# 7. VITAMINS

## definition (attributes)

- organic low molecular weight compounds
- function as biocatalysts (regulation of metabolism)
- autotrophic organisms: biosynthesis
- heterotrophic organisms: partly biosynthesis

food

gut microorganisms

# terminology and classification

• formerly connection with illnesess antixerophtalmic factor antiscorbutic factor antirachitic factor antiberiberi factor coagulation factor

- letters of alphabet, numbers
- simple trivial names, systematic names

## water soluble (hydrophilic)

- 1. thiamine (aneurin, B<sub>1</sub>)
- 2. riboflavin (lactoflavin, B<sub>2</sub>, G)
- 3. niacin (nicotinic acid, B<sub>3</sub>; nicotinamide, PP)
- 4. pantothenic acid (B<sub>5</sub>)
- 5. pyridoxine (~al, ~ol, ~amine, adermin, B<sub>6</sub>)
- 6. biotin (H)
- 7. folacin (B<sub>c</sub>, B<sub>9</sub>)
- 8. cyanocobalamin (corinoids, B<sub>12</sub>)
- 1.- 8. = group of vitamins B (B-complex)
- 9. ascorbic acid (vitamin C)

# exogenity and essentiality

thiamine niacin biotin corrinoids vitamin K vitamin D very little by gut microorganisms biosynthesis from Trp (1 mg ~ 60 mg) gut microorganisms gut microorganisms gut microorganisms vitamin or hormone

- water soluble: excretion by urine, main losses by leaching, cofactors (coenzymes, prosthetic groups)
- fat soluble: storage in liver, main losses by oxidation, possible hypervitaminosis, other function

terminology	
hypovitaminosis	insufficient intake
avitaminosis	temporary absolute shortage (malfunction of biochemical functions)
hypervitaminosis	excessive intake (failure of functions ), A, D
retention	maintaining of original amounts
restitution	addition over original amounts

A<sub>1</sub>retinol C ascorbic acid D calciferols B<sub>1</sub> thiamine K<sub>1</sub> fylloquinone

## fat soluble (lipophilic)

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

fortification	addition at higher amounts than original ones
provitamin	precursor (biologically inactive substance)
antivitamin	substances blocking biochemical usage of vitamin (vitamin antagonists)

amount (content in food) (book 2, tab. 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, 5.7, 5.8)

- biological units
- international units

vitamin A	1 IU = 0.3 $\mu$ g retinol = 0.6 $\mu$ g $\beta$ -carotene 1 RE = 1 $\mu$ g retinol = 3.33 IU
vitamin D	1 IU = 0.025 $\mu$ g vitamin D <sub>3</sub> (or D <sub>2</sub> )
vitamin E	1 IU = 1 mg all-rac $\alpha$ -tocopheryl-acetate

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

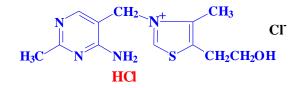
# required amount

type of organism, age, physiological state, advisable daily intake

#### application

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

# thiamine



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

# **sources** (mg / 100 g) (book 2, tab. 5.1)

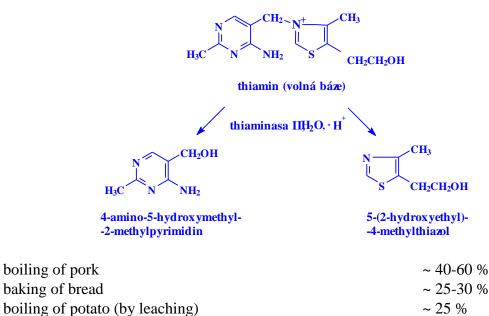
• legumes	0,1-1 mostly free thiamine
• pork	1 mostly diphosphate
• beef	0,04-0,1
• fruits	0,04-0,1
• vegetables	0,03-0,15
• potato	0,05-0,18

#### covered by (%)

• cereals products (bread)	43 (20)
• meat and meat products	18-27
• milk and dairy products	8-14
• potato	10
• legumes	5
• vegetables	12

- fruits
- eggs

#### reactions



4 2

100 %

• preservation of non-acid foods by SO<sub>2</sub>

#### applications

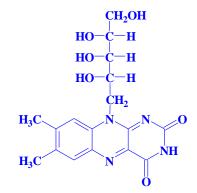
losses

•

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fortification (restitution): wheat flour, breakfast cereals, rice

## riboflavin



oxidised form (isoalloxazine, ribitol)

- free, ox. form flavoquinone, red. form flavohydroquinone (leucoflavin)
- bound (proteins), cofactor flavoproteins (FMN, FAD)
- other forms

