Vitamins

definition (attributes)

- organic low molecular weight compounds synthesized by autotrophic org.
- not a source of energy or building material
- function as biocatalysts (necessary for metabolism and regulation of metabolism)

exogenous essential biocatalysts

- **autotrophic** organisms (bio)synthesis
- **heterotrophic** organisms: - partial synthesis
  -from food
  - intestinal microflora

eg.	niacin	biosynthesis from Trp (1 mg ~ 60 mg)
	thiamin	very low amount by intestinal microflora
	biotin	high amount by intestinal microflora
	corinoids (B_{12})	high amount by intestinal microflora
	vitamin K	high amount by intestinal microflora

terminology and classification

formerly connection with illnesess

antixerophthalmic factor	A	retinol	vitamin against night blindness
antiscorbutic factor	C	ascorbic acid	against scurvy
antirachitic factor	D	calcipherols	against rickets
antiberiberi factor	B_1	thiamine	
coagulation factor	K_1	phylloquinon	

letters of alphabet, numbers D_2 (ergocalcipherol), D_3 (cholecalcipherol)

simple trivial names ascorbic acid

water soluble (hydrophilic)

1. thiamine (aneurin, B_1)
2. riboflavin (lactoflavin, B_2, formerly G)
3. niacin (nicotinic acid, B_3; nicotinamide, PP)
4. pantothenic acid (B_5)
5. pyridoxine (~al, ~ol, ~amin, B_6)
6. biotin (H)
7. folic acid (folate, B_c , B_9)
8. cyanocobalamin (corinoids, B_{12})

1.- 8. group of vitamins B (B-complex)

9. ascorbic acid (vitamin C)

fat soluble (lipophilic)

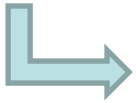
10. retinoids (A)
11. calciferols (D)
12. tocopherols (E)
13. phylloquinones (K)

water soluble :

main losses by leaching
cofactors of enzymes (coenzymes, prosthetic groups)
excess - excretion by urine

fat soluble :

main losses by oxidation
other functions
excess - storage in liver



possible hypervitaminosis

vitamin	task in metabolism	symptoms of deficiency (avitaminosis)
thiamine	met. of saccharides, proteins decarboxylases, dehydrogenases, transketolases, carboligases	muscle fatigue, loss of appetite, weight loss irritability, beri-beri (neurological disease)
riboflavin	met. of proteins (redox reactions) flavin enzymes, glucose oxidase	ariboflavinosa, accumulation of amino acids inflammatory changes of the skin, mucous membranes
niacin	met. of saccharides, proteins dehydrogenases, other enzymes in Krebs cycle	pellagra (dermatitis) malfunctions of digestive and nervous system
pyridoxine	met. of aminoacids dehydrases (lysyloxidase), aminotransferases, racemases of aminoacids, synthases	disorders of protein metabolism, synthesis of hemoglobin, dermatitis, nervous disorders (seizures in children)
pantothenic acid	met. of fats, saccharides, proteins transacylases, synthetases of fatty acids	dermatitis
biotin	met. of fats (gluconeogenese), proteins karboxylases (transfer of CO_2), transcarboxylases, decarboxylases	dermatitis
folacin	met. of proteins, nucleotides, nucleosides transferases (transfer of 1C fragments)	anemia (macrocytic) changes of erythrocytes
corinoids	met. of haem pigments transferases (transfer of 1C fragments)	anemia (pernicious)

terminology

hypovitaminosis	**insufficient intake**
avitaminosis	**temporary absolute shortage (malfunction of biochemical functions)**
hypervitaminosis	**excessive intake (failure of functions) vit. A, D**
retention	**maintaining of original amounts (in %)**
restitution	**addition to the original amount (level)**
fortification	**addition to higher then original amount**
provitamin	**precursor (biologically inactive substance)**
antivitamin	**substances blocking biochemical usage of vitamin (vitamin antagonists)**

- **structural analogues (competitive inhibitors) (oxythiamine)**
- **enzymes catalyzing the degradation of vitamins (thiaminases)**
- **substances forming unusable complexes with vitamins (avidin)**

amount (in food)

- international units

vitamin A	1 IU = 0.3 μg retinol = 0.6 μg β-carotene
	1 RE = 1 μg retinol = 3.33 IU (RE=Retinol Equivalents)
vitamin D	1 IU = 0.025 μg vitamin D_3 (or D_2)
vitamin E	1 IU = 1 mg *all-rac* α-tocopheryl-acetate

- mass units
- rich sources of vitamins x important sources of vitamins

required amount
type of organism
age
physiological state

recommended daily intake of vitamin C :

Age (years)	< 1	1-4	4-10	10-18	> 18
mg / day	35	40	40	45	45-80

recommended daily intake in Czech Republic (Annex no. 5 of the Decree no. 225/2008 Coll.)

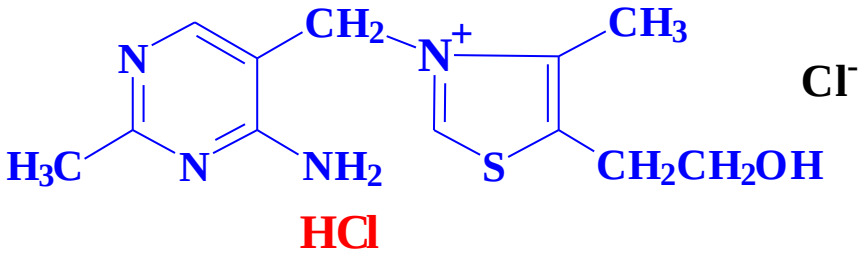
thiamine (B_1)	mg	1.4
riboflavin (B_2)	mg	1.6
niacin (B_3)	mg	18
pyridoxine (~al, ~ol, ~amin, B_6)	mg	2
pantothenic acid (B_5)	mg	6
folic acid (B_c)	µg	200
biotin (H)	mg	0.15
cyanocobalamin (corinoids, B_{12})	µg	1
ascorbic acid (C)	mg	60
retinoids (A)	µg	800
calcipherols (D)	µg	5
tocopherols (E)	mg	10

application

- additives for restitution and fortification all vitamins
- colours riboflavin, provitamins A
- antioxidants vitamin C, provitamins A, vitamin E

thiamine B_1

- free
- bound (phosphates: mono-, di-, triphosphate, diphosphate = cofactor of enzymes
- other forms (thiol, disulfide)
- thiaminchloridhydrochlorid (synth.)



pork meat

- thiamine 18%
- diphosphate 52%
- thiol 22% (decomposition in pH neutral media)
- disulphide 8% (product of thiol oxidation)

sources (mg/100 g)

• cereals, legumes	0.1-1	mainly free form
• pork meat	1	mainly diphosphate
• beef meat	0.04-0.1	
• fruit	0.04-0.1	
• vegetable	0.03-0.15	
• potatoes	0.05-0.18	
• beer	traces	mainly in yeasts

intake covered by (%)

• cereal products (bread)	43 (20)
• meat and meat products	18-27
• milk and dairy products	8-14
• potatoes	10
• legumes	5
• vegetables	12
• fruits	4
• eggs	2

losses very labile vitamin (especially in neutral and alcalic pH)

