23 °C	69–89
Fortified ready-to-eat cereal	4000 IU/oz	6 months @ 23 °C	83
Fortified potato chips	700 IU/100 g	2 months @ 23 °C	100
Carotene			
Margarine	3 mg/Ib	6 months @ 5 °C	98
		6 months @ 23 °C	89
Lard	3.3 mg/lb	6 months @ 5 °C	100
		6 months @ 23 °C	100
Dried egg yolk	35.2 mg/100 g	3 months @ 37 °C	94
		12 months @ 23 °C	80
Carbonated beverage	7.6 mg/29 oz	2 months @ 30 °C	94
		2 months @ 23 °C	94
Canned juice drinks	0.6–1.3 mg/8 fl oz	12 months @ 23 °C	85–100

Source: From E. deRitter, Stability Characteristics of Vitamins in Processed Foods, *Food Technol.,* Vol. 30, pp. 48–51, 54, 1976

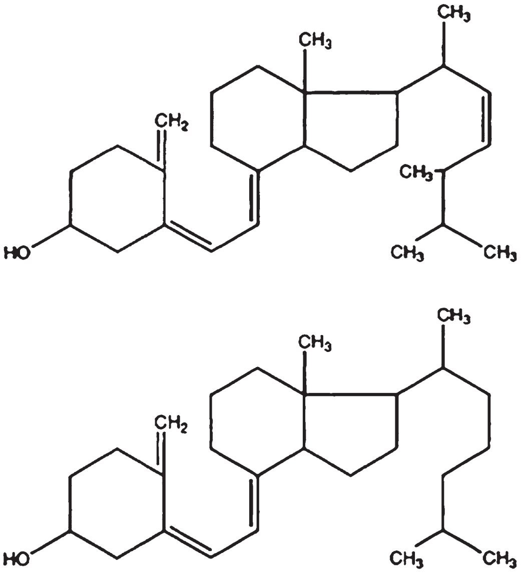


Fig. 9.5 Structural formulas of (**a**) vitamin D_2 and (**b**) vitamin D_3

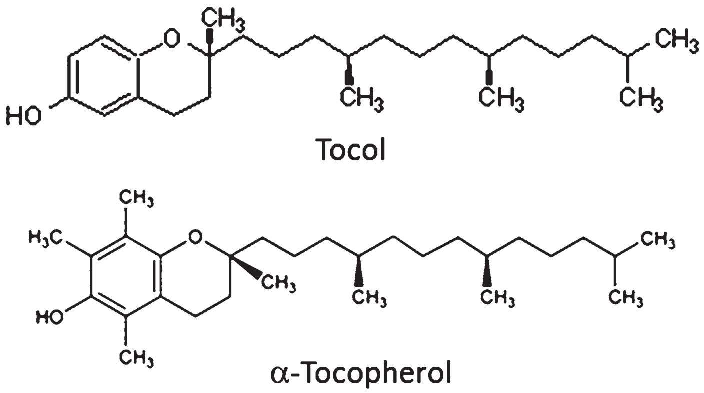
Table 9.6 Vitamin D content of some foods

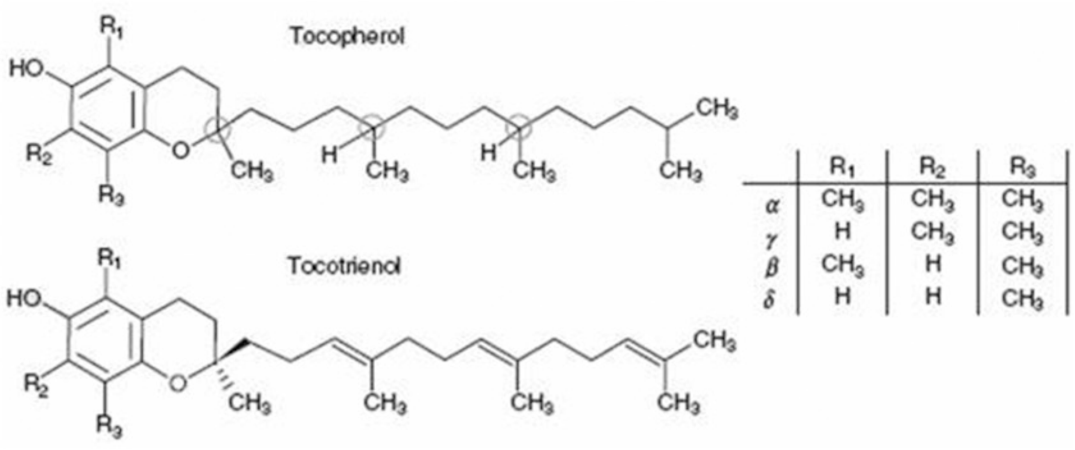
Product	Vitamin D (μg/1000 g edible portion)
Liver (beef, pork)	2–5
Eggs	44
Milk	0.9
Butter	2–40
Cheese	12–47
Herring oil	2500

On oxidation, α-tocopherol can form a meta-stable epoxide that can be irreversibly converted to α-tocopherolquinone. Reduction of the quinone yields a quinol. Tocopherolquinones occur naturally. Oxidation with nitric acid yields the *o*-quinone or tocopherol red, which is not found in nature. Alpha-tocopheronic acid and α-tocopheronolactone are some of the products of metabolism of tocopherol. Much of the biological activity of the tocopherols is related to their antioxidant activity. Because α-tocopherol is the most abundant of the different tocopherols, and because it appears to have the greatest biological activity, the α-tocopherol content of foods is usually considered to be most important.

The biological activity of the tocopherols and tocotrienols varies with the number and position of the methyl groups on the chroman ring and by

Fig. 9.6 Structural formula of tocol and α-tocopherol





	R_1	R_2	R_3
α	CH_3	CH_3	CH_3
γ	H	CH_3	CH_3
β	CH_3	H	CH_3
δ	H	H	CH_3

Fig. 9.7 Chemical structure of the tocopherols and tocotrienols

the configuration of the asymmetric carbons in the side chain. The R configuration at each chiral center has the highest biological activity. Because the different isomers have different activities, it is necessary to measure each homolog and convert these to RRR-α-tocopherol equivalents (α-TE). One α-TE is the activity of 1 mg of RRR-α-tocopherol (Eitenmiller 1997). The vitamin E activity of α-tocopherol isomers and synthetic tocopherols is listed in Table 9.7.

Tocopherols are important as antioxidants in foods, especially in vegetable oils. With few exceptions, animal and vegetable products contain from about 0.5 to 1.5 mg/100 g; vegetable oils from 10 to 60 mg/100 g; and cereal germ oils, which are a very good source, from 150 to 500 mg/100 g. Vegetable oils have the highest proportion of α-tocopherol, which amounts to about 60% of the total tocopherols. Refining of vegetable oils, carried out under normal precautions (such as excluding air), appears to result in little destruction of tocopherol. The tocopherol and tocotrienol content of selected fats and oils and their primary homologs are listed in Table 9.8. The seed oils contain only tocopherol. Tree oils, palm, palm kernel, coconut oil, and rice bran oil also contain major amounts of tocotrienols. The processing of vegetable oils by deodorization or physical refining removes a considerable portion of the tocopherols, and these steam-volatile compounds accumulate in the fatty acid distillate (Ong 1993). This product is an important source of natural vitamin E preparations. Baltes (1967) carried out tests in which two

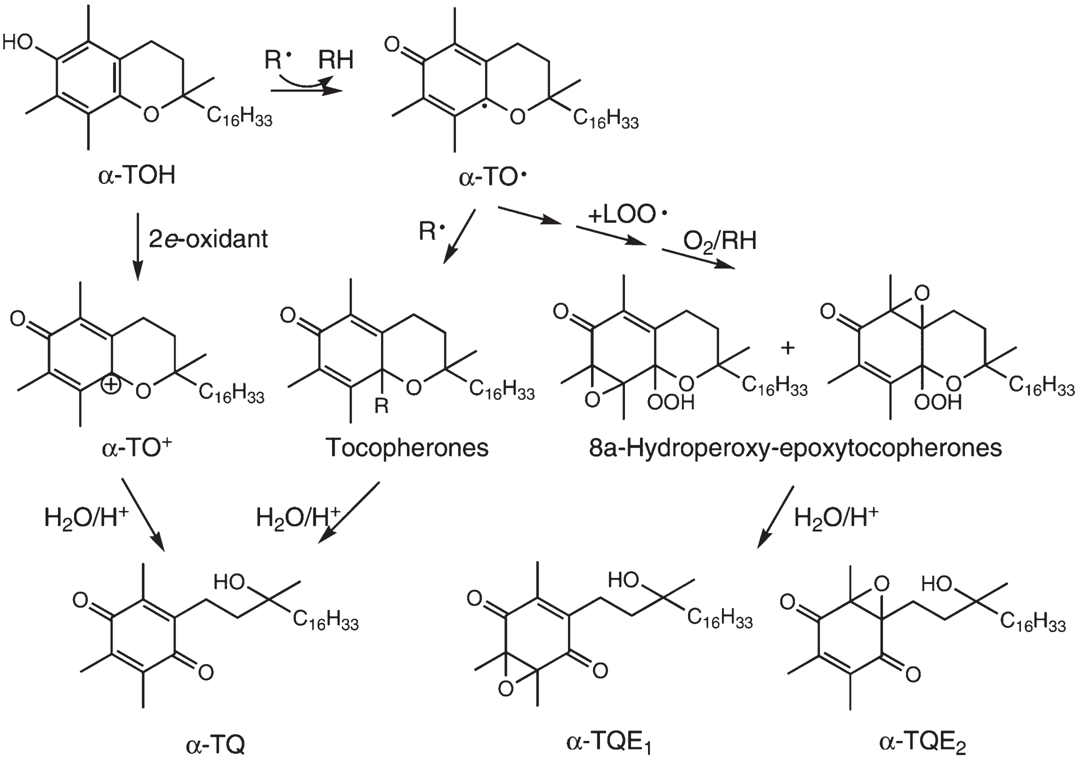


Fig. 9.8 The major pathways of α-TOH oxidation. Two-electron oxidants such as HOCl and ONOO⁻ oxidize α-TOH to the intermediate tocopheroxylium cation (α-TO$^+$), which hydrolyzes to α-tocopherylquinone (α-TQ). Radical oxidants (R) generate the α-TO that can further scavenge radicals, to produce 8a-substituted tocopherone adducts, or scavenge LOO, to produce 8a-hydroperoxy-epoxytocopherones. These hydrolyze to α-TQ and α-tocopheryl quinone epoxides (TQEs), respectively (Stocker and Kearney 2004)

