



VITAMINS





Point –point diskusi kelompok

- Rumus kimiawi dasar vitamin A/D/E/K
- Konversi provitamin A/D menjadi vitamin A/D
- Karakteristik vitamin A/D/E/K
- Sumber vitamin A/D/E/K
- Aplikasi pada proses pengolahan pangan

Referensi dari bahan kuliah yang diberikan
(Principles of Food Chemistry – deMan)

INTRODUCTION



- Minor constituents of foods
- Essential micronutrients
- Biological functions:
 - Coenzymes (thiamine, riboflavin, niacin, pantothenic acid, biotin, B6, B12, folate)
 - Components of antioxidative defence systems (ascorbic acid, certain carotenoids and tocopherols)
 - Specified functions (vit A in vision, vit K in specific carboxylation)
 - Factors involved in genetic regulation (vit A & D)

Vitamins (1)



- Many vitamins are unstable under certain conditions of processing and storage, therefore their levels in processed may be drastically reduced.
- Synthetic vitamins are used extensively to compensate for those losses and to restore vitamin levels in food.
- Fat-soluble (A, D, E,& K) and water soluble (all the other ones) vitamins

Vitamins (2)



- 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.
- Sources of vitamins in significant amounts by food groups:
 - Meats, poultry, fish, beans provide thiamin, riboflavin, niacin, pyridoxine, pantothenic acid, biotin, and vit B12.

Vitamins (3)



- Milk and milk products provide vitamins A and D, riboflavin, pyridoxine and vitamin B12.
- Bread and cereals provide thiamin, riboflavin, niacin, pyridoxine, folate, panthothenic acid and biotin.
- Fruits and vegetables provide vitamins A and K, ascorbic acid, riboflavin and folate.
- Fats and oils provide vitamins A and E.

Table 10.1 Vitamins and some commonly used synonyms

Vitamin	Synonyms
<i>Fat-soluble</i>	
vitamin A	retinol
vitamin D ₂	ergocalciferol
vitamin D ₃	cholecalciferol
vitamin E	alpha, beta and gamma tocopherols and alpha tocotrienol
vitamin K ₁	phylloquinone, phytomenadione
vitamin K ₂	farnoquinone, menaquinone
vitamin K ₃	menadione
<i>Water-soluble</i>	
vitamin B ₁	thiamin
vitamin B ₂	riboflavin
vitamin B ₆	pyridoxal, pyridoxine, pyridoxamine
vitamin B ₁₂	cobalamins, cyanocobalamin, hydroxocobalamin
niacin	nicotinic acid (vitamin PP)
niacinamide	nicotinamide (vitamin PP)
pantothenic acid	—
folic acid	folacin (vitamin M)
biotin	vitamin H
vitamin C	ascorbic acid

A decorative graphic consisting of six circles arranged in two rows of three. The top row has one white circle with a thin yellow outline on the left, and two solid yellow circles on the right. The bottom row has two solid yellow circles on the left, and one white circle with a thin yellow outline on the right. A solid yellow horizontal bar is centered across the middle of the circles, containing the text "FAT-SOLUBLE VITAMINS" in bold, dark grey, uppercase letters.

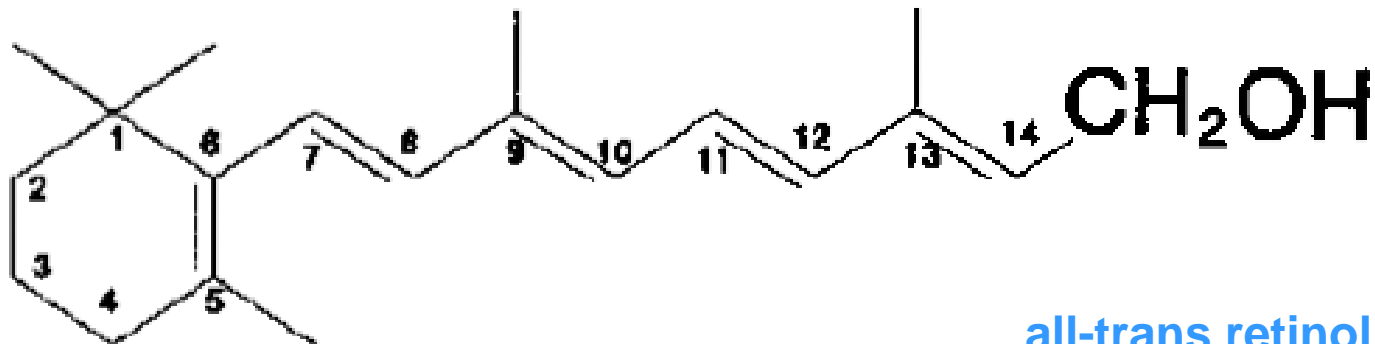
FAT-SOLUBLE VITAMINS

Vitamin A (Retinol)