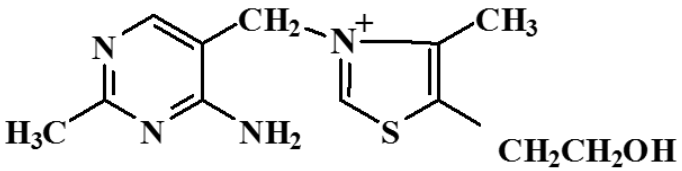
• boiling of pork meat	~ 40-60%
• baking of bread	~ 25-30%
• boiling of potato (by leaching)	~ 25%
• preservation of non-acid foods by SO_2	up to 100%

applications

•fortification (restitution) - wheat flour, breakfast cereals, rice

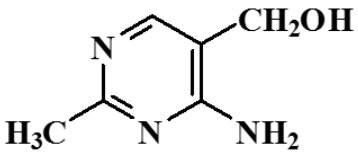
• ingredient for simulating the aroma of meat

reactions

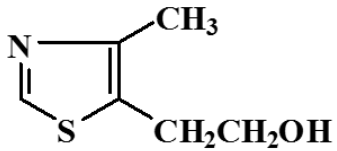


thiamine (free base)

thiaminase II, H_2O, $-H^+$

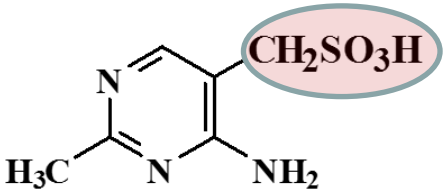


4-amino-5-hydroxymethyl-
-2-methylpyrimidin

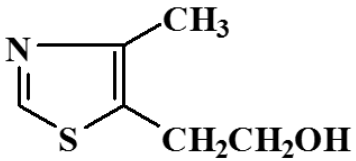


5-(2-hydroxyethyl)-
-4-methylthiazol

HSO_3^-



~ sulfonic acid

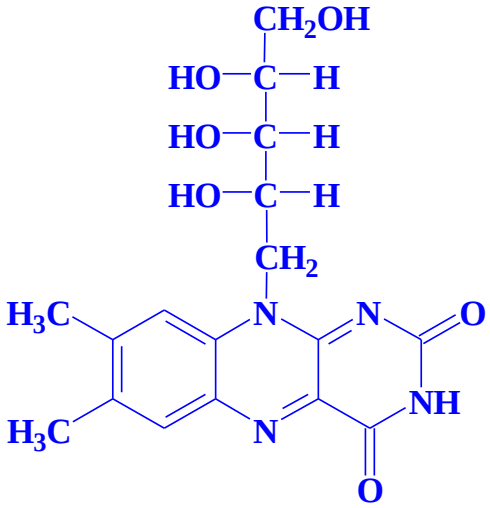


5-(2-hydroxyethyl)-
-4-methylthiazol

riboflavin B_2

from Latin flavus, "yellow"

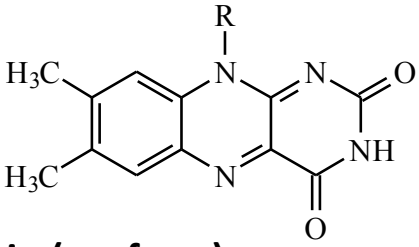
oxidised form (isoalloxazine + ribitol)



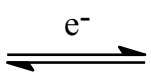
- **free**

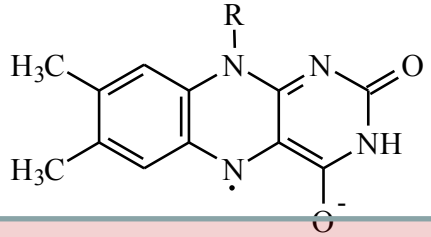
  ox. form called flavoquinone, red. form flavohydroquinone (leucoflavin)

yellow colour



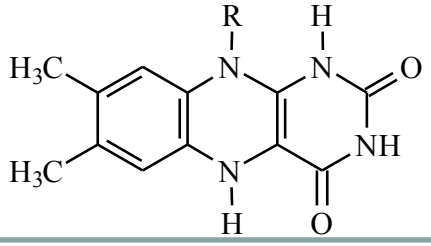
riboflavin (ox. form)



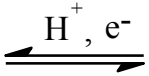


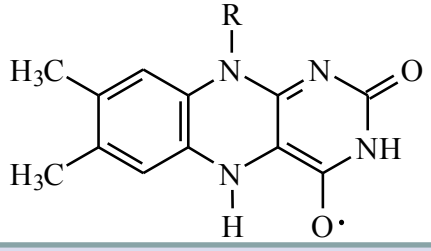
anion of radical (red)

colourless

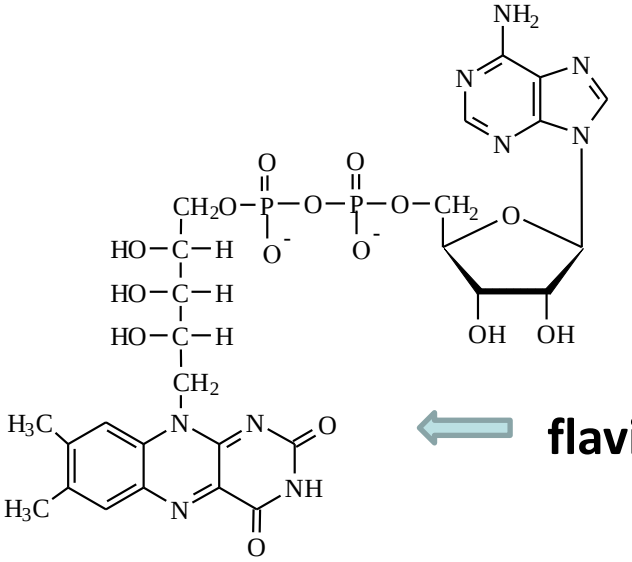


1,5-dihydroriboflavin (red. form)

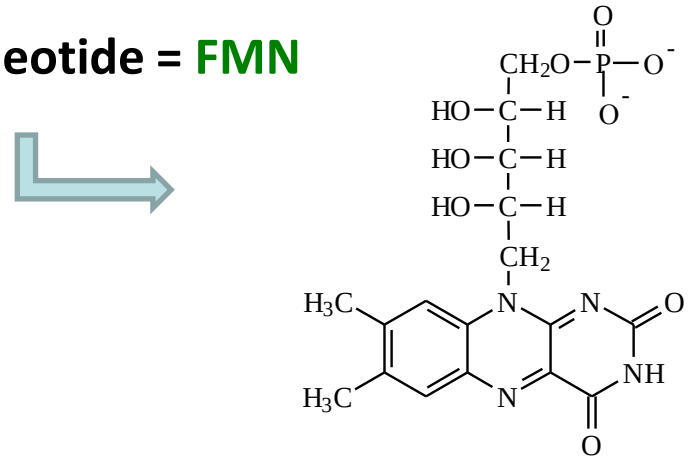




radical (blue)



flavinmononucleotide = FMN



flavinadenindinucleotide = FAD

- **bounded**
  cofactor of flavoproteins (flavin enzymes) FMN, FAD
- **other forms**
  5´-phosphate (widely), 5´-malonylriboflavin (oat)

sources (mg/100g)

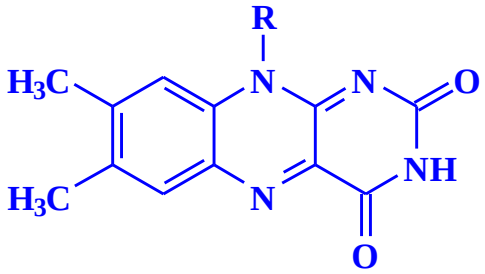
• **meat**	**0.2**
• **livers**	**3**
• **milk**	**0.2**
• **cheeses**	**0.5**
• **beer**	**0.05 (difference from thiamine)**

covered by (%)

- milk, cheeses 36% mainly riboflavin, bound to α- and β-casein
- meat 19% mainly FMN, FAD
- cereals 15%
- eggs 8% mainly riboflavin
- vegetables 8%

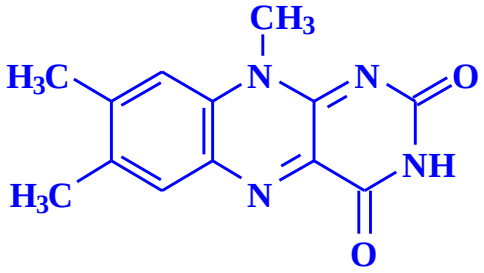
reactions in the absence of light stable

photodegradation



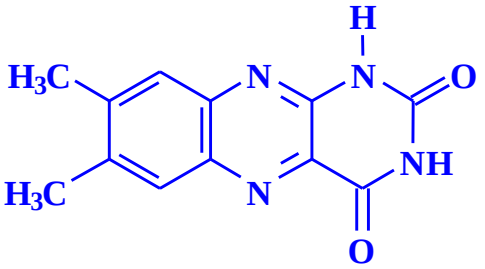
riboflavin (ox. form)

pH >10



lumiflavin

pH < 8



lumichrome
(+ traces of lumiflavin)

photosensitizer

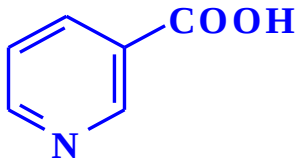
- formation of $^1O_2$ (singlet oxygen)
- destruction of vitamin C, retinol, Met