Table 9.7 Vitamin E activity of α-tocopherol isomers and synthetic tocopherols

Name	IU/mg
d-α-tocopherol (2R4′R8′R) RRR-α-tocopherol	1.49
1-α-tocopherol (2S4′R8′R)	0.46
dl-α-tocopherol all-rac-α-tocopherol	1.10
2R4′R8′S-α-tocopherol	1.34
2S4′R8′S-α-tocopherol	0.55
2S4′S8′S-α-tocopherol	1.09
2S4′S8′R-α-tocopherol	0.31
2R4′S8′R-α-tocopherol	0.85
2S4′S8′S-α-tocopherol	1.10
d-α-tocopheryl acetate RRR-α-tocopheryl acetate	1.36
dl-α-tocopherol all-rac-α-tocopherol acetate	1.00

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easily oxidizable fats, lard and partially hydrogenated whale oil, were stabilized with α-tocopherol and ascorbyl palmitate and citric acid as synergists. Without antioxidants, these fats cannot be used in the commercial food chain. Amounts of α-tocopherol ranging from 0.5 to 10 mg/100 g were effective in prolonging the storage life of some samples up to 2 years.

The tocopherol content of some animal and vegetable products as reported by Thaler (1967) is listed in Table 9.9. Cereals and cereal products are good sources of tocopherol (Table 9.10). The distribution of tocopherol throughout the kernels is not uniform, and flour of different degrees of extraction can have different tocopherol levels. This was shown by Menger (1957) in a study of wheat flour (Table 9.11).

Processing and storage of foods can result in substantial tocopherol losses. An example is

Table 9.8 Tocopherol (T) and tocotrienol (T3) content of vegetable oils and their primary homologs

Fats and oils	Total T + T3 (mg/100 g)	α-TE/100 g	%T	%T3	Primary homologs
Sunflower	46–67	35–63	100	0	α-T, γ-T
Cottonseed	78	43	100	0	α-T, γ-T
Safflower	49–80	41–46	100	0	α-T, δ-T, γ-T, β-T
Safflower—high linolenic	41	41	100	0	α-T, β-T
Safflower—high oleic	32	31	100	0	α-T, β-T, γ-T
Palm	89–117	21–34	17–55	45–83	α-T, α-T3, δ-T3, α-T, δ-T3
Canola	65	25	100	0	γ-T, α-T, δ-T, α-T3(Tr), β-T(Tr)
Corn	78–109	20–34	95	5	γ-T, α-T, δ-T, γ-T3, δ-T3
Soybean	96–115	17–20	100	0	γ-T, δ-T, α-T
Rice bran	9–160	0.9–41	19–49	51–81	γ-T3, αT, α-T3, β-T, β-T3
Peanut	37	16	100	0	γ-T, α-T, δ-T
Olive	5.1	5.1	100	0	α-T
Cocoa butter	20	3.0	99	1	γ-T, δ-T, α-T, α-T3
Palm kernel	3.4	1.9	38	62	α-T3, α-T
Butter	1.1–2.3	1.1–2.3	100	0	α-T
Lard	0.6	0.6	100	0	α-T
Coconut	1.0–3.6	0.3–0.7	31	69	γ-T3, α-T3, δ-T, α-T, β-T3

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Table 9.9 Tocopherol content of some animal and vegetable food products

Product	Total tocopherol as α-tocopherol (mg/100 g)
Beef liver	0.9–1.6
Veal, lean	0.9
Herring	1.8
Mackerel	1.6
Crab, frozen	5.9
Milk	0.02–0.15
Cheese	0.4
Egg	0.5–1.5
Egg yolk	3.0
Cabbage	2–3
Spinach	0.2–6.0
Beans	1–4
Lettuce	0.2–0.8 (0.06)
Peas	4–6
Tomato	0.9 (0.4)
Carrots	0.2 (0.11)
Onion	0.3 (0.22)
Potato	(0.12)
Mushrooms	0.08

Source: From H. Thaler, Concentration and Stability of Tocopherols in Foods, in *Tocopherols*, K. Lang, ed., 1967, Steinkopff Verlag, Darmstadt, Germany

Table 9.10 Tocopherol content of cereals and cereal products

Product	Total tocopherol as α-tocopherol (mg/100 g)
Wheat	7–10
Rye	2.2–5.7
Oats	1.8–4.9
Rice (with hulls)	2.9
Rice (polished)	0.4
Corn	9.5
Whole wheat meal	3.7
Wheat flour	2.3–5.4
Whole rye meal	2.0–4.5
Oat flakes	3.85
Corn grits	1.17
Corn flakes	0.43
White bread	2.15
Whole rye bread	1.3
Crisp bread	4.0

Source: From H. Thaler, Concentration and Stability of Tocopherols in Foods, in *Tocopherols,* K. Lang, ed., 1967, Steinkopff Verlag, Darmstadt, Germany

given in Table 9.12, where the loss of tocopherol during frying of potato chips is reported. After only 2 weeks' storage of the chips at room

Table 9.11 Tocopherol content of wheat and its milling products

Product	Ash (%)	Tocopherol mg/100 g (dry basis)
Whole wheat	2.05	5.04
Flour 1 (fine)	1.68	5.90
Flour 2	1.14	4.27
Flour 3	0.84	3.48
Flour 4	0.59	2.55
Flour 5	0.47	2.35
Flour 6 (coarse)	0.48	2.13
Germ	4.10	25.0

Source: From A. Menger, Investigation of the Stability of Vitamin E in Cereal Milling Products and Baked Goods, *Brot. Gebäck*, Vol. 11, pp. 167–173, 1957 (German)

Table 9.12 Tocopherol losses during processing and storage of potato chips

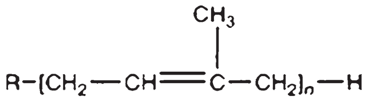
	Tocopherol (mg/100 g)	Loss (%)
Oil before use	82	–
Oil after use	73	11
Oil from fresh chips	75	–
After 2 weeks at room temperature	39	48
After 1 month at room temperature	22	71
After 2 months at room temperature	17	77
After 1 month at −12 °C	28	63
After 2 months at −12 °C	24	68

temperature, nearly half of the tocopherol was lost. The losses were only slightly smaller during storage at freezer temperature. Boiling of vegetables in water for up to 30 min results in only minor losses of tocopherol. Baking of white bread results in a loss of about 5% of the tocopherol in the crumb.

The human daily requirement of vitamin E is estimated at 30 IU. Increased intake of polyunsaturated fatty acids increases the need for this vitamin.

Vitamin K

This vitamin occurs in a series of different forms, and these can be divided into two groups. The first is vitamin K_1 (Fig. 9.9), characterized by one double bond in the side chain. The vitamins K_2 have a side chain consisting of a number of regular units of the type.



$$R-[CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2]_n-H$$

where *n* can equal 4, 5, 6, 7, and so forth.

Vitamin K_1 is slowly decomposed by atmospheric oxygen but is readily destroyed by light. It is stable against heat, but unstable against alkali.

The human adult requirement is estimated at about 4 mg per day. Menadione (2-methyl 1,4-naphtoquinone) is a synthetic product and has about twice the activity of naturally occurring vitamin K.

Vitamin K occurs widely in foods and is also synthesized by the intestinal flora. Good sources of vitamin K are dark green vegetables such as spinach and cabbage leaves, and also cauliflower, peas, and cereals. Animal products contain little vitamin K_1, except for pork liver, which is a good source.

The Vitamin K levels in some foods, expressed in menadione units, are given in Table 9.13.

Water-Soluble Vitamins

Vitamin C (L-Ascorbic Acid)

This vitamin occurs in all living tissues, where it influences oxidation-reduction reactions. The major source of L-ascorbic acid in foods is vegetables and fruits (Table 9.14).