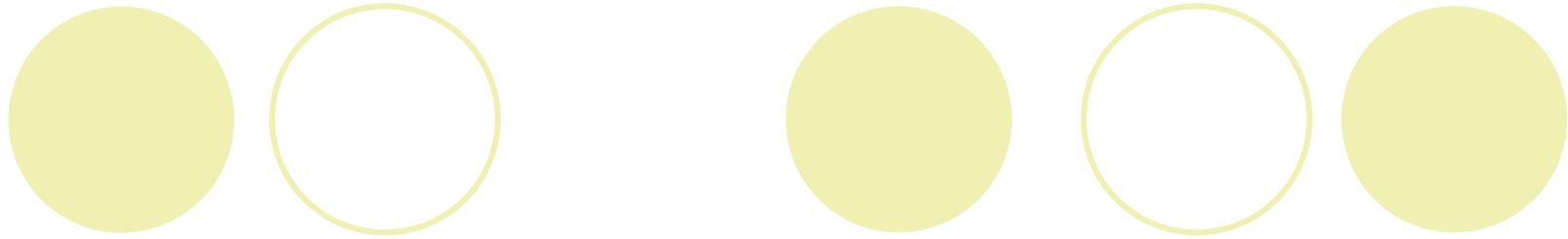
- Vitamin A is the generic descriptor for compounds with the qualitative biological activity of retinol, i.e. retinoids and some (pro-vitamin A) carotenoids.
- Vitamin A-active substances are hydrophobic and, thus are insoluble in aqueous environments.
- Vitamin A was discovered by its ability to prevent night blindness.

Essential features of the chemical structure

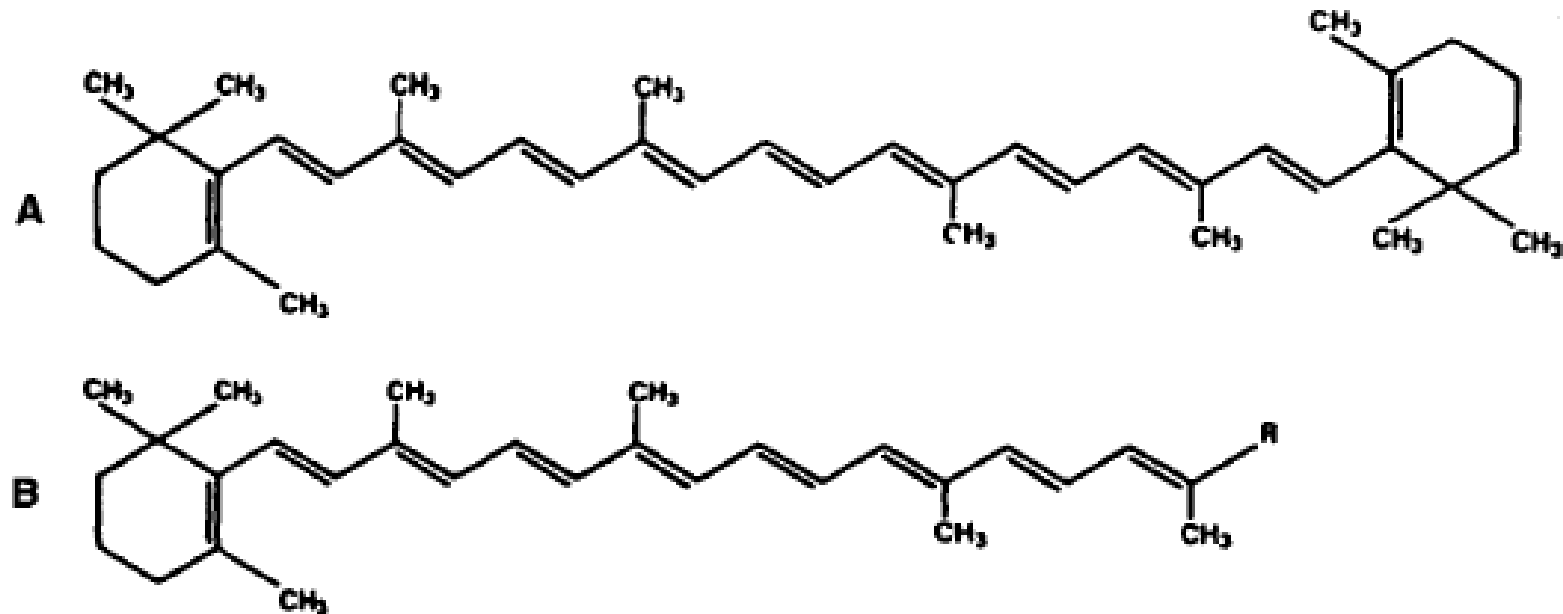
- Substituted β -ionone ring (4-[2,6,6-trimethyl-2cyclohexen-1-yl]-3-buten-2-one)
- Side-chain composed of 3 isoprenoid units joined head to tail at the 6-position of the β -ionone ring
- Conjugated double bond system among the side-chain and 5,6-ring carbon atoms