milk, wine: sun off-flavour

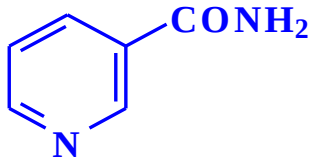
applications

- fortification
- colour ⟶ yellow-green colour

niacin B_3

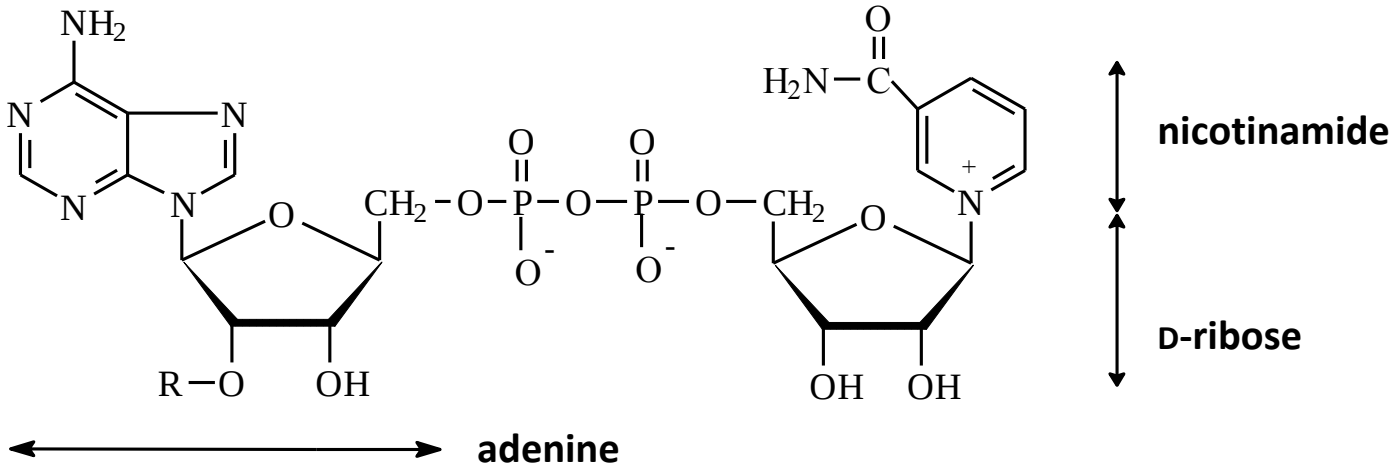


nicotinic acid



nicotinamide

- free (acid-plants, amide-animals) - low amount
- bound (proteins): NAD a NADP - cofactors of hundreds of enzymes

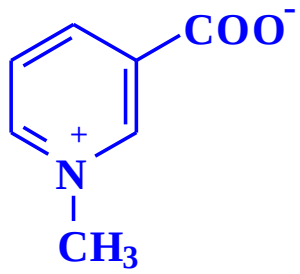


Nicotinamide Adenine Dinucleotide - NAD

(ox. form = NAD^+ and red. form = NADH) NAD^+ R = H,

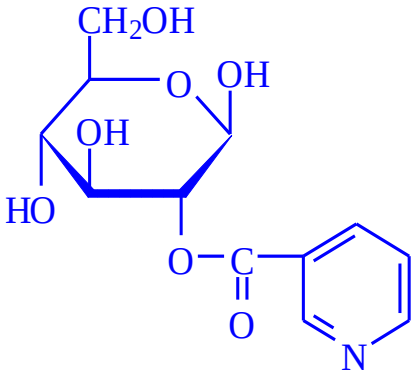
Nicotinamide Adenine Dinucleotide Phosphate - NADP ($NADP^+$ and NADPH) $NADP^+$ R=PO_3H_2

- **other forms:**



trigonellin

alkaloid (coffee, legumes, cereals)



+ polypeptide

niacin bounded on glycopeptides

sorghum, maize

Sorghum - grains are grown for human consumption (eg flour), animal feed or for technical purposes

sources (mg / 100 g)

- meat 5-15
- legumes, fruits, vegetables 0.7-2
- eggs 0.1
- coffee roasted 50
  green (unroasted) 2

intake covered by (%)

- meat 33
- milk 13
- cereals 21
- potatoes 9

reactions

- limited hydrolysis of the amide, acid is stable

losses

- by leaching

Calcium hydroxide, traditionally called slaked lime, is an inorganic compound with the chemical formula $Ca(OH)_2$

Because of its low toxicity and the mildness of its basic properties, slaked lime is widely used in the food industry to:

- make corn tortillas - it helps the corn flour (masa) bind together

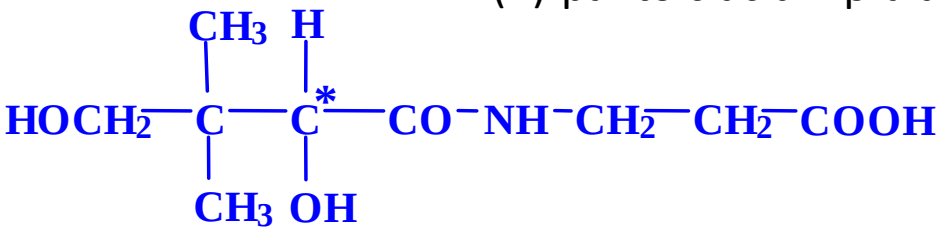
Mexican tortilla (from corn flour + lime milk)

material	free vitamin (mg/kg)
raw corns	0.4
boiled in water	3.8
boiled in lime milk	24.6 (100 %)

pantothenic acid B_5

(*R*)-isomer

(*R*)-pantoic acid + β-alanine



- **free form (low amount)**
- **bound - coenzyme A (CoA) - component of transacylases,**
  the most common is acetyl-CoA
  - Acyl-Carrier Protein (ACP) – coenzyme of synthetases of FA

sources

- **meat, fishes**
- **cheese (in milk only low amount)**
- **whole cereal products**
- **legumes**
- **fruits, vegetables (low amount)**

intake covered by (%)

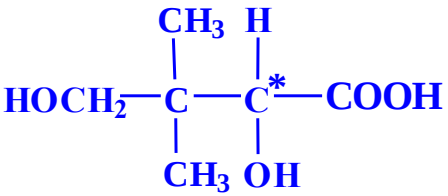
sufficient coverage

reactions more stable only in pH 4-5

hydrolysis: pantothenic acid

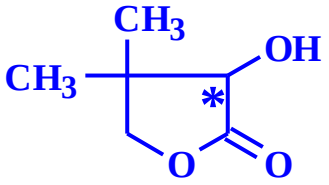
pH > 7

pH < 7



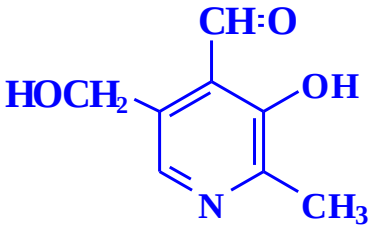
pantoic acid

β-alanine

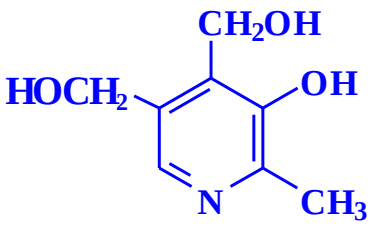


pantolactone

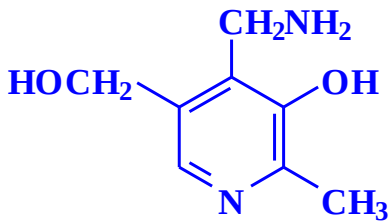
pyridoxine B_6



pyridoxal

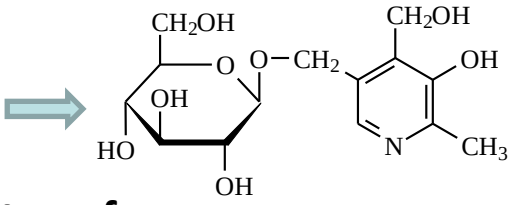


pyridoxol



pyridoxamine

- free form
- their 5´- phosphates (metabolically active form)
- 5-*O*-β-D-glucoside (5-70% in cereals, fruits, vegetables)



