

# C3181

# Biochemie I

04-Koenzymy a vitaminy

FRVŠ **1647/2012**

# Obsah

- Koenzymy a vitaminy. Koenzymy oxidoreduktáz (nikotinamid a NAD, flaviny, chinony, hemy, železosírné proteiny, lipoát,) transferáz (ATP, UDP, CDP, biotin, thiamin, koenzym A, THF, pyridoxalfosfát, vit B<sub>12</sub>).
- Vitamin C, lipofilní vitaminy (A, D, K).

# Typy kofaktorů

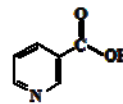
- Rozdělení podle reakcí
  - Někdy spadají do více skupin (THF)
- Jako prekurzory slouží vitaminy
  - Většinou, někdy jiné esenciální složky
  - Možnost syntézy z neesenciálních prekurzorů – hem
- Relativita pojmu
  - Kofaktor x druhý substrát (ATP)
  - Vazba kovů
  - Produkty přeměny aminoacylů – PQQ

# Kofaktory oxidoreduktas

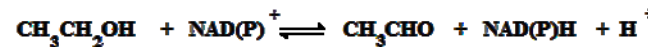
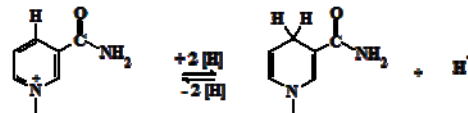
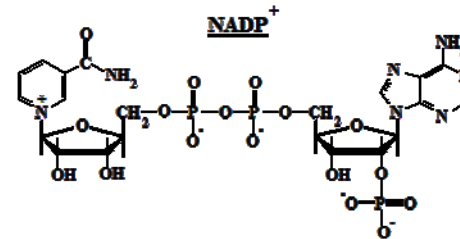
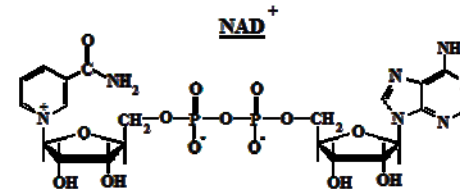
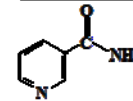
- Nikotinamidové
- Koenzymy
- Prekurzor niacin
- Disociabilní
- 2e<sup>-</sup> redukce
- Přenos H<sup>-</sup>
- NAD<sup>+</sup> - respirace
- NADP<sup>+</sup> - redukce
- Změna spektra
- $A_{340} = f(c)$