all-trans retinol



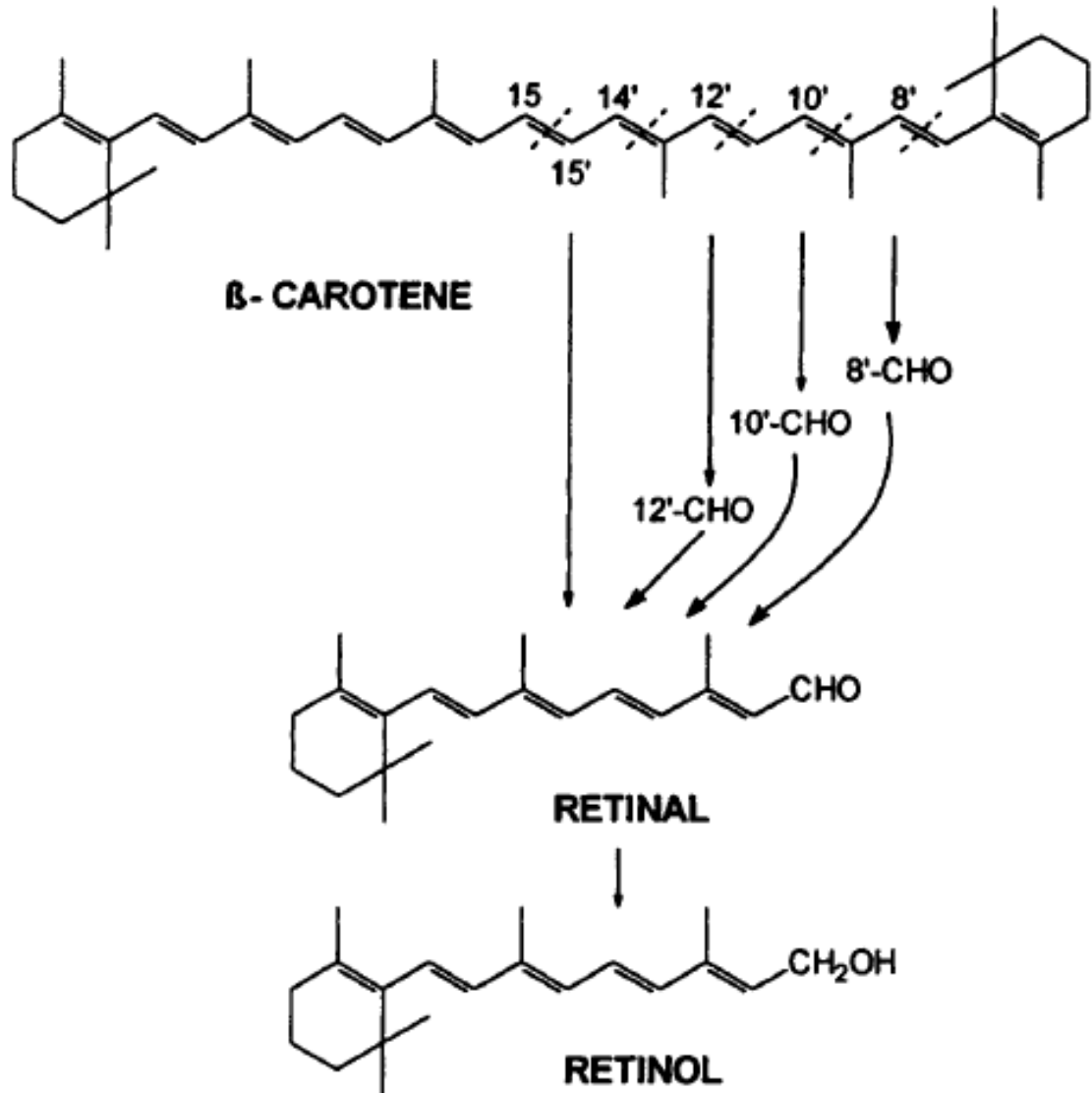
- The all-trans form is the most active biologically. It is an alcohol that occurs in nature predominantly in the form of fatty acid esters.
- The synthetic vitamin A is made as acetate or palmitate and marketed commercially in the form of oil solutions, stabilized powders, or aqueous emulsions. The compounds are insoluble in water but soluble in fats, oils and fat solvents.



Structural Formulas of Some Provitamins A. (A) β -carotene, and (B) apocarotenal (R = CHO) and apocarotenoic acid ester (R = COOC_2H_5).

- There are several provitamins A; these belong to the carotenoid pigments.
- The most important one is β -carotene and its derivations.
- One molecule of β -carotene can yield two molecules of vitamin A.
- Other provitamins are α - and γ -carotene and cryptoxanthin.

The conversion of β -carotene to vitamin A



- The enzyme 15-15'-dioxygenase is able to cleave a β -carotene molecule symmetrically to produce two molecules of vitamin A.
- This enzyme occurs in intestinal mucosa, but the actual conversion is much less efficient.
Or..
- After cleavage of the β -carotene, the first reaction product is retinal, which is reduced to retinol.



The unit of vitamin A

- Vitamin A levels are frequently expressed in International Units (IU), although this unit is officially no longer accepted.
- **One IU equals** 0.344 μg of crystalline vitamin A acetate, or 0.300 μg vitamin A alcohol, or **0.600 μg β -carotene.**
- 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 (1974) states that **1 retinol equivalent** is equal to **3.3 IU of retinol** or **10 IU of β -carotene.**



Vitamin A Sources

- Vitamin A occurs only in animals and not in plants. The A1 form (retinol) occurs in all animals and fish. The A2 form (dihydroretinol) in freshwater fish and not in land animals.
- 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.

Vitamin A and Carotene Sources

Product	Vitamin A (IU/100 g)	Carotene (mg/100 g)
Beef (grilled sirloin)	37	0.04
Butter	2363 – 3452	0.43 – 0.77
Cheddar cheese	553 – 1078	0.07 – 0.71
Eggs (boiled)	165 - 488	0.01 – 0.15
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



The application of vitamin A



- Vitamin A is used to fortify margarine and skim milk.
- It is added to margarine at a level of 3,525 IU per 100 g.
- Some of the carotenoids (provitamin A) are used as food colors.