L-ascorbic acid (Fig. 9.10) is a lactone (internal ester of a hydroxycarboxylic acid) and is characterized by the enediol group, which makes it a strongly reducing compound. The D form has no biological activity. One of the isomers, D-isoascorbic acid, or erythorbic acid, is produced commercially for use as a food additive. L-ascorbic acid is readily and reversibly oxidized to dehydro-L-ascorbic acid (Fig. 9.11), which retains vitamin C activity. This compound can be further oxidized to diketo-L-gulonic acid, in a nonreversible reaction. Diketo-L-gulonic

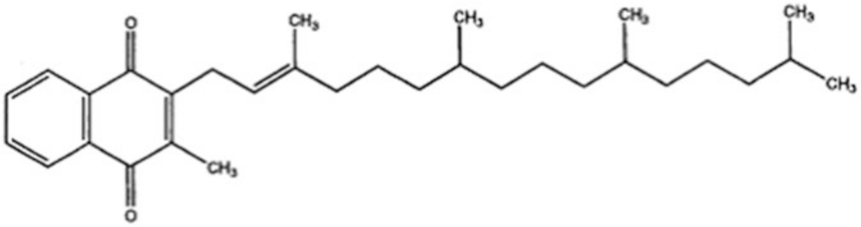


Fig. 9.9 Structural formula of vitamin K_1

Table 9.13 Vitamin K in some foods (expressed as menadione units per 100 g of edible portion)

Product	Units/100 g
Cabbage, white	70
Cabbage, red	18
Cauliflower	23
Carrots	5
Honey	25
Liver (chicken)	13
Liver (pork)	111
Milk	8
Peas	50
Potatoes	10
Spinach	161
Tomatoes (green)	24
Tomatoes (ripe)	12
Wheat	17
Wheat bran	36
Wheat germ	18

Table 9.14 Vitamin C content of some foods

Product	Ascorbic acid (mg/100 g)
Black currants	200
Brussels sprouts	100
Cauliflower	70
Cabbage	60
Spinach	60
Orange	50
Orange juice	40–50
Lemon	50
Peas	25
Tomato	20
Apple	5
Lettuce	15
Carrots	6
Milk	2.1–2.7
Potatoes	30

acid has no biological activity, is unstable, and is further oxidized to several possible compounds, including 1-threonic acid. Dehydration and decarboxylation can lead to the formation of furfural, which can polymerize to form brown pigments or combine with amino acids in the Strecker degradation.

Humans and guinea pigs are the only primates unable to synthesize vitamin C. The human requirement of vitamin C is not well defined. Figures ranging from 45 to 75 mg/day have been listed as daily needs. Continued stress and drug therapy may increase the need for this vitamin.

Vitamin C is widely distributed in nature, mostly in plant products such as fruits (especially citrus fruits), green vegetables, tomatoes, potatoes, and berries. The only animal sources of this vitamin are milk and liver. Although widely distributed, very high levels of the vitamin occur only in a few products, such as rose hips and West Indian cherries. The concentration varies widely in different tissues of fruits; for example, in apples, the concentration of vitamin C is two to three times as great in the peel as in the pulp.

Vitamin C is the least stable of all vitamins and is easily destroyed during processing and storage. The rate of destruction is increased by the action of metals, especially copper and iron, and by the action of enzymes. Exposure to oxygen, prolonged heating in the presence of oxygen, and exposure to light are all harmful to the vitamin C content of foods. Enzymes containing copper or iron in their prosthetic groups are efficient catalysts of ascorbic acid decomposition. The most important enzymes of this group are ascorbic acid oxidase, phenolase, cytochrome oxidase, and peroxidase. Only ascorbic acid oxidase involves a direct reaction among enzyme,

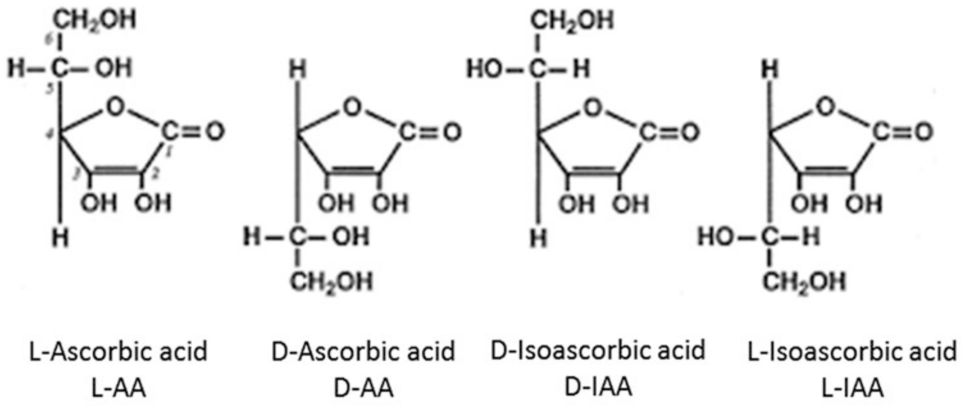


Fig. 9.10 Structural formulas of L-ascorbic acid and its stereoisomers

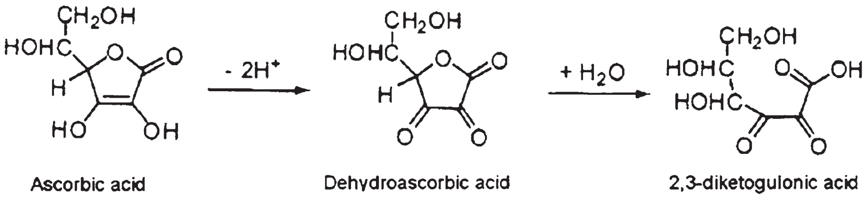


Fig. 9.11 Oxidation of L-ascorbic acid

substrate, and molecular oxygen. The other enzymes oxidize the vitamin indirectly. Phenolase catalyzes the oxidation of mono and dihydroxy phenols to quinones. The quinones react directly with the ascorbic acid. Cytochrome oxidase oxidizes cytochrome to the oxidized form and this reacts with L-ascorbic acid.

Peroxidase, in combination with phenolic compounds, utilizes hydrogen peroxide to bring about oxidation. The enzymes do not act in intact fruits because of the physical separation of enzyme and substrate. Mechanical damage, rot, or senescence lead to cellular disorganization and initiate decomposition. Inhibition of the enzymes in vegetables is achieved by blanching with steam or by electronic heating. Blanching is necessary before vegetables are dried or frozen. In fruit juices, the enzymes can be inhibited by pasteurization, deaeration, or holding at low temperature for a short period. The effect of blanching methods on the ascorbic acid content of broccoli was reported by Odland and Eheart (1975). Steam blanching was found to result in significantly smaller losses of ascorbic acid (Table 9.15). The retention of ascorbic acid in frozen spinach depends on storage temperature. At a very low temperature (−29 °C), only 10% of the initially present ascorbic acid was lost after 1 year. At −12°, the loss after 1 year was much higher, 55%. The presence of metal chelating compounds stabilizes vitamin C. These compounds include anthocyanins and flavonols, polybasic or polyhydroxy acids such as malic and citric acids, and polyphosphates.

Table 9.15 Effect of blanching method on ascorbic acid levels of broccoli

	Ascorbic acid (mg/100 g)		
Factor effect	Reduced	Dehydro	Total
Raw	94.0	4.0	98.2
Water blanch	45.3	5.7	51.0
Steam blanch	48.8	7.4	56.2

Source: From D. Ödland and M.S. Eheart, Ascorbic Acid, Mineral and Quality Retention in Frozen Broccoli Blanched in Water, Steam, and Ammonia-Steam, *J. Food Sci*., Vol. 40, pp. 1004–1007, 1975

Ascorbic acid is oxidized in the presence of air under neutral and alkaline conditions. At acid pH (for example, in citrus juice), the vitamin is more stable. Because oxygen is required for the breakdown, removal of oxygen should have a stabilizing effect. For the production of fruit drinks, the water should be deaerated to minimize vitamin C loss. The type of container may also affect the extent of ascorbic acid destruction. Use of tin cans for fruit juices results in rapid depletion of oxygen by the electrochemical process of corrosion. In bottles, all of the residual oxygen is available for ascorbic acid oxidation. To account for processing and storage losses, it is common to allow for a loss of 7–14 mg of ascorbic acid per 100 mL of fruit juice. Light results in rapid destruction of ascorbic acid in milk. It has been shown (Sattar and deMan 1973) that transparent packaging materials permit rapid destruction of vitamin C (Fig. 9.12). The extent of ascorbic acid destruction is closely parallel to the development of off-flavors. The destruction of ascorbic acid in milk by light occurs under the influence of riboflavin as a sensitizer. The reaction occurs in the presence of light and oxygen, and the riboflavin is converted to lumichrome.

Factors that affect vitamin C destruction during processing include heat treatment and leaching. The severity of processing conditions can often be judged by the percentage of ascorbic acid that has been lost. The extent of loss depends on the amount of water used. During blanching, vegetables that are covered with water may lose 80%; half covered, 40%; and quarter covered, 40% of the ascorbic acid. Particle size affects the size of the loss; for example, in blanching small pieces of carrots, losses may range from 32 to 50%, and in blanching large pieces, only 22 to 33%. Blanching of cabbage may result in a 20% loss of ascorbic acid, and subsequent dehydration may increase this to a total of 50%. In the processing of milk, losses may occur at various stages. From an initial level of about 22 mg/L in raw milk, the content in the product reaching the consumer may be well below 10 mg/L. Further losses may occur in the household during storage of the opened container.

The processing of milk into various dairy products may result in vitamin C losses. Ice cream contains no vitamin C, nor does cheese. The production of powdered milk involves a 20–30% loss, evaporated milk a 50–90% loss. Bullock (1968) studied the stability of added vitamin C in evaporated milk and found that adding 266 mg of sodium ascorbate per kg was sufficient to ensure the presence of at least 140 mg/L of ascorbic acid during 12 months of storage at 21 °C. Data on the stability of vitamin C in fortified foods have been assembled by deRitter (1976) (Table 9.16).