## NIKOTINAMIDOVÉ KOENZYMY

k. nikotinová

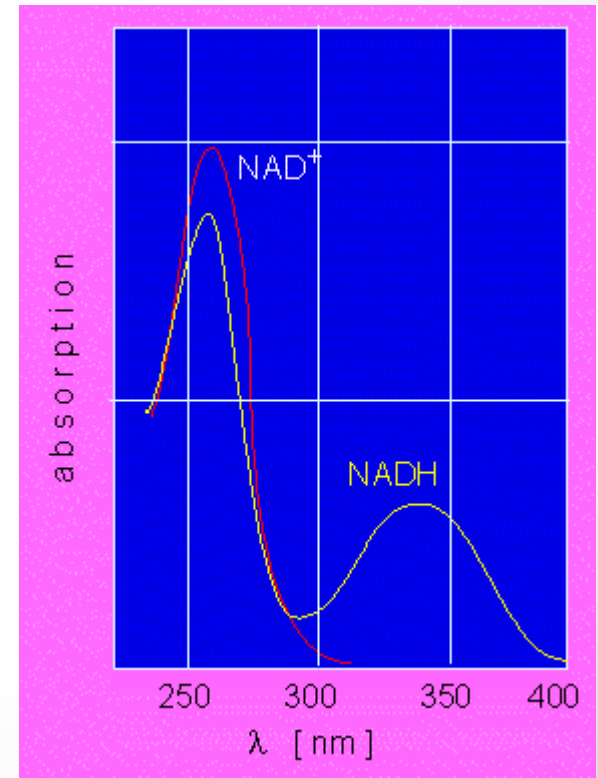
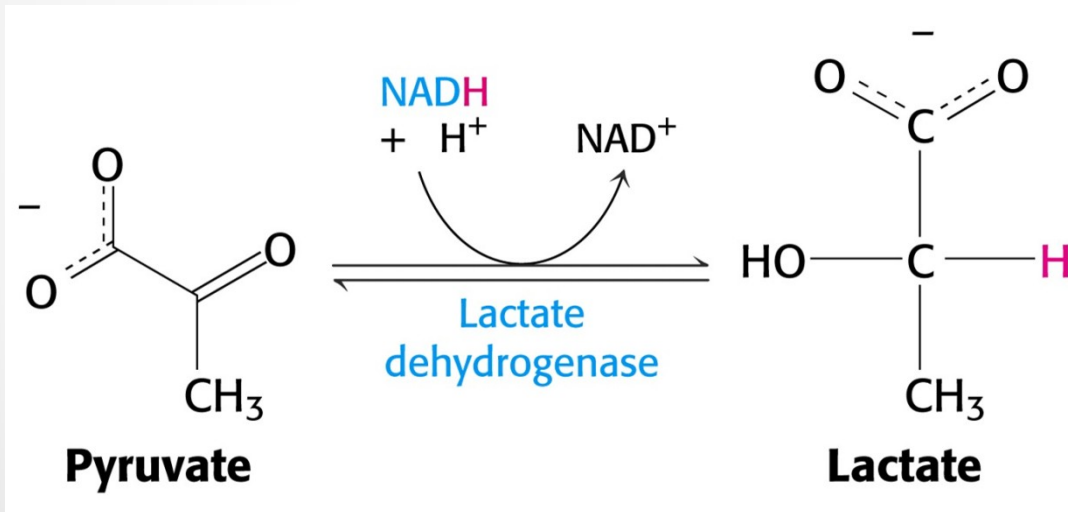