The stability of vitamin A

- Vitamin A is relatively stable to heat in the absence of oxygen.
- Vitamin A and the carotenoids have good stability during various food processing operations. Losses may occur at high temperatures in the presence of oxygen.
- It is quite susceptible to oxidation (especially under the influence of light).
- It is unstable in the presence of mineral acids but stable in alkali.
- Vitamin A and the carotenoids are also susceptible to oxidation by lipid peroxides, and other conditions favoring lipid oxidation.

Table 9-4 Vitamin A and Carotene Stability in Foods

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

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



The stability of vitamin A

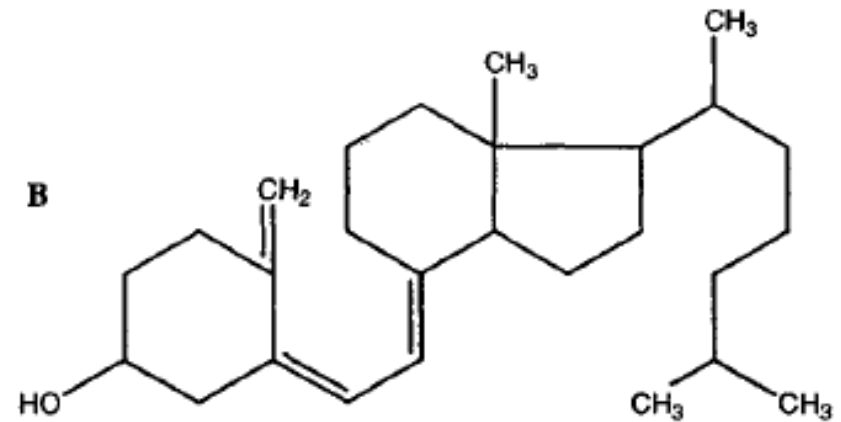
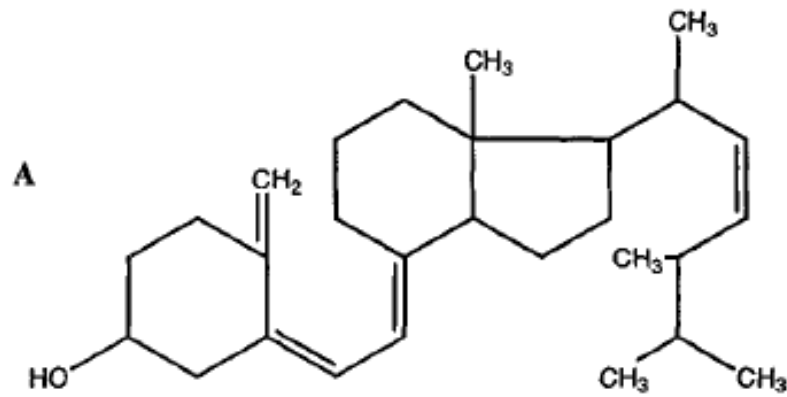


- The form in which vitamin A is added to food products may influence its stability.
- Vitamin A in beadlet form is more stable than that added as a solution in oil.
- The beadlets are stabilized by a protective coating. If this coating is damaged by water, the stability of the vitamin is greatly reduced.
- Vitamin A added to milk is more easily destroyed by light than the native vitamin A, because these two types of vit A are dispersed differently in the milk.

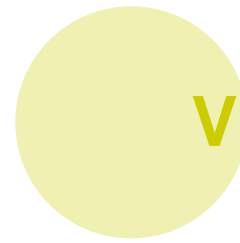
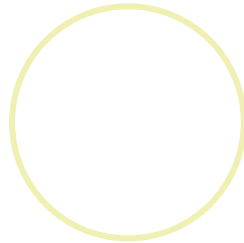
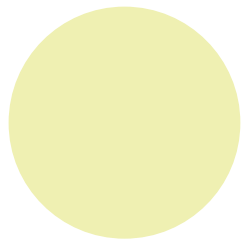
Vitamin D

- This vitamin occurs in several forms; the two most important are vitamin D2, or ergocalciferol, and vitamin D3, or cholecalciferol.
- Vitamin D is the generic descriptor for steroids exhibiting qualitatively the biological activity of cholecalciferol
- Most vitamers D are hydrophobic and thus are insoluble in aqueous environments
- Vitamin D is not required in the diets of animals or humans adequately exposed to sources of UV