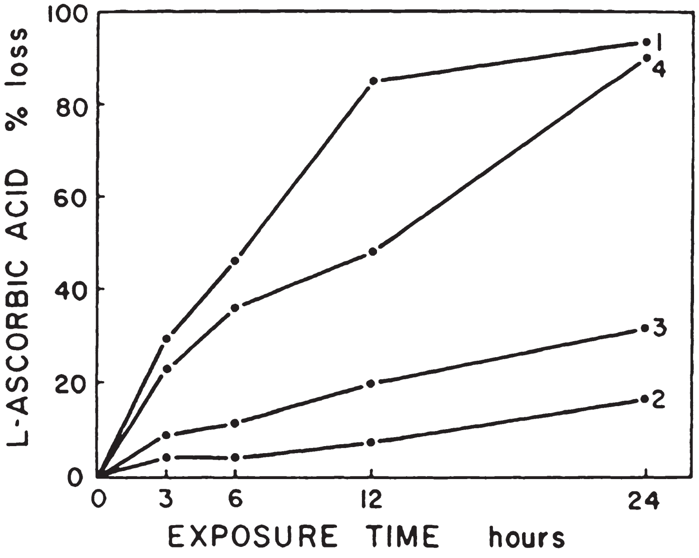


Fig. 9.12 Effect of exposure time at light intensity of 200 Ft-C on the loss of ascorbic acid in milk. Packaging materials: (1) clear plastic pouch, (2) laminated nontransparent pouch, (3) carton, (4) plastic 3-quart jug. *Source:* From A. Sattar and J.M. deMan, Effect of Packaging Material on Light Induced Quality Deterioration of Milk, *Can. Inst. Food Sci. Technol. J.*, Vol. 6, pp. 170–174, 1973

Table 9.16 Vitamin C stability in fortified foods and beverages after storage at 23 °C for 12 months, except as noted

Product	No. of samples	Retention: Mean (%)	Retention: Range (%)
Ready-to-eat cereal	4	71	60–87
Dry fruit drink mix	3	94	91–97
Cocoa powder	3	97	80–100
Dry whole milk, air pack	2	75	65–84
Dry whole milk, gas pack	1	93	–
Dry soy powder	1	81	–
Potato flakes[a]	3	85	73–92
Frozen peaches	1	80	–
Frozen apricots[b]	1	80	–
Apple juice	5	68	58–76
Cranberry juice	2	81	78–83
Grapefruit juice	5	81	73–86
Pineapple juice	2	78	74–82
Tomato juice	4	80	64–93
Vegetable juice	2	68	66–69
Grape drink	3	76	65–94
Orange drink	5	80	75–83
Carbonated beverage	3	60	54–64
Evaporated milk	4	75	70–82

[a] Stored for 6 months at 23 °C

[b] Thawed after storage in freezer for 5 months

Source: From E. deRitter, Stability Characteristics of Vitamins in Processed Foods, *Food Technol.*, Vol. 30, pp. 48–51, 54, 1976

There are many technical uses of ascorbic acid in food processing. It is used to prevent browning and discoloration in vegetables and fruit products; as an antioxidant in fats, fish products, and dairy products; as a stabilizer of color in meat; as an improver of flour; as an oxygen acceptor in beer processing; as a reducing agent in wine, partially replacing sulfur dioxide; and as an added nutrient. The vitamin is protected by sulfur dioxide, presumably by inhibiting polyphenolase.

Vitamin B_1 (Thiamin)

This vitamin acts as a coenzyme in the metabolism of carbohydrates and is present in all living tissues. It acts in the form of thiamin diphosphate in the decarboxylation of α-keto acids and is referred to as cocarboxylase. Thiamin is available in the form of its chloride or nitrate, and its structural formula is shown in Fig. 9.13. The molecule contains two basic nitrogen atoms; one is in the primary amino group, the other in the quaternary ammonium group. It forms salts with inorganic and organic acids. The vitamin contains a primary alcohol group, which is usually present in the naturally occurring vitamin in esterified form with ortho-, di-, or triphosphoric acid. In aqueous solution, the compound may occur in different forms, depending on pH. In acid solution, the equilibrium favors the formation of positive ions (Fig. 9.14). The thiol- form is favored in alkaline medium. This form can react with compounds containing sulfhydryl groups to form disulfide bridges. It has been suggested that thiamin occurs in some foods linked to protein by disulfide bridges.

Small quantities of thiamin are present in almost all foods of plant and animal origin. Good sources are whole cereal grains; organ meats such as liver, heart, and kidney; lean pork; eggs; nuts; and potatoes (Table 9.17). Although thiamin content is usually measured in mg per 100 g of a food, another unit has been used occasionally, the IU corresponding to 3 μg of thiamin-hydrochloride. The human daily requirement is related to the carbohydrate level of the diet. A minimum intake of 1 mg per 2000 kcal is considered essential. Increased metabolic activity, such as that which results from heavy work, pregnancy, or disease, requires higher intake.

Thiamin is one of the more unstable vitamins. Various food processing operations may considerably reduce thiamin levels. Heat, oxygen, sulfur dioxide, leaching, and neutral or alkaline pH may all result in destruction of thiamin. Light has no effect. The enzyme is stable under acid conditions; at pH values of 3.5 or below, foods can be autoclaved at 120 °C with little or no loss of thiamin. At neutral or alkaline pH, the vitamin is destroyed by boiling or even by storage at room temperature. Even the slight alkalinity of water used for processing may have an important effect. Bender (1971) reports that cooking rice in distilled water reduced thiamin content negligibly, whereas cooking in tap water caused an 8–10% loss, and cooking in well water caused a loss of up to 36%.

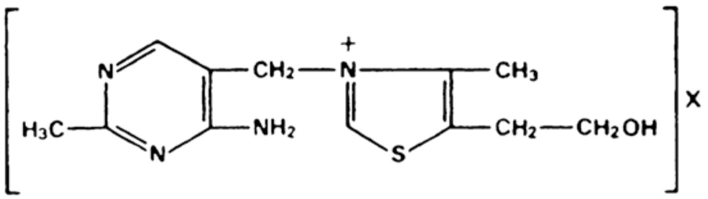


Fig. 9.13 Structural formula of thiamin. Hydrochloride: X=Cl$^-$, HCl;mononitrate:X=NO_3^-

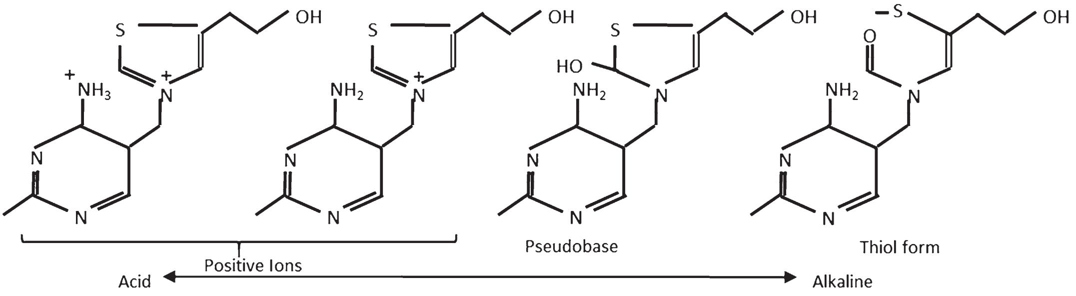


Fig. 9.14 Behavior of thiamin in aqueous solutions

Table 9.17 Thiamin content of some foods

Product	Thiamin (mg/100 g) edible portion
Almonds	0.24
Corn	0.37
Egg	0.11
Filberts	0.46
Beef heart	0.53
Beef liver	0.25
Macaroni (enriched)	0.88
Macaroni (not enriched)	0.09
Milk	0.03
Peas	0.28
Pork, lean	0.87
Potatoes	0.10
Wheat (hard red spring)	0.57
Wheat flour (enriched)	0.44
Wheat flour (not enriched)	0.08

Some fish species contain an enzyme that can destroy thiamin. Sulfur dioxide rapidly destroys thiamin. For this reason, sulfur dioxide is not permitted as an additive in foods that contain appreciable amounts of thiamin.

Baking of white bread may result in thiamin loss of 20%. Thiamin loss in milk processing is as follows: pasteurization, 3–20%; sterilization, 30–50%; spray drying, 10%; and roller drying, 20–30%. Cooking of meat causes losses that are related to size of cut, fat content, and so on. Boiling loss is 15–40%; frying, 40–50%; roasting, 30–60%; and canning, 50–75%. Similar losses apply to fish. Because thiamin and other vitamins are located near the bran of cereal grains, there is a great loss during milling. White flour, therefore, has a greatly reduced content of B vitamins and vitamin E (Fig. 9.15). Not only is thiamin content lowered by milling, but also storage of whole grain may result in losses. This depends on moisture content. At normal moisture level of 12%, 5 months' storage results in a 12% loss; at 17% moisture, a 30% loss; and at 6% moisture, no loss at all. Because of the losses that are likely to occur in cereal grain processing and in the processing of other foods, a program of fortification of flour is an important factor in preventing vitamin deficiencies. Table 9.18 lists the nutrients and recommended levels for grain products fortification (National Academy of Sciences 1974b). A summary of data relating processing treatment to thiamin stability has been given by deRitter (1976) (Table 9.19).