pyridoxal 5´-phosphate – cofactor of decarboxylases, aminotransferases,…

sources

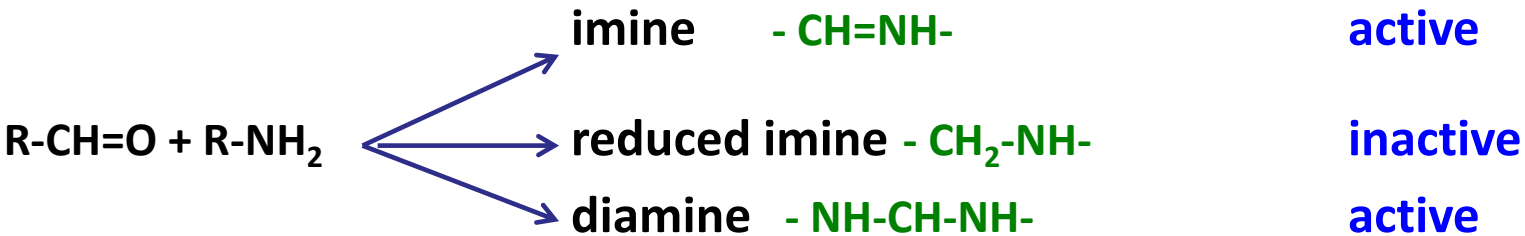
- animal food: pyridoxal, pyridoxol — meat, yolk
- plant food: pyridoxal, pyridoxamin — germ of cereals

intake covered by (%)

- meat 40
- vegetables 22
- milk 12
- cereals 10
- fruits 8
- legumes 5

reactions - lower stability in neutral and alcalic pH

Maillard reaction



losses

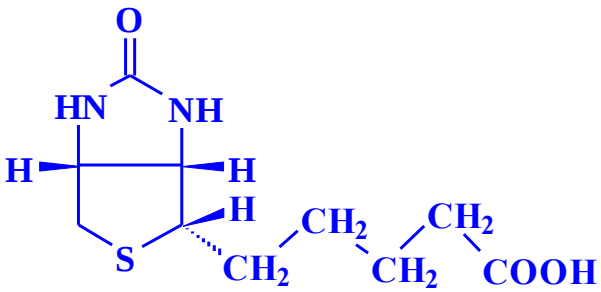
- dried milk 30-70%

  (reaction with Lys and Cys)

applications

- fortification

biotin H



(+)-biotin, *(3aS, 4S*, 6*aR*)-isomer

biotin - cofactor of enzymes catalyzing CO_2 transfer
carboxylases, transcarboxylases and decarboxylases

sources - egg yolk, liver, whole grain cereal products, vegetables, yeast

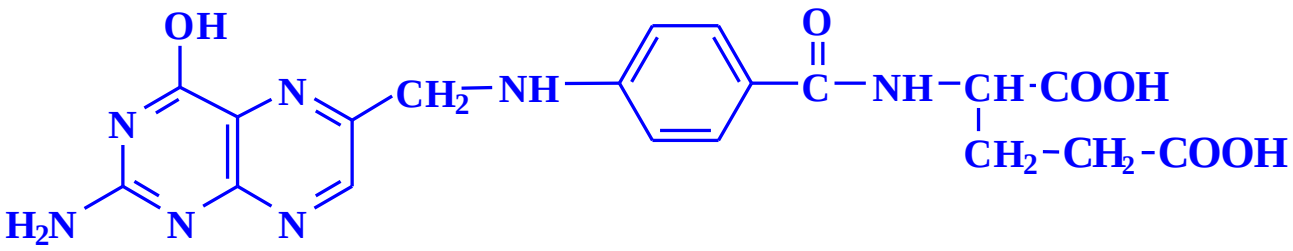
deficiency is rare

when consuming excessive amounts of raw eggs, as raw egg white contains a glycoprotein avidin, which forms a very strong biotin complex

folacin B_c or B_9

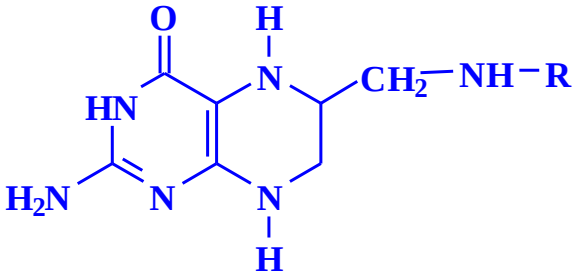
derivatives of folic (pteroylglutamic) acid

3-8 molecules Glu



pteroic 4-aminobenzoic Glu

active form: tetrahydrofolic acid ⇨



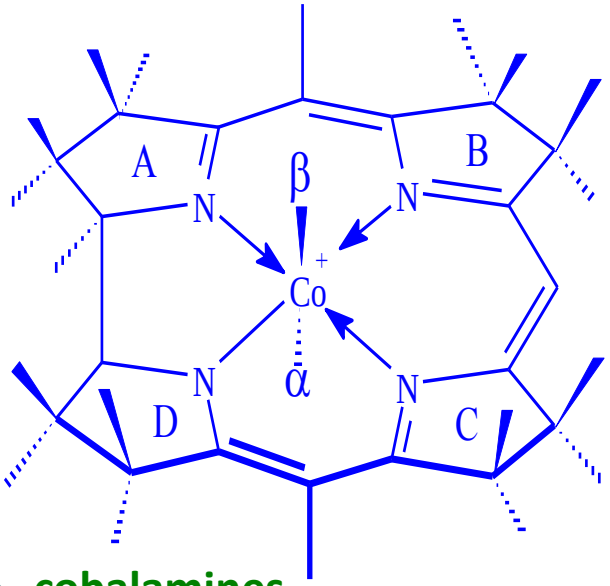
cofactor of enzymes
transfer of 1C groups
(methyl (CH_3-), formyl (-CHO)

in the diet usually short supply deficiency = anemia

sources - leaf vegetables, cereals (in the surface layers of the caryopsis), liver, eggs, yeast

corrinoids B_{12}

substituted corrin cycles with central Co atom
4 pyrrols without CH bridge between cycles A-D



central atom Co **up to 6 coordination bonds**

5. coord. bond - α = 5,6-dimethylbenzimidazole ⇨ cobalamines

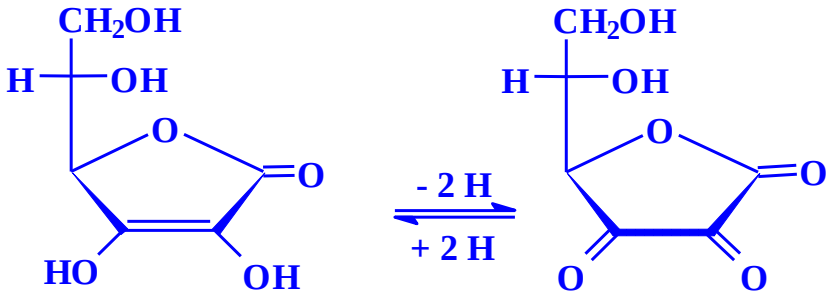
6. coord. bond - β = **OH** **hydroxycobalamine**
H_2O **aquacobalamine**
CH_3 **methylcobalamine**
CN **cyanocobalamine (synthetic form – in multivitamine preparates)**

coenzyme B_{12} - prosthetic group of many enzymes

is not present in plant foods
sources – meat (70%), milk and dairy products (20%), eggs (9%)

vitamin C (ascorbic and dehydroascorbic acid)