The structure of vitamin D



Structural Formulas of (A) Vitamin D2 and (B) Vitamin D3

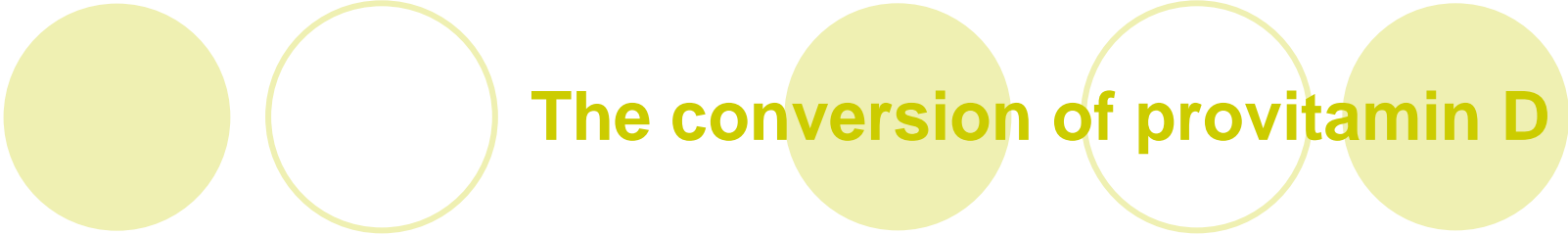


Vitamin D sources

- Vitamin D does not occur in plant products.
- Vitamin D2 occurs in small amounts in fish liver oils.
- Vitamin D3 is widely distributed in animal products, but large amounts occur only in fish liver oils. Smaller quantities of vitamin D3 occur in eggs, milk, butter, and cheese.

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	2,500

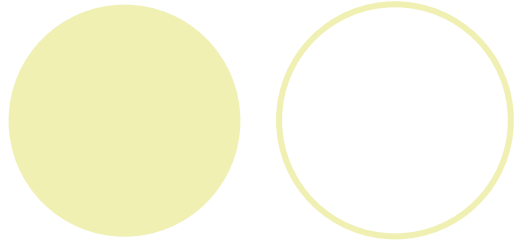


The conversion of provitamin D

- The precursors of vitamins D2 and D3 are ergosterol and 7-dehydrocholesterol, respectively.
- These precursors or provitamins can be converted into the respective D vitamins by irradiation with ultraviolet light.
- 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.



- 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 D2 or D3.



The stability of vitamin D



- 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.
- 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.



Increasing vitamin D concentration in food

- Feeding cows substances that are high in vitamin D activity, such as irradiated yeast
- Irradiating milk (it has been discontinued due to the effect of irradiation on other milk components).
- Adding vitamin D concentrates (the most common procedure).



The application of vitamin D

- 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.
- 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 550IU per 100 g.



The application of vitamin D

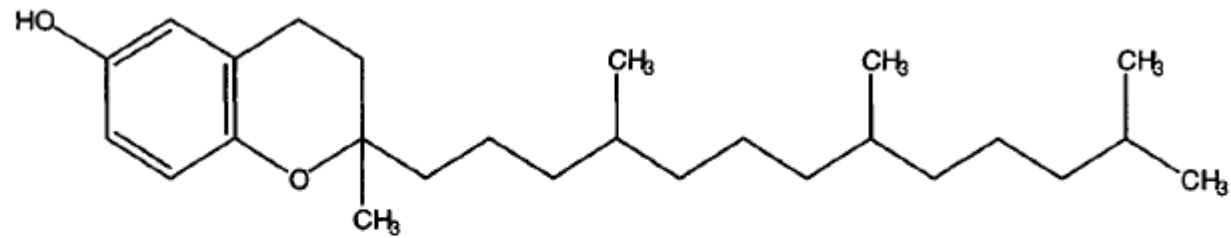
- Both vitamins D₂ and D₃ are manufactured for commercial use.
- Preparations of vitamin D in edible oils are more stable than the crystalline forms, and the vitamin is normally provided for commercial usage as an oil preparation or stabilised powder containing an antioxidant (usually tocopherol).

Vitamin E (Tocopherols)

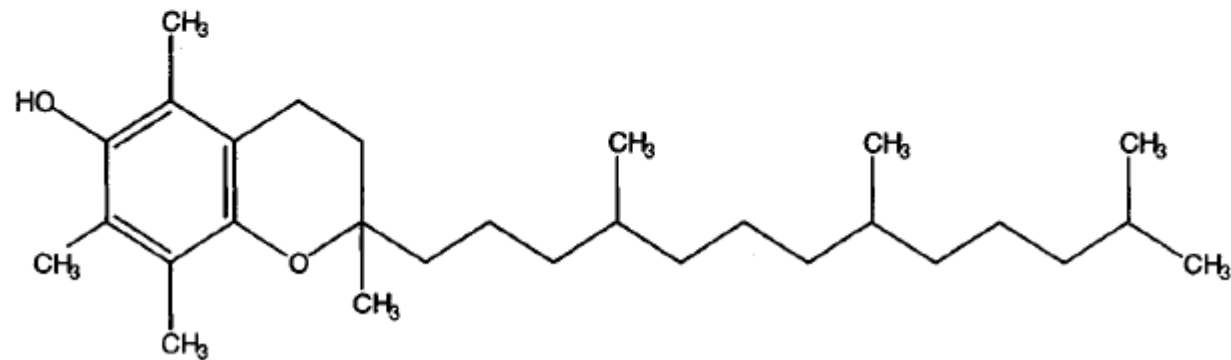
- Vitamin E is the generic descriptor for all tocol and trienol derivatives exhibiting qualitatively the biological activity of α -tocopherol.
- There are four tocopherols and four tocotrienols
- The tocotrienols have three unsaturated isoprenoid groups in the side chain.