Vitamin B_2 (Riboflavin)

The molecule consists of a d-ribitol unit attached to an isoalloxazine ring (Fig. 9.16). Anything more than a minor change in the molecule results

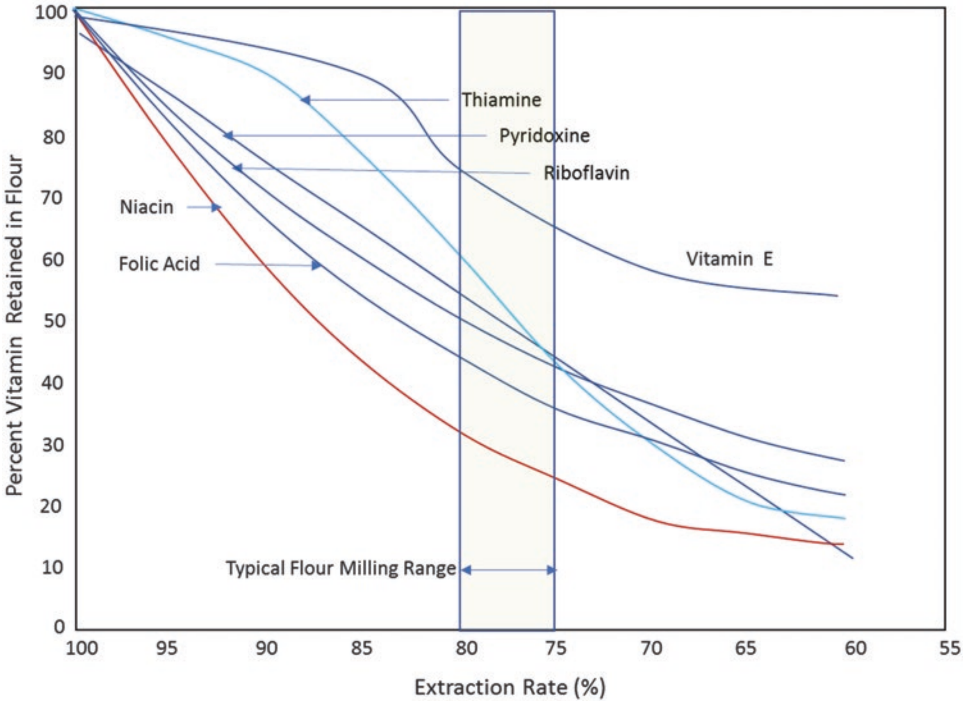


Fig. 9.15 Typical losses of vitamins during flour milling

Table 9.18 Nutrients and levels recommended for inclusion in fortification of cereal-grain products[a]

Nutrient	Level (mg/Ib)	(mg/100 g)
Vitamin A[b]	2.2	0.48
Thiamin	2.9	0.64
Riboflavin	1.8	0.40
Niacin	24.0	5.29
Vitamin B_6	2.0	0.44
Folic acid	0.3	0.07
Iron	40	8.81
Calcium	900	198.2
Magnesium	200	44.1
Zinc	10	2.2

[a] Wheat flour, corn grits, cornmeal, rice. Other cereal-grain products in proportion to their cereal-grain content

[b] Retinol equivalent

Source: Reprinted with permission from National Academy of Sciences, Recommended Dietary Allowances, 8th rev. ed., © 1974, National Academy of Sciences

Table 9.19 Thiamin stability in foods

Product	Treatment	Retention (%)
Nine canned vegetables	Processing	31–89
Four canned vegetables	Storage, 2–3 months @ room temperature	73–94
Cereals	Extrusion cooking	48–90
Fortified ready-to-eat cereal	Storage, 12 months @ 23 °C	100
Bread (white, whole wheat)	Commercial baking	74–79
Devil's food cake (pH 9)	Baking	0–7

Source: From E. deRitter, Stability Characteristics of Vitamins in Processed Foods, *Food Technol.,* Vol. 30, pp. 48–51, 54, 1976

in a loss of vitamin activity. Aqueous solutions of riboflavin are yellow with a yellowish-green fluorescence. The vitamin is a constituent of two coenzymes, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). FMN is riboflavin-5′-phosphate and forms part of several enzymes, including cytochrome c reductase. The flavoproteins serve as electron carriers and are involved in the oxidation of glucose, fatty acids, amino acids, and purines.

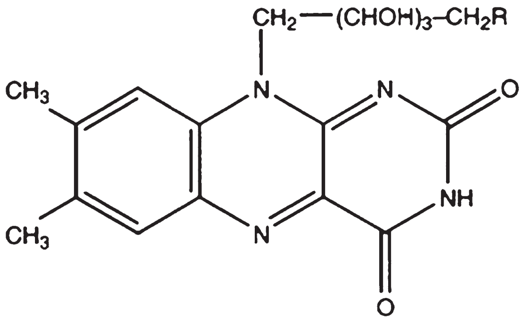


Fig. 9.16 Structural formula of riboflavin. Riboflavin: *R=OH; Riboflavin phosphate: R=*PO_3NaOH

Table 9.20 Riboflavin content of some foods

Product	Riboflavin (mg/100 g) edible portion
Beef	0.16
Cabbage	0.05
Eggs	0.30
Chicken	0.19
Beef liver	3.26
Chicken liver	2.49
Beef kidney	2.55
Peas	0.29
Spinach	0.20
Tomato	0.04
Yeast (dry)	5.41
Milk	0.17
Nonfat dry milk	1.78

Very good sources of riboflavin are milk and milk products; other sources are beef muscle, liver, kidney, poultry, tomatoes, eggs, green vegetables, and yeast (Table 9.20).

Riboflavin is stable to oxygen and acid pH but is unstable in alkaline medium and is very sensitive to light. When exposed to light, the rate of destruction increases as pH and temperature increase. Heating under neutral or acidic conditions does not destroy the vitamin.

The human requirement for riboflavin varies with metabolic activity and body weight and ranges from 1 to 3 mg per day. Normal adult requirement is 1.1–1.6 mg per day. In most cases, the riboflavin of foods is present in the form of the dinucleotide, the phosphoric acid ester, or is bound to protein. Only in milk does riboflavin occur mostly in the free form.

Under the influence of light and alkaline pH, riboflavin is transformed into lumiflavin, an inactive compound with a yellowish green fluorescence. Under acid conditions, riboflavin is transformed into another inactive derivative, lumichrome, and ribitol. This compound has a blue fluorescence. The transformation into lumiflavin in milk results in the destruction of ascorbic acid.

The light sensitivity of riboflavin results in losses of up to 50% when milk is exposed to sunlight for 2 h. The nature of the packaging material significantly affects the extent of riboflavin destruction. It appears that the wavelengths of light responsible for the riboflavin destruction are in the visible spectrum below 500–520 nm. Ultraviolet light has been reported to have no destructive effect on riboflavin (Hartman and Dryden 1978). Riboflavin is stable in dry milk for storage periods of up to 16 months. Pasteurization of milk causes only minor losses of riboflavin.

Vitamin B_6 (Pyridoxine)

There are three compounds with vitamin B_6 activity. The structural formula of pyridoxine is presented in Fig. 9.17. The other two forms of this vitamin are different from pyridoxine—they have another substituent on carbon 4 of the benzene ring. Pyridoxal has a –CHO group in this position and pyridoxamine has a $-CH_2NH_2$ group. All three compounds can occur as salts. Vitamin B_6 plays an important role in the metabolism of amino acids, where it is active in the

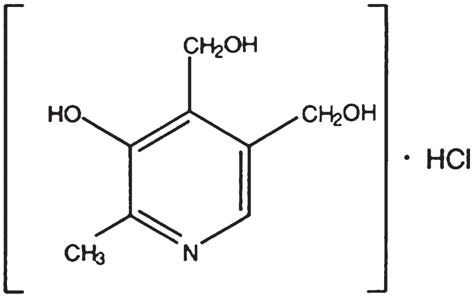


Fig. 9.17 Structural formula of pyridoxine

coenzyme form pyridoxal-5-phosphate. The three forms of vitamin B_6 are equally active in rats; although it can be expected that the same applies for humans, this has not been definitely established.

Vitamin B_6 is widely distributed in many foods (Table 9.21), and deficiencies of this vitamin are uncommon. The recommended allowance for adults has been established at 2 mg per day. The requirement appears to increase with the consumption of high-protein diets.

Vitamin B_6 occurs in animal tissues in the form of pyridoxal and pyridoxamine or as their phosphates. Pyridoxine occurs in plant products.

Pyridoxine is stable to heat and strong alkali or acid; it is sensitive to light, especially ultraviolet light and when present in alkaline solutions. Pyridoxal and pyridoxamine are rapidly destroyed when exposed to air, heat, or light. Pyridoxamine is readily destroyed in food processing operations.

Because it is difficult to determine this vitamin in foods, there is a scarcity of information on its occurrence. Recent data establish the level in milk as 0.54 mg per L. Other sources are meats, liver, vegetables, whole grain cereals, and egg yolk.