# **sources** (mg/100g) (book 2, tab. 5.1)

٠	meat	0,2
٠	liver	3
٠	milk	0,2
٠	cheese	0,5
٠	beer	0,05 (difference from thiamine)

## covered by (%)

• milk, cheeses 36% mostly riboflavin, bound on  $\alpha$ - a  $\beta$ -casein

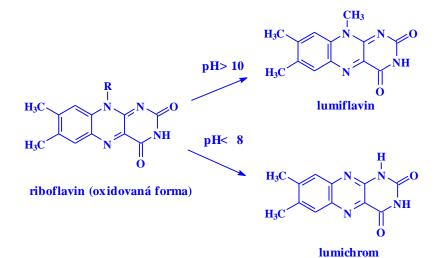
- meat 19% mostly FMN, FAD
- cereals 15%
  - eggs 8% mostly riboflavin

8%

vegetables

# reactions

photodegradation



#### losses

- milk, wine: sun off-flavour
- formation of  ${}^{1}O_{2}$  (singlet oxygen)
- destruction of vitamin C, retinol, Met

# application

- fortification
- colouring matter

## niacin



- free (low quantity) (acid: plants, amide: animals)
- bound (to proteins): NAD (DPN) and NADP (TPN)
- other forms

trigonelline (coffee, legumes, cereals) sorghum, corn



trigonelline

**sources** (mg / 100 g) (book 2, tab. 5.1)

٠	meat		5-15
٠	legumes	s, fruits, vegetables	0,7-2
٠	eggs		0,1
٠	coffee	roasted	50
		green	2

covered by (%)

•	meat	33 %
•	milk	13 %
•	cereals	21 %
•	potatoes	9 %

#### reactions

• limited hydrolyses of amide, acid stable

## losses

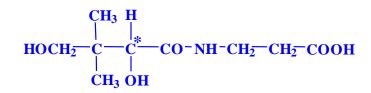
• by leaching

# application

fortification

• white flour

# pantothenic acid



- free, (*R*)-isomer
- bound (CoA, ACP)

**sources** (mg / 100 g) (book 2, tab. 5.1)

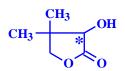
- meat, fish
- cheeses (milk, little)
- whole cereal products
- legumes
- fruits, vegetables (little)

covered by (%) sufficient

## reactions

 $\begin{array}{c} CH_3 H \\ | & | \\ HOCH_2 - C - C - C - COOH \\ | & | \\ CH_3 OH \end{array}$ 

NH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-COOH



pantoic acid

β-alanine

pantolactone

# pyridoxine



- free
- their 5'-phosphates
- 5-*O*-β-D-glucoside of pyridoxol (5-70 % in cereals, fruits, vegetables)

## sources (book 2, tab. 5.1)

- animal food: pyridoxal, pyridoxol meat, yolk
- plant food: pyridoxal, pyridoxamine cereals

# covered by (%)

•	meat	40
•	vegetables	22
•	milk	12
•	cereals	10
•	fruits	8
•	legumes	5
•	vegetables	2

#### reactions

- Maillard reaction
- transamination

#### losses

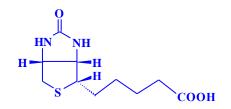
• powder milk 30-70% (reaction with Lys and Cys)

# application

fortification

• baby food

# biotin

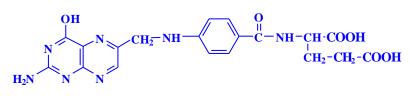


(+)-biotin, (*3aS*, *4S*, 6*aR*)-isomer

broadly distributed deficiency = raw eggs (avidine)

sources (book 2, tab. 5.1)

# folacin



CH=O (10) CH<sub>3</sub> (5)

3-8 molecules of Glu

Glu

pteroic acid pteroylglutamic (folic acid) tetrahydrofolic acid

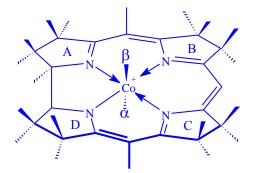


4-aminobenzoic acid

sources mostly leaf vegetables (book 2, tab. 5.1)

## corrinoids

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



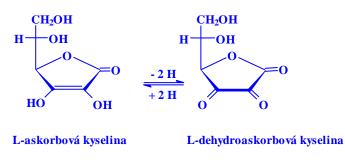
central Co atom: 6 coordination bonds cobalamins  $\alpha = 5,6$ -dimethylbenzimidazole  $\beta = OH$  $H_2O$  $CH_3$ CN

hydroxocobalamin aquocobalamin methylcobalamin cyanocobalamin

deoxyadenosylcobalamin coenzym B12

sources (book 2, tab. 5.2), not present in foods of plant origin

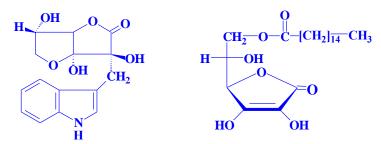
vitamin C (ascorbic and dehydroascorbic acid, redox system)