The structure of vitamin E

A

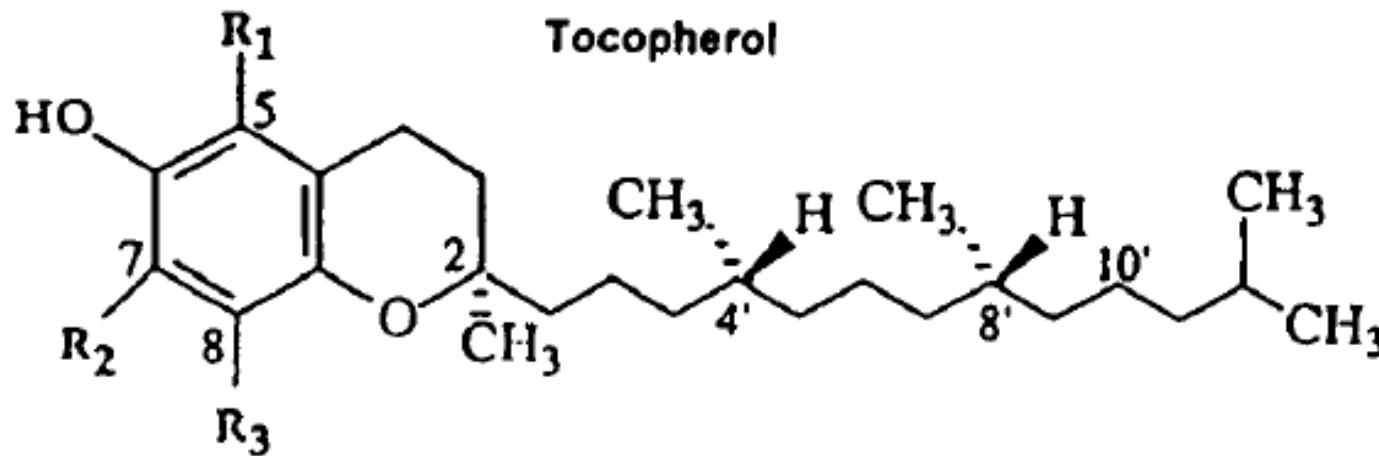


B



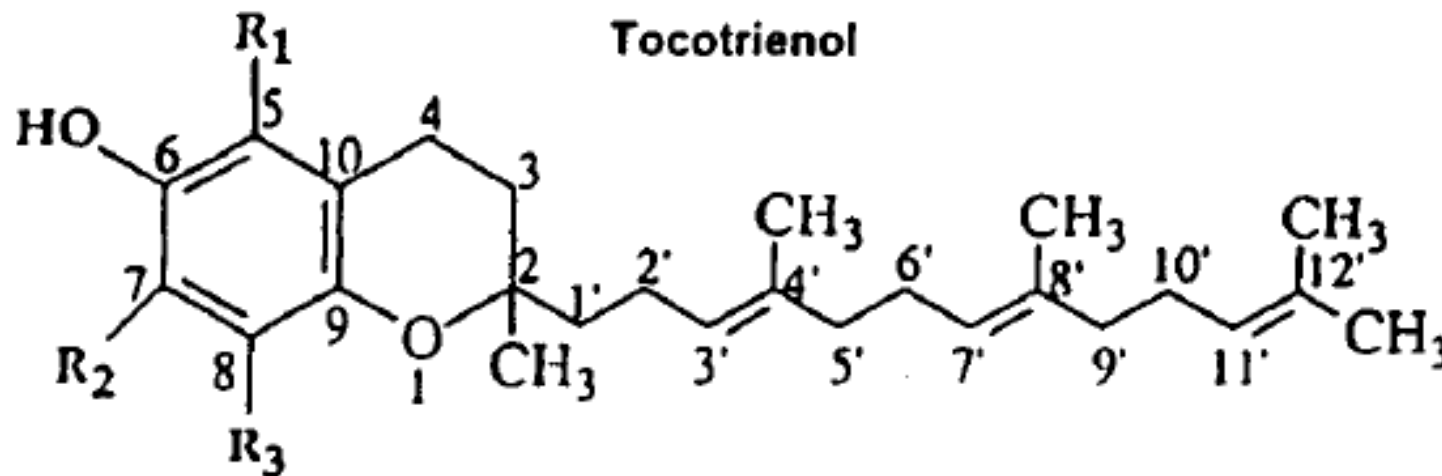
Structural Formula of (A) Tocol and (B) α -Tocopherol

- The four tocopherols are characterized by a saturated side chain consisting of three isoprenoid units.

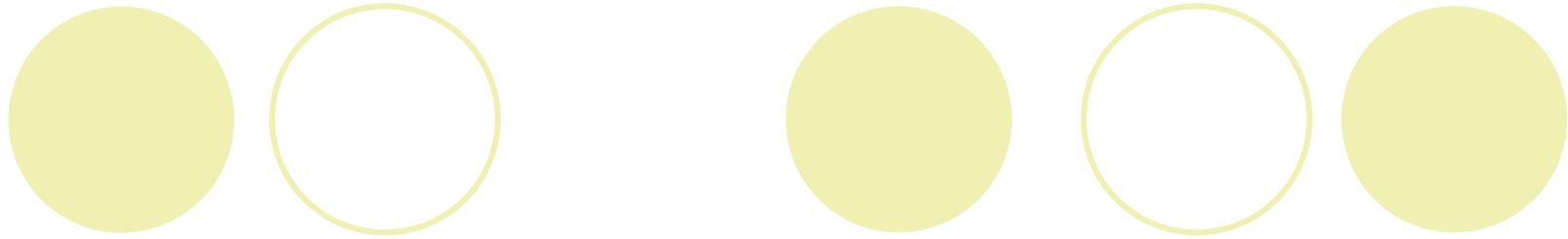


Tocopherol	Tocopherol	R ₁	R ₂	R ₃
α	5,7,8 - Trimethyl	CH ₃	CH ₃	CH ₃
β	5,8 - Dimethyl	CH ₃	H	CH ₃
γ	7,8 - Dimethyl	H	CH ₃	CH ₃
δ	8 - Methyl	H	H	CH ₃