Table 9.21 Vitamin B_6 content of some foods

Product	Vitamin B_6 (μg/g)
Wheat	3.2–6.1
Whole wheat bread	4.2
White bread	1.0
Orange juice	0.52–0.60
Apple juice	0.35
Tomatoes	1.51
Beans, canned	0.42–0.81
Peas, canned	0.44–0.53
Beef muscle	0.8–4.0
Pork muscle	1.23–6.8
Milk, pasteurized	0.5–0.6
Yeast	50

The effects of processing on pyridoxine levels in milk and milk products have been reviewed by Hartman and Dryden (1978). No significant losses have been reported to result from pasteurization, homogenization, or production of dried milk. Heat sterilization of milk, however, has been reported to result in losses ranging from 36 to 49%. Losses occur not only during the heat treatment but also during subsequent storage of milk. These storage losses have been attributed to a conversion of pyridoxal to pyridoxamine and then to a different form of the vitamin. Wendt and Bernhart (1960) have identified this compound as *bis*-4-pyridoxal disulfide (Fig. 9.18). This compound is formed by reaction of pyridoxal and active sulfhydryl groups. The latter are formed during heat treatment of milk proteins. Exposure of milk to daylight in clear glass bottles for 8 h resulted in a vitamin B_6 loss of 21%.

Food canning results in losses of vitamin B_6 of 20–30%. Milling of wheat may result in losses of up to 80–90%. Baking of bread may result in losses of up to 17%.

A review of some stability data of vitamin B_6 as prepared by deRitter (1976) is given in Table 9.22.

Niacin

The term *niacin* is used in a generic sense for both nicotinic acid and nicotinamide (Fig. 9.19). Nicotinamide acts as a component of two important enzymes, NAD and NADP, which are involved in glycolysis, fat synthesis, and tissue respiration. Niacin is also known as the pellagra

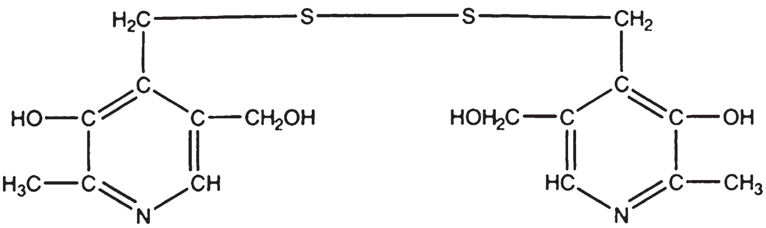


Fig. 9.18 Structural formula of *bis*-4-pyridoxal disulfide

Table 9.22 Vitamin B_6 stability in foods

Product	Treatment	Retention (%)		
Bread (added B_6)	Baking	100		
Enriched corn meal	12 months @ 38 °C + 50% relative humidity	90–95		
Enriched macaroni	12 months @ 38 °C + 50% relative humidity	100		
		Saccharomyces Carlsbergensis	Chick	Rat
Whole milk	Evaporation and sterilization	30	55	65
	Evaporation and sterilization +6 months @ room temperature	18	44	41
Infant formula, liquid	Processing and sterilization	33–50 (natural) 84 (added)		
Infant formula, dry	Spray drying	69–83		
Boned chicken	Canning	57		
	Irradiation (2.79 megarads)	68		

Source: From E. deRitter, Stability Characteristics of Vitamins in Processed Foods, *Food Technol.,* Vol. 30, pp. 48–51, 54, 1976

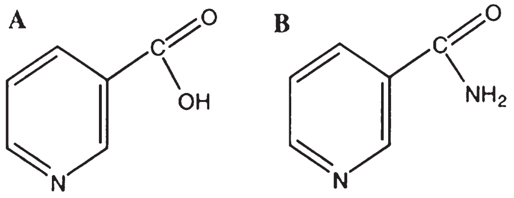


Fig. 9.19 Structural formulas of (**a**) nicotinic acid and (**b**) nicotinamide

Table 9.23 Niacin content of some foods

Product	Niacin (mg/100 g) edible portion
Barley (pearled)	3.1
Beans (green, snap)	0.5
Beans (white)	2.4
Beef (total edible)	4.4
Beef kidney	6.4
Beef liver	13.6
Chicken (dark meat)	5.2
Chicken (light meat)	10.7
Corn (field)	2.2
Haddock	3.0
Milk	0.1
Mushrooms	4.2
Peanuts	17.2
Peas	2.9
Potatoes	1.5
Spinach	0.6
Wheat	4.3
Yeast (dry)	36.7

preventive factor. The incidence of pellagra has declined but is still a serious problem in parts of the Near East, Africa, southeastern Europe, and in North American populations that subsist on com diets. When com is treated with alkali or lime, as for the tortilla preparation in Central America, the amount of available niacin can be greatly increased. Tryptophan can be converted by the body into niacin. Many diets causing pellagra are low in good quality protein as well as in vitamins. Corn protein is low in tryptophan. The niacin of corn and other cereals may occur in a bound form, called niacytin, that can be converted into niacin by alkali treatment.

The human requirement of niacin is related to the intake of tryptophan. Animal proteins contain approximately 1.4% of tryptophan, vegetable proteins about 1%. A dietary intake of 60 mg of tryptophan is considered equivalent to 1 mg of niacin. When this is taken into account, average diets in the United States supply 500–1000 mg tryptophan per day and 8–17 mg niacin for a total niacin equivalent of 16–33 mg. The RDA for adults, expressed as niacin, is 6.6 mg per 1000 kcal, and not less than 13 mg when caloric intake is less than 2000 kcal.

Good dietary sources of this vitamin are liver, kidney, lean meat, chicken, fish, wheat, barley, rye, green peas, yeast, peanuts, and leafy vegetables. In animal tissues, the predominant form of niacin is the amide. Niacin content of some foods are listed in Table 9.23.

Niacin is probably the most stable of the B vitamins. It is unaffected by heat, light, oxygen, acid, or alkali. The main loss resulting from processing involves leaching into the process water. Blanching of vegetables may cause a loss of about 15%. Processes in which brines are used may cause losses of up to 30%. Processing of milk, such as pasteurization, sterilization, evaporation, and drying have little or no effect on nicotinic acid level. Virtually all the niacin in milk occurs in the form of nicotinamide. In many foods, application of heat, such as roasting or baking, increases the amount of available niacin. This results from the change of bound niacin to the free form.

Vitamin B_{12} (Cyanocobalamine)

This vitamin possesses the most complex structure of any of the vitamins and is unique in that it has a metallic element, cobalt, in the molecule (Fig. 9.20). The molecule is a coordination complex built around a central tervalent cobalt atom and consists of two major parts—a complex cyclic structure that closely resembles the porphyrins and a nucleotide-like portion, 5,6-dimethyl-l-(α-D-ribofuranosyl) benzimidazole-3′-phosphate. The phosphate of the nucleotide is esterified with l-amino-2-propanol; this, in turn, is joined by means of an amide bond with the propionic acid side chain of the large cyclic structure. A second

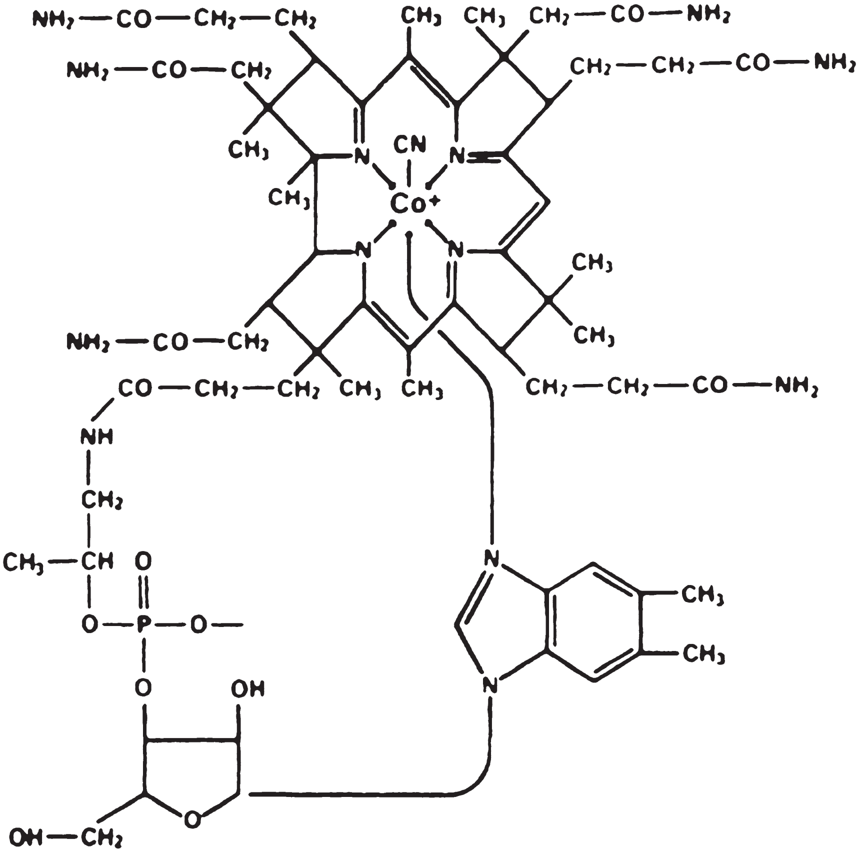


Fig. 9.20 Structural formula of cyanocobalamine

linkage with the large structure is through the coordinate bond between the cobalt atom and one of the nitrogen atoms of the benzimidazole. The cyanide group can be split off relatively easily, for example, by daylight. This reaction can be reversed by removing the light source. The cyano group can also be replaced by other groups such as hydroxo, aquo, and nitroto. Treatment with cyanide will convert these groups back to the cyano form. The different forms all have biological activity.

Cyanocobalamine is a component of several coenzymes and has an effect on nucleic acid formation through its action in cycling 5-methyltetrahydrofolate back into the folate pool. The most important dietary sources of the vitamin are animal products. Vitamin B_{12} is also produced by many microorganisms. It is not surprising that vitamin B_{12} deficiency of dietary origin only occurs in vegetarians.