reversibile redox system

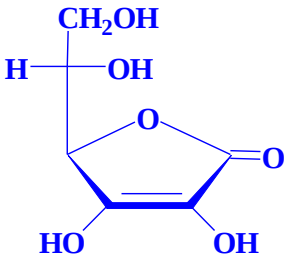


L-ascorbic acid

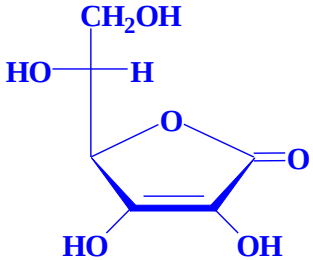
L-dehydroascorbic acid

two-electron oxidation product

4 stereoisomers

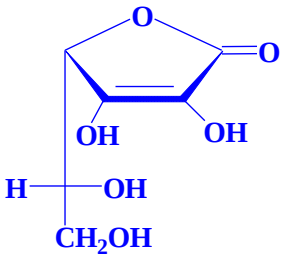


L-ascorbic

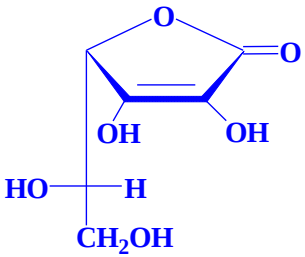


D-isoascorbic

5-20% activity



D-ascorbic

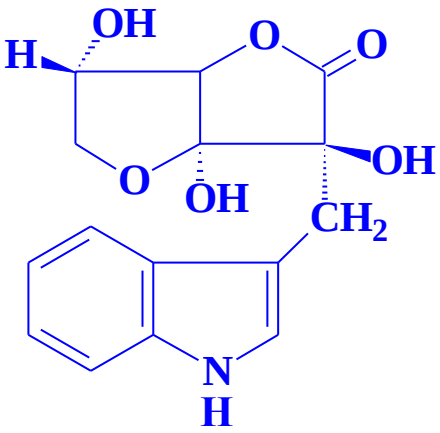


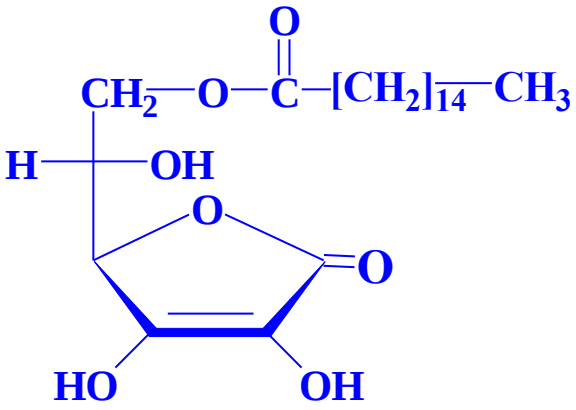
L-isoascorbic

- free
- bound

ascorbigen in brassica vegetables

ascorbyl palmitate (antioxidant) E304 - fats, oils, margarines, cereal products





ascorbigen

L-ascorbyl-6-palmitate

15-20% activity

full activity

vit. C - Involved in – hydroxylation of Pro to Hyp and Lys to Hyl in procollagene
- absorption and transport of ions (Fe, Na, Cl, Ca)

sources

fruits	**(mg/kg)**
rose hips	**2 500-10 000**
blackcurrant	**1 100-3 000**
strawberries	**400-700**
citrus fruits	**240-700**
apples	**15-50**

vegetables	
curly parsley	**1 500-2 700**
peppers	**620-3 000**
cabbage	**170-700**
potatoes	**80-400**

intake covered by (%)

potatoes	**20-30**
vegetables	**30-40**
fruits	**30-35**
milk	**9**

0.5-2 mg / 100 ml

synthesize

- green plants (photoautotrophic)
- part of animals

vitamin is for:

- humans
- primates
- guinea pigs

acerola, Barbados cherry (*Malpighia emarginata*)
(Spanish pronunciation: [aseˌɾoˌla]

native to South America, southern Mexico, and Central America, but is now also being grown in subtropical areas of Asia, such as India

extremely rich in vitamin C 17-46 g/kg

The fruit can be used to make juices and pulps, vitamin C concentrate, and baby food, among other things

reactions

- losses by leaching
- in presence of O_2: enzymatic oxidation and autoxidation
- in absence of O_2: degradation catalyzed by acids

  total losses: 20-80%

enzymatic oxidation

ascorbatoxidase, ascorbase, peroxidase (in damaged plant tissues)

the resulting reaction:

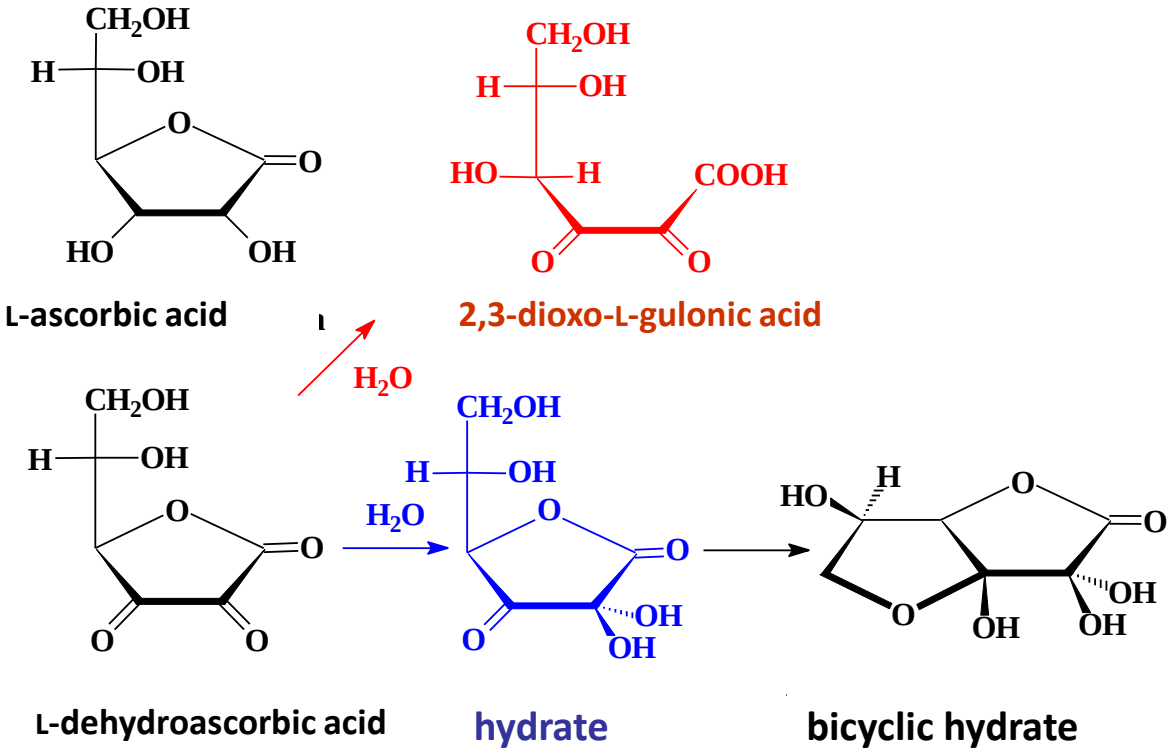
$$2\ H_2A + O_2 \longrightarrow 2\ A + 2\ H_2O$$

H_2A= ascorbic acid

A=dehydroascorbic acid

dehydroascorbic acid - unstable

hydrolysis in neutral and alkaline pH



prevention: blanching (pre-cooking), reduction by SO_2

autoxidation

catalyzed by metals : Fe^{3+}, Cu^{2+}

the resulting reaction :

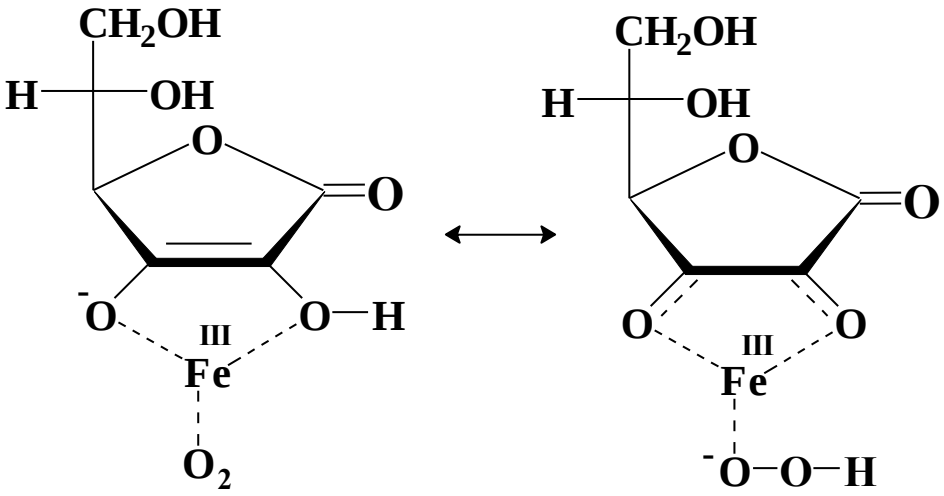
$$2\ H_2A + O_2 \longrightarrow 2\ A + 2\ H_2O$$

mechanism:

$$H_2A + O_2 \longrightarrow A + H_2O_2$$

$$H_2A + H_2O_2 \longrightarrow A + 2\ H_2O$$

ternary complex



consequences :

oxidation of other components H_2O_2 (myoglobin, lipids, anthocyans)