- The tocotrienols have three double bonds at the 3', 7', and 11' carbons of the isoprenoid side chain



Tocotrienol	Tocotrienol	R ₁	R ₂	R ₃
α	5,7,8 - Trimethyl	CH ₃	CH ₃	CH ₃
β	5,8 - Dimethyl	CH ₃	H	CH ₃
γ	7,8 - Dimethyl	H	CH ₃	CH ₃
δ	8 - Methyl	H	H	CH ₃



- The vitamers E are hydrophobic and thus insoluble in aqueous environments.
- By the virtue of phenolic hydrogen on the C-6 ring-hydroxyl group, the vitamers E have antioxidant activities in vitro.
- Much of the biological activity of the tocopherols is related to their antioxidant activity.
- α -tocopherol is the most abundant of the different tocopherols, and have the greatest biological activity



Vitamin E Sources

- 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.
- Cereals and cereal products are good sources of tocopherol.

Table 9-7 Tocopherol (T) and Tocotrienol (T3) Content of Vegetable Oils and Their Primary Homologs

<i>Fats and Oils</i>	<i>Total T+T3 (mg/100g)</i>	<i>α-TE/ 100g</i>	<i>%T</i>	<i>%T3</i>	<i>Primary Homologs</i>
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, α-T, 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

Table 9–8 Tocopherol Content of Some Animal and Vegetable Food Products

<i>Product</i>	<i>Total Tocopherol as α-Tocopherol (mg/100 g)</i>
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

Table 9–9 Tocopherol Content of Cereals and Cereal Products

<i>Product</i>	<i>Total Tocopherol as α- Tocopherol (mg/100 g)</i>
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

- Flour of different degrees of extraction can have different tocopherol levels.

Table 9–10 Tocopherol Content of Wheat and Its Milling Products

<i>Product</i>	<i>Ash (%)</i>	<i>Tocopherol mg/100 g (Dry Basis)</i>
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



The stability of vitamin E



- Processing and storage of foods can result in substantial tocopherol losses.
Example: potato chips (by frying) --- only two weeks' storage of the chips at room temperature, nearly half of the tocopherol was lost, the losses were only slightly smaller during storage at freezer temperature.
- The processing of vegetable oils by deodorization or physical refining removes a considerable portion of the tocopherols.

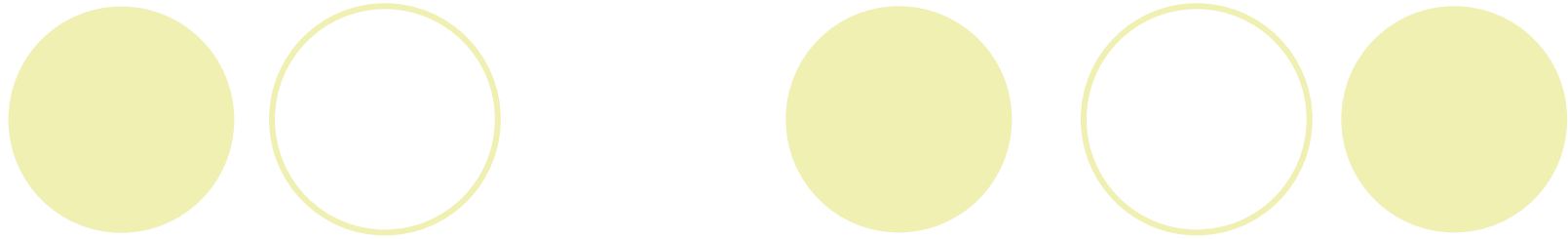


- Boiling of vegetables in water for up to 30 minutes results in only minor losses of tocopherol.
- Baking of white bread results in a loss of about 5 percent of the tocopherol in the crumb.



Table 9–11 Tocopherol Losses During Processing and Storage of Potato Chips

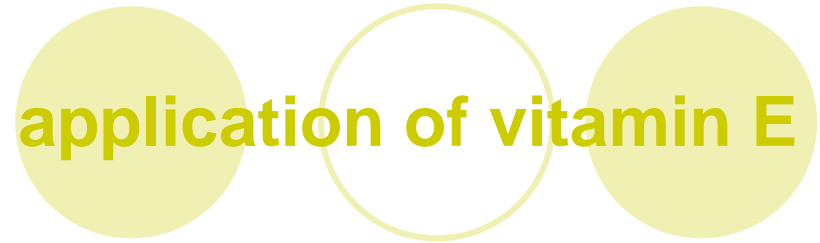
	<i>Tocopherol (mg/100 g)</i>	<i>Loss (%)</i>
Oil before use	82	—
Oil after use	73	11
Oil from fresh chips	75	—
After two weeks at room temperature	39	48
After one month at room temperature	22	71
After two months at room temperature	17	77
After one month at -12°C	28	63
After two months at -12°C	24	68



- α -Tocopherol is readily oxidised by air. It is stable to heat in the absence of air but is degraded if heated in the presence of air and is readily oxidised during the processing and storage of foods.
- DL- α -Tocopheryl acetate is relatively stable in air but is hydrolysed by moisture in the presence of alkalis or strong acids to free tocopherols.