The average diet in the United States is considered to supply between 5 and 15 μg/day. In foods, the vitamin is bound to proteins via peptide linkages but can be readily absorbed in the intestinal tract. The RDA is 3 μg for adults and adolescents.

Few natural sources are rich in vitamin B_{12}. However, only very small amounts are required in the diet. Good sources are lean meat, liver, kidney, fish, shellfish, and milk (Table 9.24). In milk, the vitamin occurs as cobalamine bound to protein.

Table 9.24 Vitamin B_{12} content of some foods

Product	Vitamin B_{12}
Beef muscle	0.25–3.4 μg/100 g
Beef liver	14–152 μg/100 g
Milk	3.2–12.4 μg/L
Shellfish	600–970 μg/100 g (dry wt)
Egg yolk	0.28–1.556 μg/100 g

Vitamin B_{12} is not destroyed to a great extent by cooking, unless the food is boiled in alkaline solution. When liver is boiled in water for 5 min, only 8% of the vitamin B_{12} is lost. Broiling of meat may result in higher losses. Pasteurization causes only a slight destruction of vitamin B_{12} in milk; losses range from 7 to 10% depending on pasteurization method. More drastic heat treatment results in higher losses. Boiling milk for two to 5 min causes a 30% loss, evaporation about 50%, and sterilization up to 87%. The loss in drying of milk is smaller; in the production of dried skim milk, the vitamin B_{12} loss is about 30%. Ultra-high-temperature sterilization of milk does not cause more vitamin B_{12} destruction than does pasteurization.

Folic Acid (Folacin)

Folic acid is the main representative of a series of related compounds that contain three moieties: pterin, *p*-aminobenzoic acid, and glutamic acid (Fig. 9.21). The commercially available form contains one glutamic acid residue and is named pteroylglutamic acid (PGA). The naturally occurring forms are either PGA or conjugates with varying numbers of glutamic acid residues, such as tri- and heptaglutamates. It has been suggested that folic acid deficiency is the most common vitamin deficiency in North America and Europe. Deficiency is especially likely to occur in pregnant women.

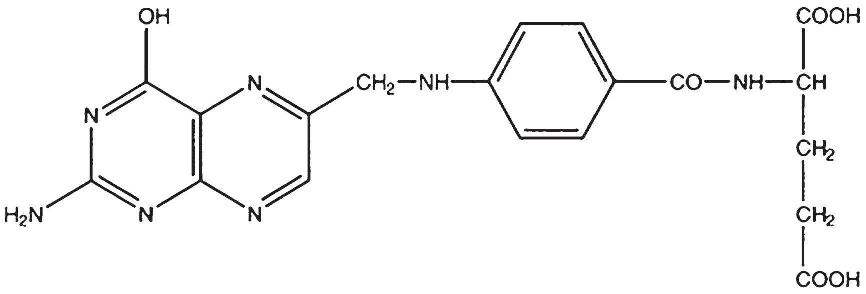


Fig. 9.21 Structural formula of folic acid

The vitamin occurs in a variety of foods, especially in liver, fruit, leafy vegetables, and yeast (Table 9.25) (Hurdle et al. 1968; Streiff 1971). The usual form of the vitamin in these products is a polyglutamate. The action of an enzyme (conjugase) is required to liberate the folic acid for metabolic activity; this takes place in the intestinal mucosa. The folacin of foods can be divided into two main groups on the basis of its availability to *L. casei*: (1) the so-called free folate, which is available to *L. casei* without conjugase treatment; and (2) the total folate, which also includes the conjugates that are not normally available to *L. casei.* About 25% of the dietary folacin occurs in free form. The folate in vegetables occurs mainly in the conjugated form; the folate in liver occurs in the free form.

The RDA for folacin is 400 μg for adults. There is an additional requirement of 400 μg/day during pregnancy and 200 μg/day during breastfeeding.

Many of the naturally occurring folates are extremely labile and easily destroyed by cooking. Folic acid itself is stable to heat in an acid medium but is rapidly destroyed under neutral and alkaline conditions. In solution, the vitamin is easily destroyed by light. Folate may occur in a form more active than PGA; this is called folinic acid or citrovorum factor, which is N5-formyl-5, 6, 7, 8-tetrahydro PGA (Fig. 9.22). The folate of milk consists of up to 20% of folinic acid. It has been reported that pasteurization and sterilization of milk involve only small losses or no loss. Hurdle et al. (1968) reported that boiling of milk causes no loss in folate; however, boiling of potato results in a 90% loss and boiling of cabbage a 98% loss. Reconstitution of dried milk followed by sterilization as can occur with baby formulas may lead to significant folacin losses. Fermentation of milk and milk products may result in greatly increased folate levels. Blanching of vegetables and cooking of meat do not appear to cause folic acid losses. Table 9.26 contains a summary of folate stability data prepared by deRitter (1976). Citrus fruit and juices are relatively good sources of folic acid, which is present mostly as the reduced 5-methyl tetrahydro folate (monoglutamate form). There are also polyglutamate derivatives present White (1991).

Table 9.25 Folate content of some foods

Product	Folate (μg/g)
Beef, boiled	0.03
Chicken, roasted	0.07
Cod, fried	0.16
Eggs, boiled	0.30
Brussels sprouts, boiled	0.20
Cabbage, boiled	0.11
Lettuce	2.00
Potato, boiled	0.12
Spinach, boiled	0.29
Tomato	0.18
Orange	0.45
Milk	0.0028
Bread, white	0.17
Bread, brown	0.38
Orange juice, frozen reconstituted	0.50
Tomato juice, canned	0.10

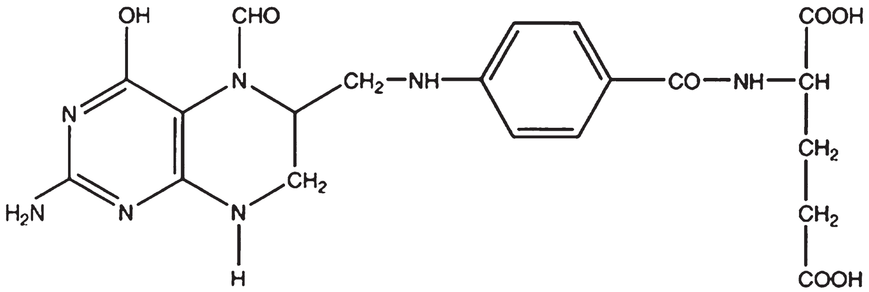


Fig. 9.22 Structural formula of folinic acid

Table 9.26 Folic acid stability in foods

Product	Treatment	Retention of folic acid	
		Free (%)	Total (%)
Cabbage	Boiled 5 min	32	54
Potatoes	Boiled 5 min	50	92
Rice	Boiled 15 min	–	10
Beef, pork, and chicken	Boiled 15 min	<50	<50
Various foods	Cooked	27	55

Source: From E. deRitter, Stability Characteristics of Vitamins in Processed Foods, *Food Technol.*, Vol. 30, pp. 48–51, 54, 1976

Pantothenic Acid

The free acid (Fig. 9.23) is very unstable and has the appearance of a hygroscopic oil. The calcium and sodium salts are more stable. The alcohol (panthenol) has the same biological activity as the acid. Only the dextrorotatory or D form of these compounds has biological activity. Pantothenic acid plays an important role as a component of coenzyme A, and this is the form in which it occurs in most foods.

Pantothenic acid occurs in all living cells and tissues and is, therefore, found in most food products. Good dietary sources include meats, liver, kidney, fruits, vegetables, milk, egg yolk, yeast, whole cereal grains, and nuts (Table 9.27). In animal products, most of the pantothenic acid is present in the bound form, but in milk only about one-fourth of the vitamin is bound.

There is no recommended dietary allowance for this vitamin because of insufficient evidence to base one on. It is estimated that adult dietary intake in the United States ranges from 5 to 20 mg/day, and 5 to 10 mg/day probably represents an adequate intake.

The vitamin is stable to air, and labile to dry heat. It is stable in solution in the pH range of 5–7 and less stable outside this range. Pasteurization and sterilization of milk result in very little or no loss. The production and storage of dried milk involves little or no loss of pantothenic acid. Manufacture of cheese involves large losses during processing, but during ripening the pantothenic acid content increases, due to synthesis by microorganisms. Blanching of vegetables may involve losses of up to 30%. Boiling in water involves losses that depend on the amount of water used.

Biotin

The structural formula (Fig. 9.24) contains three asymmetric carbon atoms, and eight different stereoisomers are possible. Only the dextrorotatory D-biotin occurs in nature and has biological activity. Biotin occurs in some products in free form (vegetables, milk, and fruits) and in other products is bound to protein (organ meats, seeds, and yeast). Good sources of the vitamin are meat, liver, kidney, milk, egg yolk, yeast, vegetables, and mushrooms (Table 9.28).

Biotin is important in a number of metabolic reactions, especially in fatty acid synthesis. The biotin supply of the human organism is only partly derived from the diet.

An important factor in biotin's availability is that some of the vitamin is derived from synthesis by intestinal microorganisms; this is demonstrated by the fact that three to six times more biotin is excreted in the urine than is ingested with the food. The daily intake of biotin is between 100 and 300 μg. No recommended dietary allowance has been established. Biotin is deactivated by raw egg white. This is caused by the glycoprotein avidin. Heating of avidin will destroy the inactivator capacity for biotin.