4 stereoisomers

- free
- bound

ascorbigen v brassica vegetables ascorbylpalmitate (antioxidant)



# **sources** (mg / 100 g) (book 2, tab. 5.3)

fruits	
rose hips	250-1000
blackcurrant	110-300
strawberry	40-70
citrus fruits	24-70
apples	1,5-5
vegetables	
parsley	150-270
peppers	62-300
cabbage	17-70
potatoes	8-40
covered by (%)	
potatoes	24
leaves vegetables	13
fruits	34
milk	9 (5-20 mg/l)

## reactions

- losses by leaching
- presence of O<sub>2</sub>: enzymatic oxidation and autoxidation
- absence of O<sub>2</sub>: degradation catalysed by acids total losses: 20-80 %

## enzymatic oxidation

ascorbatoxidase, ascorbase, peroxidase

final reaction: 2 H<sub>2</sub>A + O<sub>2</sub>  $\rightarrow$  2 A + 2 H<sub>2</sub>O

prevention: (precooking), addition of SO2

# autooxidation

catalysed by metals:  $Fe^{3+}$ ,  $Cu^{2+}$ final reaction:  $2 H_2A + O_2 \rightarrow 2 A + 2 H_2O$ 

mechanisms:

 $\begin{array}{l} H_2A+O_2 \rightarrow A+H_2O_2 \\ H_2A+H_2O_2 \rightarrow A+2 \; H_2O \end{array}$ 

consequences:

oxidation of others components by H2O2 (myoglobin, lipids, anthocyanes)

prevention:

- contact with O<sub>2</sub> (air) inert atmosphere, deaeration, glucoseoxidase+catalase, HSO<sub>3</sub><sup>-</sup>, fermentation
- Fe<sup>3+</sup>, Cu<sup>2+</sup> complexing agents
- unfavourable conditions (lower a<sub>w</sub>, pH)

# degradation catalysed by acids

main product: furan-2-carbaldehyde

# application

- vitamin
- antioxidant
- complexing agent

# in food technologies

- canning (prevention of aroma, colour, removal of O<sub>2</sub>, inhibition of browning)
- fermentation (prevention of turbidity)
- meat (improvement and a acceleration of curing, NO<sub>2</sub><sup>-</sup>)
- fats (antioxidant)
- cereals (formation of disulphide bridges in protein dough)

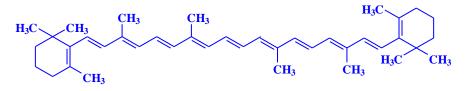
# vitamin A

retinol

CH<sub>3</sub> CH<sub>3</sub> H<sub>3</sub>C CH<sub>3</sub> CH<sub>2</sub>OH

all-*trans*-retinol, vitamin A<sub>1</sub> (diterpene)

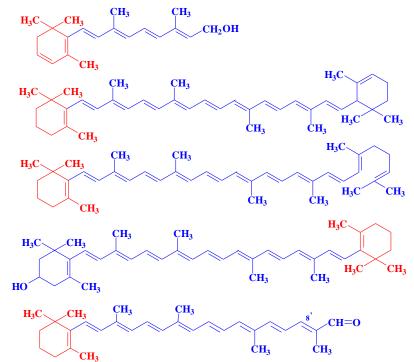
provitamins A (retinoids, isoprenoids)



β-carotene (tetraterpene)

further active substances ( $\beta$ -ionon cycle)

- 3-dehydroretinol (vitamin A<sub>2</sub>)
- α-carotene
- γ-carotene
- cryptoxanthin
- β-apo-8'-carotenal



## sources (mg/kg) (book 2, tab. 5.4)

boul ceb (1115/115) (book 2, tub.	5.1)	
• animal materials (retin	ol / provitamins A	A)
meat		0.1 / 0.4
liver		30-400 / 300
butter		5-10 / 4-8
fish liver oil, margari	nes	
• plant materials (provite	amins A)	
carrot		20-95
spinach		50-480
apricots		6-20
covered by (%)		
• liver	23	esters, mostly C <sub>16:0</sub>
• butter	17	
• milk cream	15	