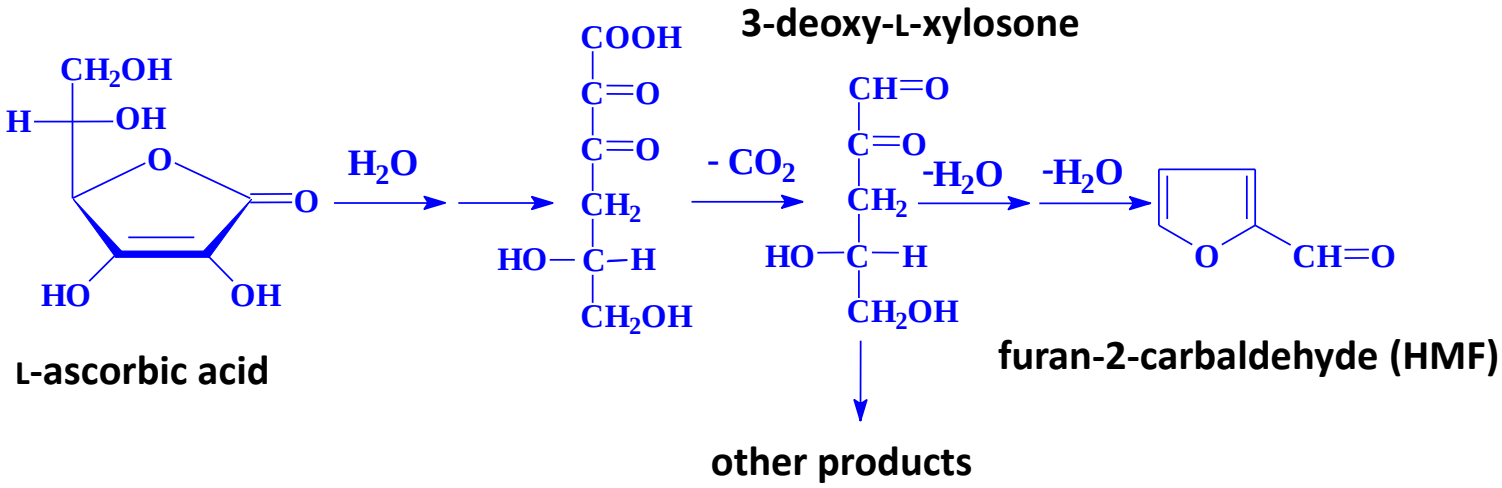
prevention :

- **preventing access of oxygen (air)**
  inert atmosphere, deaeration, HSO_3^-, fermentation
- **reduction of ions Fe^{3+}, Cu^{2+}**
  by addition a chelating agent

unfavorable conditions(lower a_w , pH)

acid catalyzed degradation

lower speed than reactions catalyzed by metals
max. = pH 4, min. = pH 2



the main cause of losses in canned products in the absence of oxygen
fruit juice at 50 °C - the loss at 12 weeks 70-95% of vitamin C

application

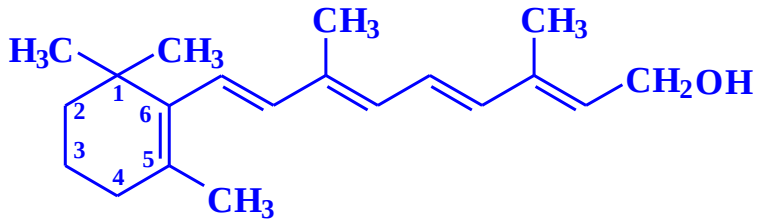
- vitamin
- antioxidant
- complexing agent

in food technologies :

- canning (prevention of aroma and colour changes, removal of O_2, inhibition of browning)
- fermentation (prevention of turbidity)
- meat (improvement and a acceleration of curing, NO_2^-) + inhibits the formation of nitrosamines
- fats (antioxidant)
- cereals (formation of disulphide bridges in proteins in dough)

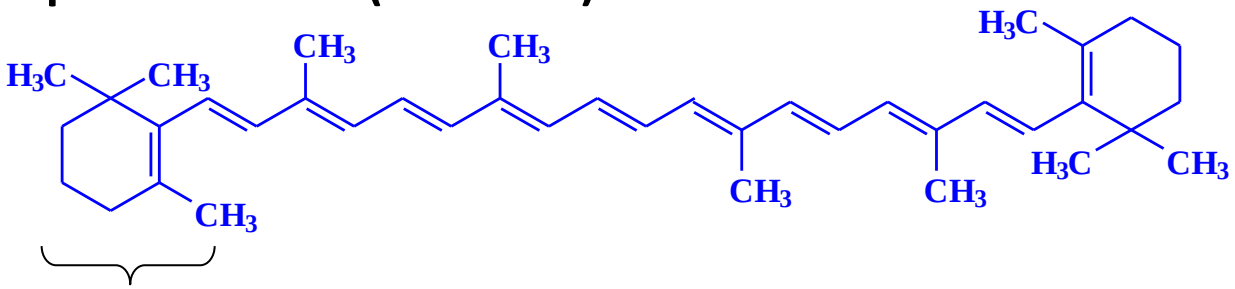
vitamin A

retinol
(isoprenoid)



all-*trans*-retinol
vitamin A_1 (diterpene)

provitamins A (retinoids)



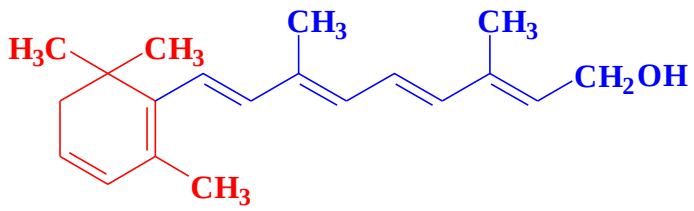
β-carotene
(tetraterpene)

β-ionon cycle

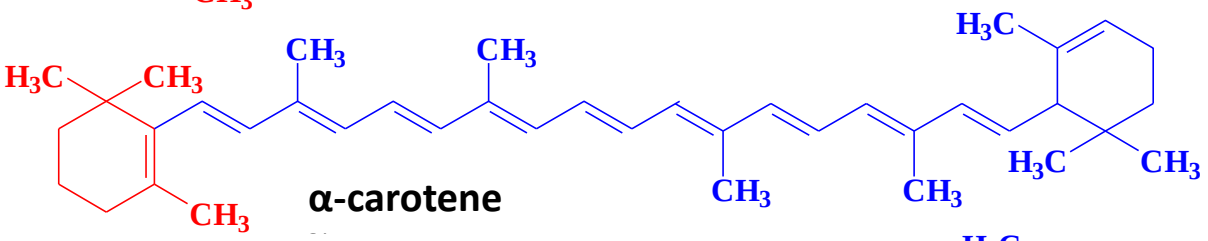
further active substances (50 natural + 2500 synthetic derivatives)

- **3-dehydroretinol (vitamin A_2)**
- **α-carotene**
- **γ-carotene**
- **cryptoxanthin and others**

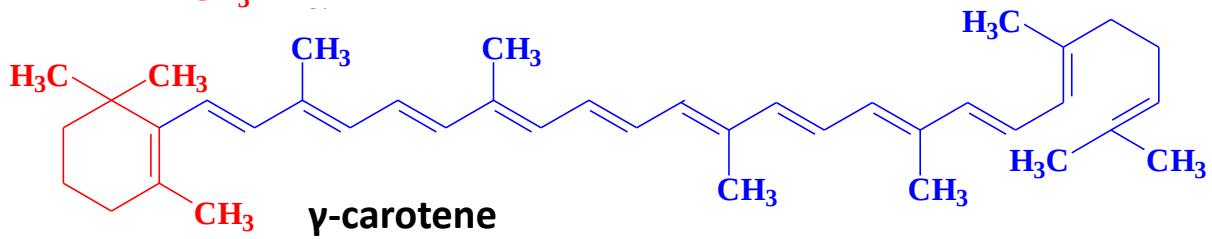
vit. A - of particular importance in biochemistry of visual perception