Data on the stability of biotin are limited. The vitamin appears to be quite stable. Heat treatment results in relatively small losses. The vitamin is stable to air and is stable at neutral and acid pH. Pasteurization and sterilization of milk result in losses of less than 10%. In the production of evaporated and dried milk, losses do not exceed 15%.

$$CH_2OH—C(CH_3)_2—CHOH—CO—NH—CH_2—CH_2—R$$

Fig. 9.23 Structural formula of pantothenic acid. Pantothenic acid: R=COOH; Panthenol: R=CH_2OH

Table 9.27 Pantothenic acid content of some foods

Product	Pantothenic acid (μg/g)
Beef, lean	10
Wheat	11
Potatoes	6.5
Split peas	20–22
Tomatoes	1
Orange	0.7
Walnuts	8
Milk	1.3–4.2
Beef liver	25–60
Eggs	8–48
Broccoli	46

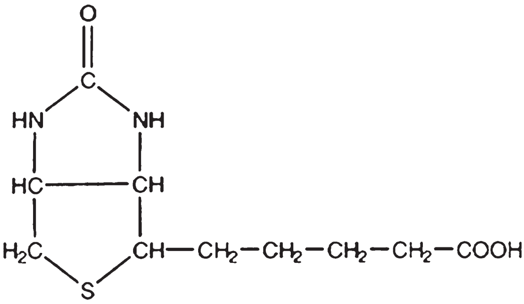


Fig. 9.24 Structural formula of biotin

Table 9.28 Biotin content of some foods

Product	Biotin (μg/100 g)
Milk	1.1–3.7
Tomatoes	1
Broad beans	3
Cheese	1.1–7.6
Wheat	5.2
Beef	2.6
Beef liver	96
Lettuce	3.1
Mushrooms	16
Potatoes	0.6
Spinach	6.9
Apples	0.9
Oranges	1.9
Peanuts	34

Vitamins as Food Ingredients

In addition to their role as essential micronutrients, vitamins may serve as food ingredients for their varied functional properties (Institute of Food Technologists 1987). Vitamin C and vitamin E have found widespread use as antioxidants. In lipid systems, vitamin E may be used as an antioxidant in fats that have little or no natural tocopherol content. Ascorbic acid in the form of its palmitic acid ester, ascorbyl palmitate, is an effective antioxidant in lipid systems. Ascorbyl palmitate prevents the formation of lipid free radicals (Fig. 9.25) and thereby delays the initiation of the chain reaction that leads to the deterioration of the fat (Liao and Seib 1987). Ascorbyl palmitate is used in vegetable oils because it acts synergistically with naturally occurring tocopherols. The tocopherols are fat-soluble antioxidants that are used in animal fats. Ascorbic acid reduces nitrous acid to nitric oxide and prevents the formation of N-nitrosamine. The reaction of nitrous acid and ascorbic acid is given in Fig. 9.26 (Liao and Seib 1987). Ascorbic acid is also widely used to prevent enzymic browning in fruit products. Phenolic compounds are oxidized by polyphenoloxidase to quinones. The quinones rapidly polymerize to form brown pigments. This reaction is easily reversed by ascorbic acid (Fig. 9.27).

The carotenoids β-carotene and β-apo-8-carotenal are used as colorants in fat-based as well as water-based foods.

Other functions of ascorbic acid are inhibition of can corrosion in canned soft drinks, protection of flavor and color of wine, prevention of black spot formation in shrimp, stabilization of cured meat color, and dough improvement in baked goods (Institute of Food Technologists 1987).

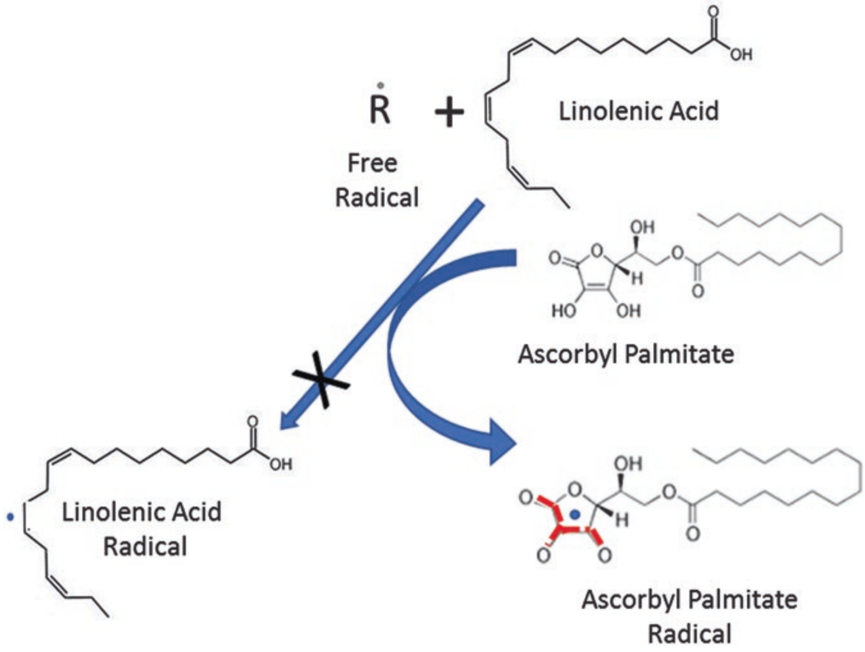
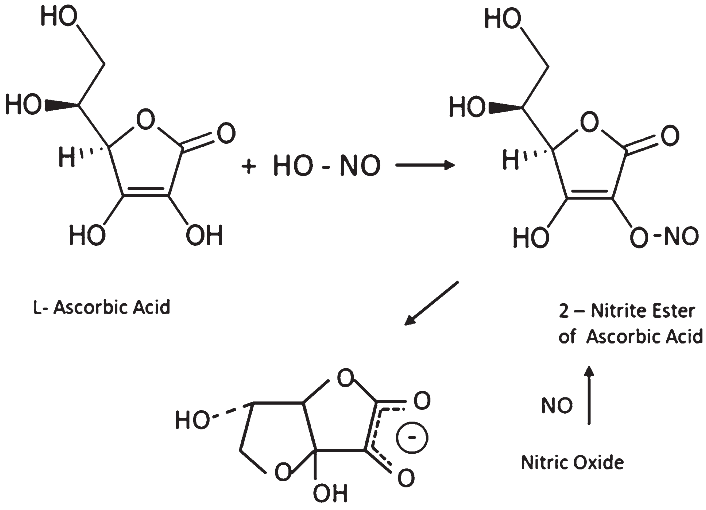


Fig. 9.25 Prevention of lipid free radical formation in linoleic acid by ascorbyl palmitate

Fig. 9.26 Reaction between nitrous acid and ascorbic acid. *Source:* From M.L. Liao and P.A. Seib, Selected Reactions of L-Ascorbic Acid Related to Foods, *Food Technol.*, Vol. 41, no. 11, pp. 104–107, 1987



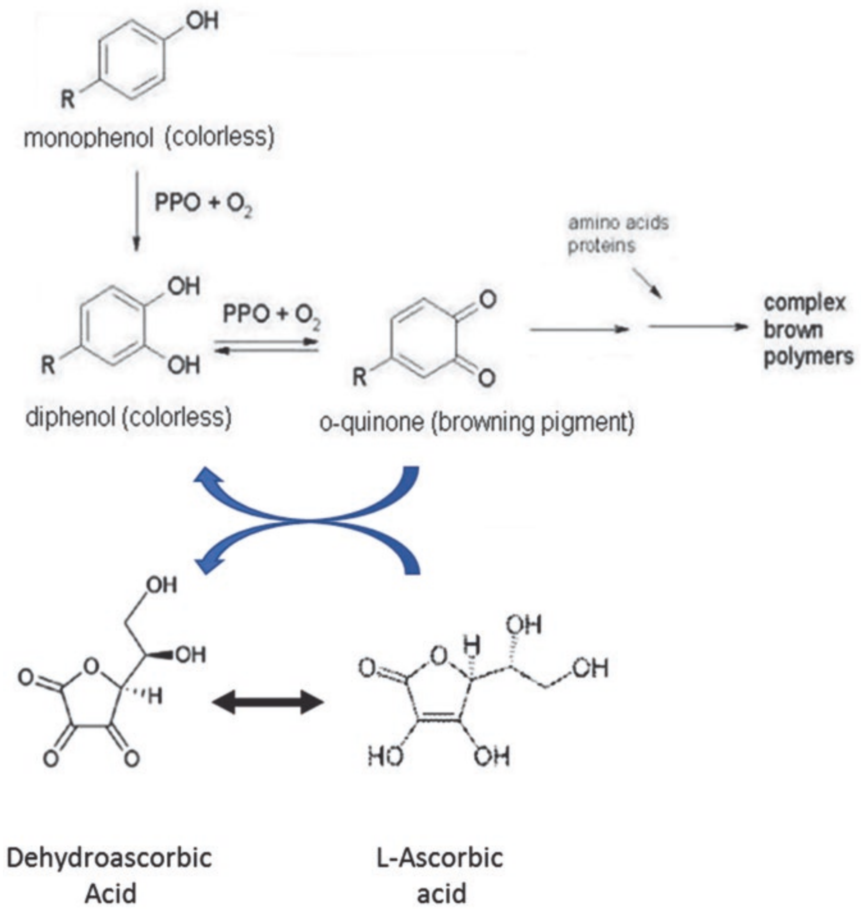


Fig. 9.27 Reduction of ortho-quinone by ascorbic acid during enzymatic browning

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