- milk, creamcarrot14
- margarines 9 retinyl acetate

## reactions

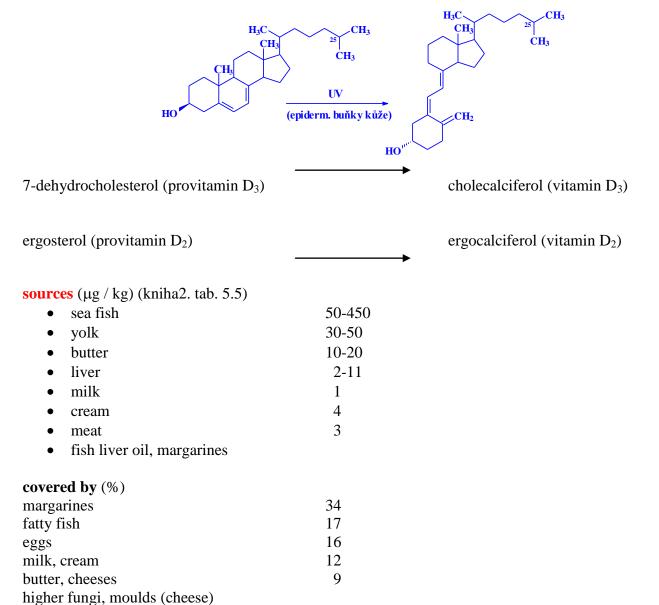
isomeration (mostly 13-cis a 9-cis), oxidation

consequences

- flour bleaching
- colour changing of citrus juices
- food aroma

# vitamin D (calciferols)

9,10-secosteroids cholecalciferol (vitamin D<sub>3</sub>)



## reactions

autooxidation (alcohols, ketones) isomeration photodegradation (vitamins D from provitamins D, tachysterols, lumisterols and others)

# application

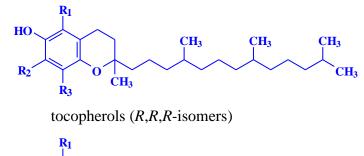
fortification

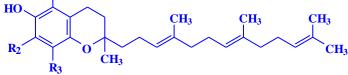
• margarines

- milk
- cereal breakfast

# vitamin E (tocopherols and tocotrienols)

6-hydroxychromans, phytol (C<sub>20</sub>), tocol





tocotrienols (trans-isomers)

Derivative	R <sub>1</sub>	R <sub>2</sub>	<b>R</b> <sub>3</sub>
α-	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>
β-	$CH_3$	Н	CH <sub>3</sub>
γ-	Н	$CH_3$	CH <sub>3</sub>
δ-	Н	Н	CH <sub>3</sub>

**sources** (mg / 100 g) (book 2, tab. 5.6, 5.7)

٠	plant oils	50-200
٠	plant materials	< 0.5
٠	animal materiala	little

vitamin activity:  $\alpha$ -T >  $\beta$ -T >  $\gamma$ -T >  $\delta$ -T  $\alpha$ -TT (1,00-0,27-0,13-0,01-0,30), in dependence on content of unsaturated fatty acids in food

antioxidative activity:  $\delta\text{-}T > \gamma\text{-}T > \beta\text{-}T > \alpha\text{-}T$ 

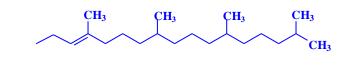
## reactions

oxidation, quinone, dimers and other products

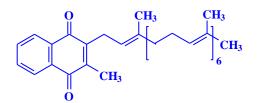
# vitamin K

similar structure of coenzymes Q, 1,4-naftoquinone terpenoid chain (phytol C<sub>20</sub>), basic substance: menadione (naphtho-1,4-quinone)





vitamin  $K_1$  (phylloquinone) R = phytyl C<sub>20</sub> 4 isoprenoid units (3 reduced)



vitamin  $K_2$  (farnoquinone) bacteria of intestinal tract 7 isoprenoid units (commonly 4-10, even 0-13) (30 atoms C = dipharnesyl), 3-multiprenyl-

<b>sources</b> (mg / 100 g) (kniha2. tab. 5.8)				
leaf vegetables (cabbage, spinach)	3-4			
garden pea, tomato (meat including liver)	0,1-0,4			
milk	0,002-0,02			

pork liver (forms)

K<sub>1</sub>, MK-4, MK 7-10

## reactions

photodegradation oxidation (epoxides, 2,3-epoxides)

# other biologically active compounds

mostly B group vitamins (B-complex)		
$B_8, B_4$	adenylic acid (adenine)	
B <sub>13</sub>	orotic acid	
B <sub>15</sub>	pangamic acid	
B <sub>t</sub>	carnitine	
$\mathbf{B}_{\mathbf{x}}, \mathbf{H}_{1}$	4-aminobenzoic acid	
	lipoic acid	
F	essential fatty acids	
Р	rutin (bioflavonoids)	
U	S-methylmethionine	
	choline	
	<i>myo</i> -inositol	
	taurine	
	coenzymes Q	