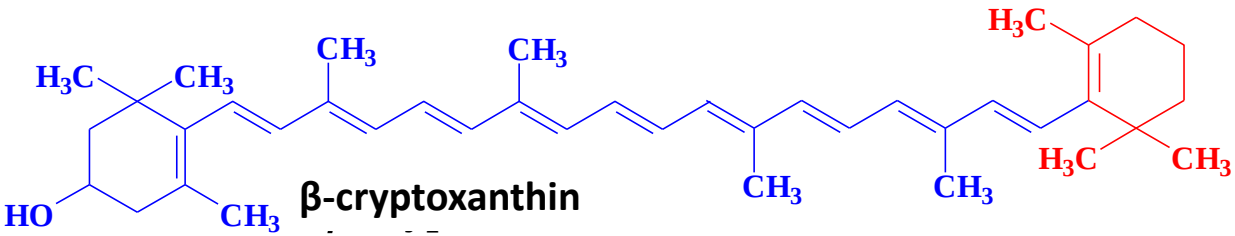
3-dehydroretinol (vitamin A 2)



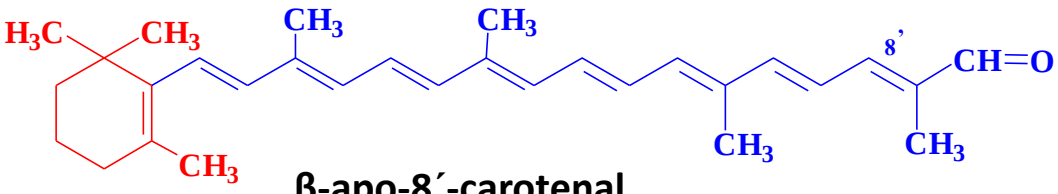
α-carotene



γ-carotene



β-cryptoxanthin



β-apo-8´-carotenal

sources (mg/kg)

- **animal materials (retinol / provitamins A)**

meat	0.1 / 0.4
liver	30-400 / 300
butter	5-10 / 4-8
fish liver oil, margarines	

- **plant materials (provitamins A)**

carrot	20-95
spinach	50-480
apricots	6-20

intake covered by (%)

• liver	23	esters, mainly $C_{16:0}$
• butter	17	
• milk, cream	15	
• carrot	14	
• margarines	9	retinyl acetate, retinyl palmitate

reactions unstable (especially on light, oxidation by atmospheric oxygen)

isomeration —light→ mainly 13-*cis* a 9-*cis*

oxidation —metals, radicals→ oxidation of $-CH_2OH$
cleavage of β-ionon cycle
(epoxides)

reaction with free radicals act as antioxidants

⇩

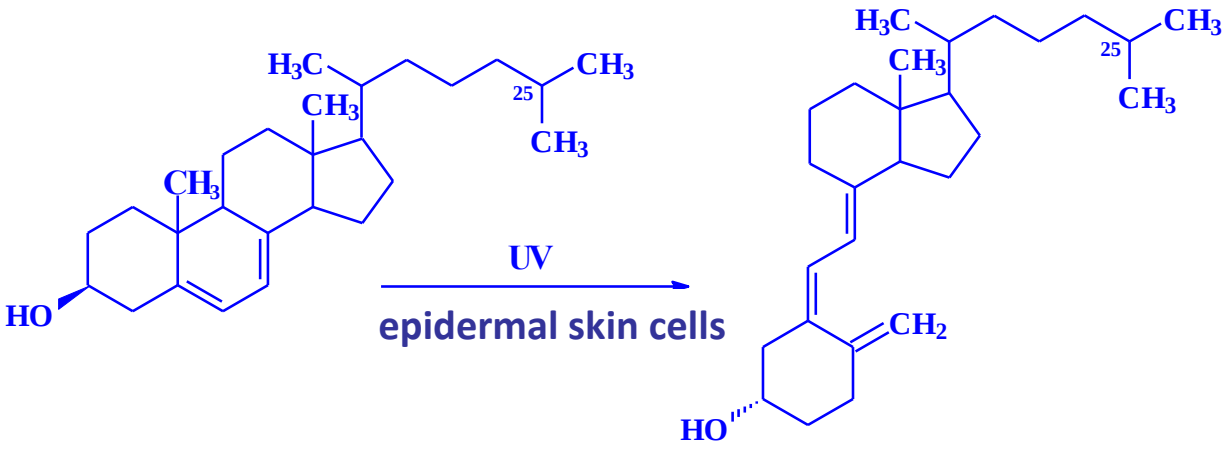
scavengers of singlet oxygen and hydroxyl radicals

(can quench singlet oxygen)

vitamin D (calciferols)

9,10-secosteroids

cholecalciferol (vitamin D_3)



7-dehydrocholesterol (provitamin D_3) → **cholecalciferol (vitamin D_3)**

ergosterol (provitamin D_2) → **ergocalciferol (vitamin D_2)**

sources (μg /kg)

• sea fish	50-450
• egg yolk	30-50
• butter	10-20
• liver	2-11
• milk	1
• cream	4
• meat	3

fish liver oil, margarines

intake covered by (%)

margarines	34
fatty fish	17
eggs	16
milk, cream	12
butter, cheeses	9

higher fungi, moulds (cheese)

reactions

autoxidation $\xrightarrow{O_2}$ alcohols, ketones

pyrolysis $\xrightarrow{\Delta}$ pyro- and isopyrovitamins D

isomeration $\xrightarrow{H^+}$ isovitamins D and isotachysterols

photodegradation $\xrightarrow[UV]{\text{záření}}$ vitamins D from provitamins D (tachysterols, lumisterols and others)

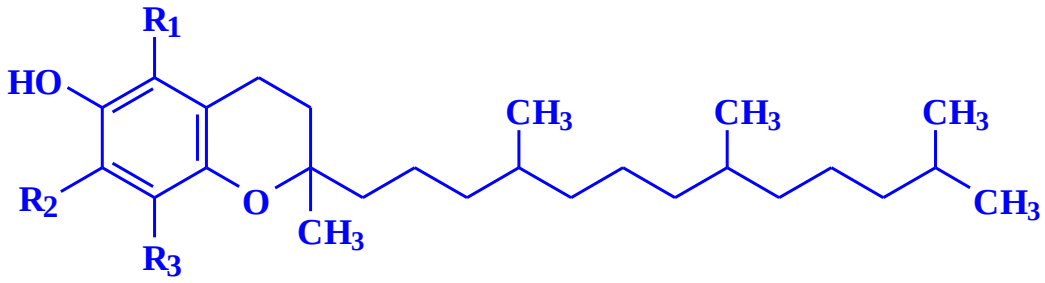
application

fortification

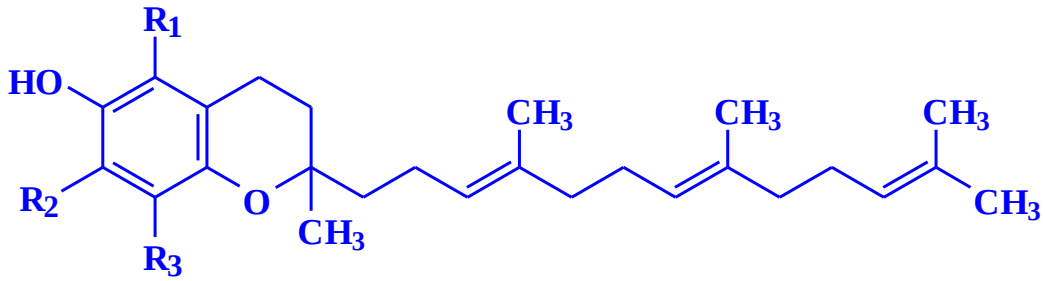
- margarins
- milk
- breakfast cereals

vitamin E (tocopherols and tocotrienols)

6-hydroxychromans, phytol (C_{20}), tocol



tocopherols (*R*,*R*,*R*-isomers)



tocotrienols (*trans*-isomers)

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

sources (mg/100 g)

- plant oils 50-200
- plant materials < 0.5
- animal materials low amount

oils

% vitamin E	α-T	β-T	γ-T	δ-T	∑TT
soy	11	-	66	23	-
corn	18	-	81	1	-
wheat germ	60	34	-	-	6