nikotinamid



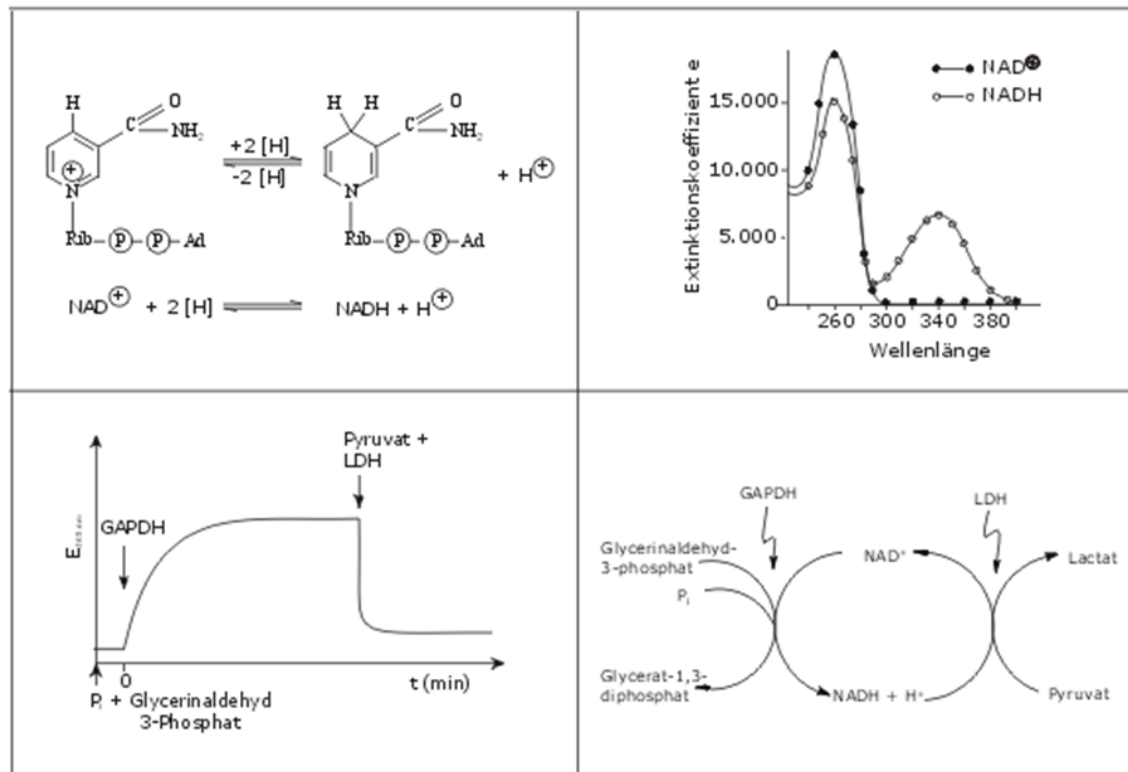
# Kofaktory oxidoreduktas

- Warburgův optický test



# Warburgův optický test

## Prinzip des Optischen Tests nach WARBURG



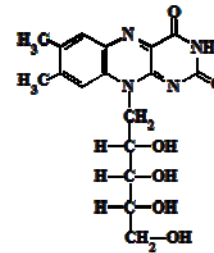
Folie 7.11

# Kofaktory oxidoreduktas

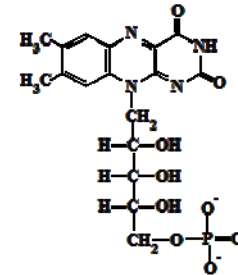
- Flavinové kofaktory
- Prekurzor riboflavin
- Prostetické skupiny
- 2  $1e^-$  kroky
- Semichinony, radikály (zdroj ROS)
- Změna A nevýrazná
- Žlutá (ox) x leukoforma (red)

## FLAVINOVÉ KOENZYMY

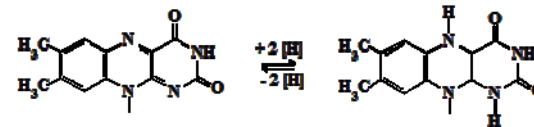
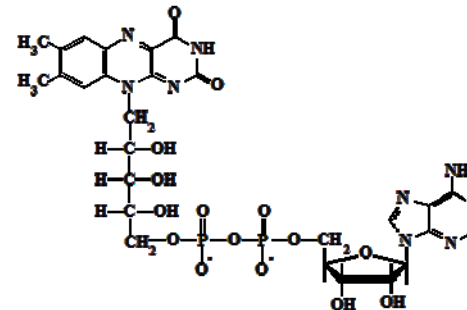
riboflavin



FMN

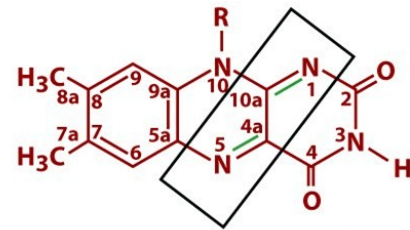


FAD

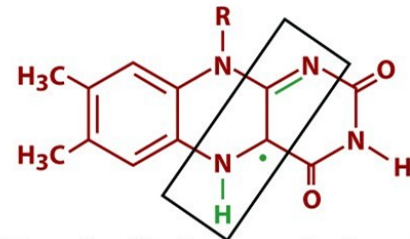


# Kofaktory oxidoreduktas

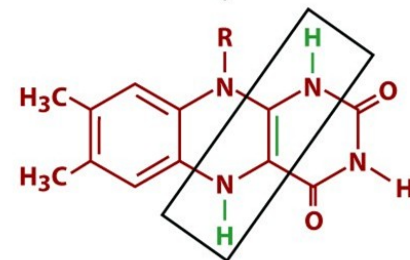
- Redukce FAD



**Flavin adenine dinucleotide (FAD)  
(oxidized or quinone form)**



**FADH · (radical or semiquinone form)**



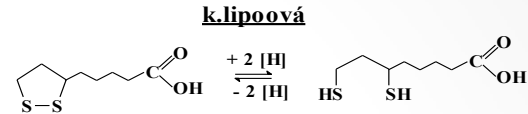
**FADH<sub>2</sub> (reduced or hydroquinone form)**