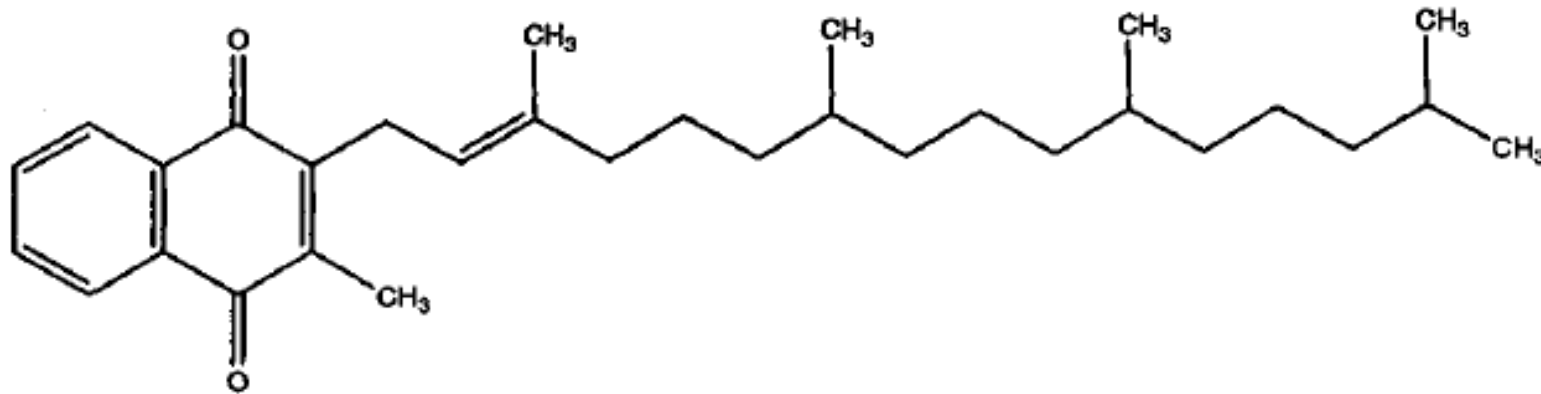
The application of vitamin E



- 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 two years.

Vitamin K

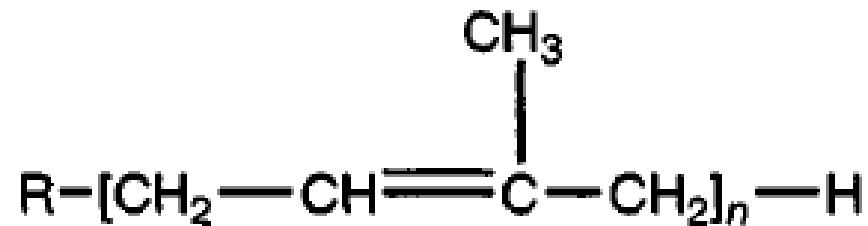
- Vitamin occurs in a series of different forms, and these can be divided into two groups, including K_1 (phylloquinone) and K_2 (menaquinone).
- Vitamin K_1 characterized by one double bond in the side chain.





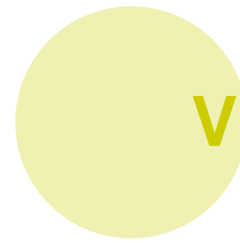
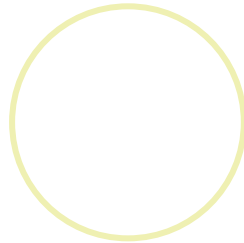
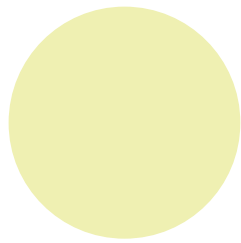
The structure of Vitamin K

- The vitamins K₂ have a side chain consisting of a number of regular units of the type



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

- Vitamin K₃ or menadione (2-methyl 1,4-naphthoquinone) is a synthetic product and has about twice the activity of naturally occurring vitamin K.

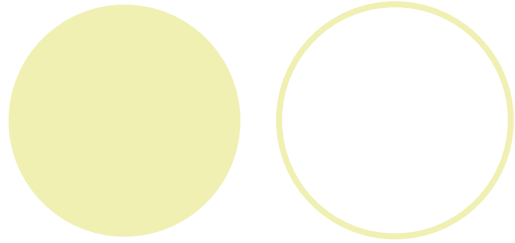


Vitamin K sources

- 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 K₁, except for pork liver, which is a good source.

Table 9–12 Vitamin K in Some Foods (Expressed as Menadione Units per 100 g of Edible Portion)

<i>Product</i>	<i>Units/100 g</i>
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



The stability of Vitamin K



- Vitamin K₁ is slowly decomposed by atmospheric oxygen but is readily destroyed by light. It is stable against heat, but unstable against alkali.



The application of vitamin E

- Vitamin K is rarely added to food products and the most common commercially available form is K₁ (phytomenadione), which is insoluble in water.
- A water-soluble K₃ is available as menadione sodium bisulphite.