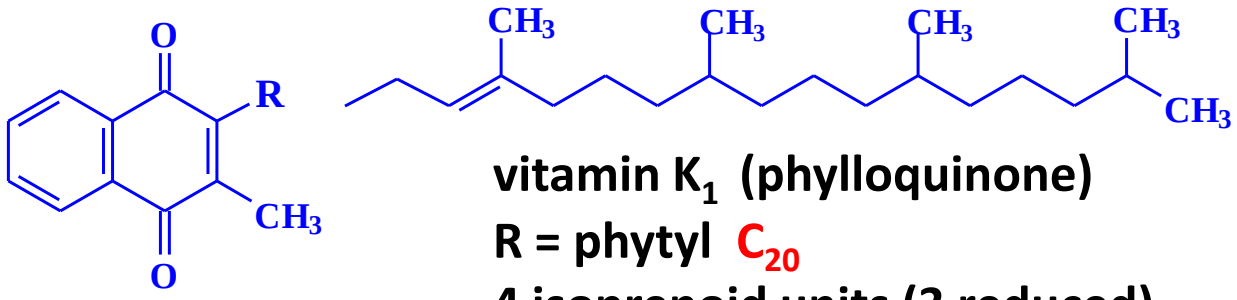
1.00 0.,27 0.13 0.01 0.30

activity of vitamin: α-T > β-T > γ-T > δ-T α-TT

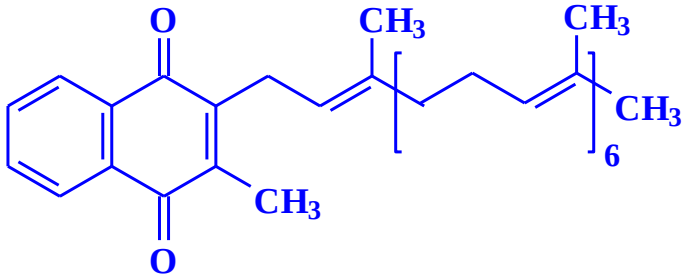
antioxidant effect: δ-T > γ-T > β-T > α-T
(vitamin E and Se)

vitamin K

similar structure to coenzymes Q, 1,4-naphthoquinone,
terpenoid chain (phytol C_{20})
basic substance menadione



vitamin K_1 (phylloquinone)
R = phytyl C_{20}
4 isoprenoid units (3 reduced)



vitamin K_2 (farnoquinone)
bacteria of intestinal tract

7 isoprenoid units (commonly 4-10, even 0-13)

sources

	(mg / 100 g)
leaf vegetables (cabbage, spinach)	3-4
pea, tomatoes, meat (including liver)	0.1-0.4
milk	0.002-0.02
pork liver (forms)	K_1, MK-4, MK 7-10

reactions

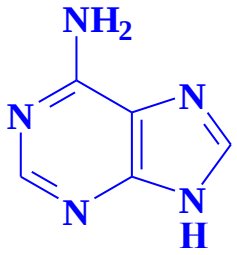
photodegradation $\xrightarrow{UV}$

oxidation $\xrightarrow[OH^-]{O_2}$ epoxides (2,3-epoxides)

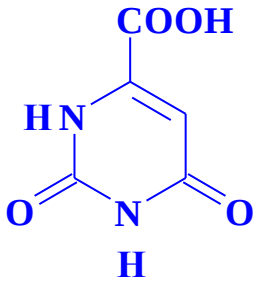
other biologically active compounds

mostly B group vitamins (B-complex)

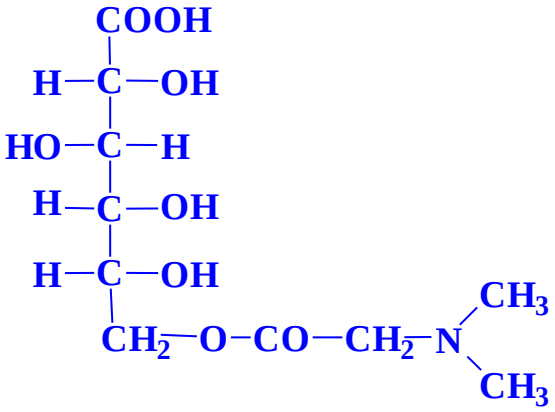
B_8, B_4	adenylic acid (adenine)
B_{13}	orotic acid
B_{15}	pangamic acid
B_t	carnitine
B_x, H_1	4-aminobenzoic acid
F	essential fatty acids
P	rutin (bioflavonoids)
U	*S*-methylmethionine
	choline
	myo-inositol
	taurine
	coenzymes Q



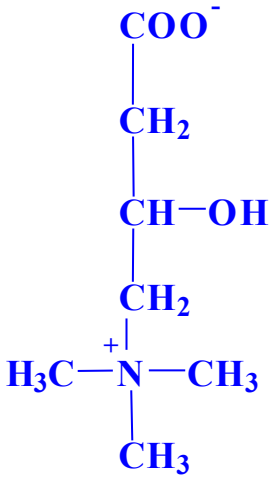
adenylic acid



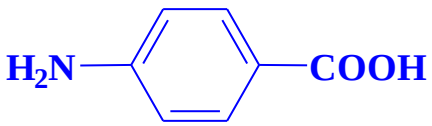
orotic acid



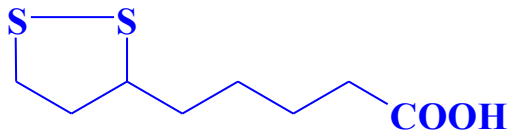
pangamic acid



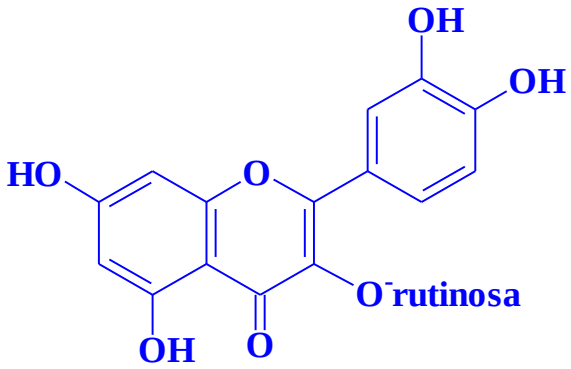
carnitine



4-aminobenzoic acid (H_1)



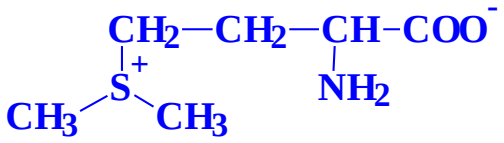
lipoic acid



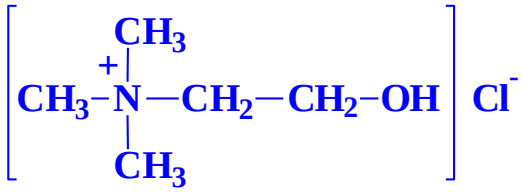
rutin (P) (quercetin -3-β-rutinoside,
rutinose = rhamnose, glucose)

rue (*Ruta graveolens)*

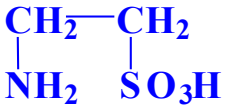
-name comes from the name of rue (*Ruta graveolens*) – formerly medicinal herb
-rue have a culinary use if used sparingly, but it is bitter and gastric discomfort may be experienced by some individuals



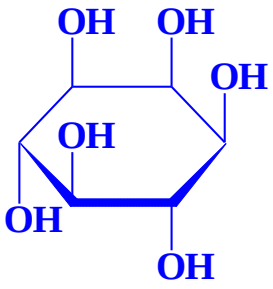
S-methylmethionine



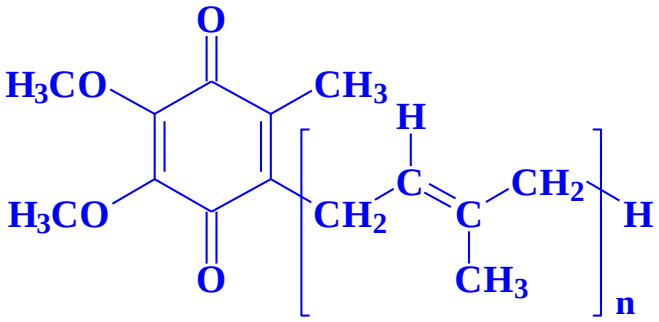
choline



taurine



myo-inositol



coenzymes Q