Figure 13-12 Fundamentals of Biochemistry, 2/e  
© 2006 John Wiley & Sons

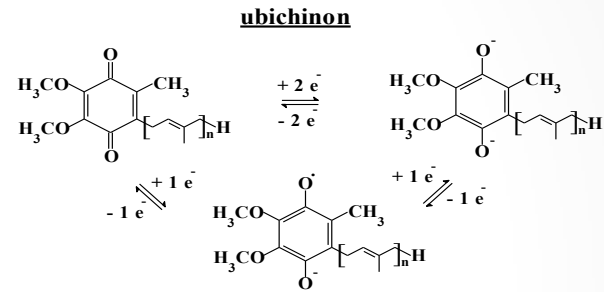


# Kofaktory oxidoreduktas

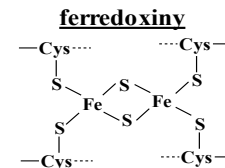
- Kys. lipoová (thioktová)
  - Vitamin
  - Vázán amidicky na apoprotein
  - Odtud lipoamid



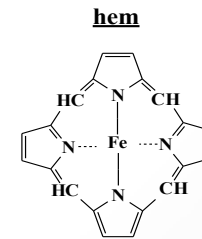
- Ubichinon, CoQ
  - Volná interakce
  - UQ-5n, CoQ<sub>n</sub>, n = 6 – 10
  - Semichinony, radikály, ROS



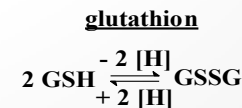
- Ferredoxinové typy
  - Nehemově vázané Fe, FeS proteiny
  - Klastry Fe-S různé struktury



- Hemově vázané Fe
  - Různé substituenty, též lipofilní
  - Různý způsob vazeb

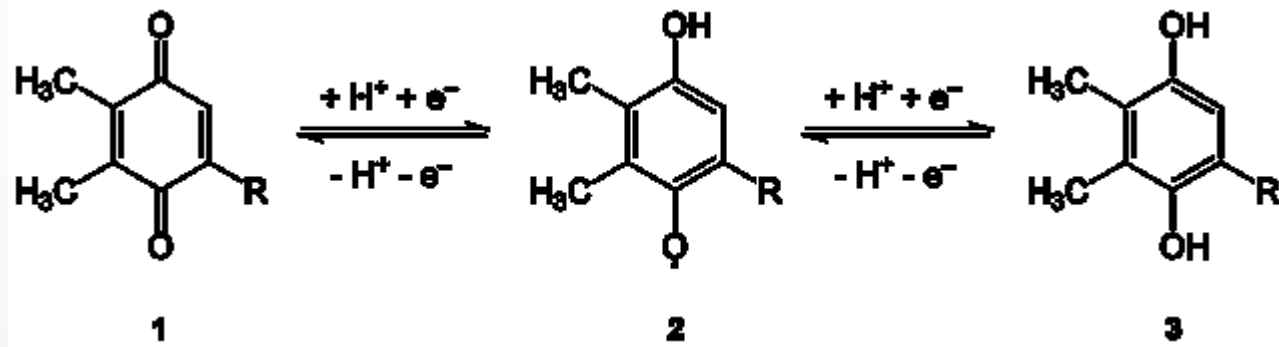
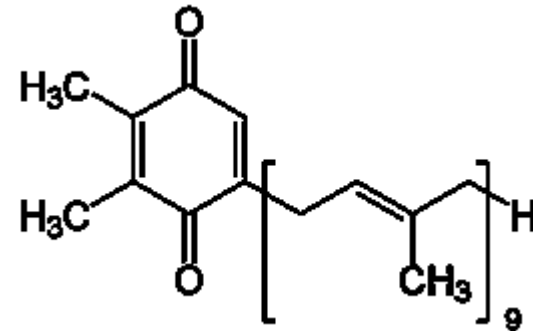


- GSH
  - Detoxikace, GSH peroxidasa x reduktasa
  - Též přenos skupin, xenobiotika



# Kofaktory oxidoreduktas

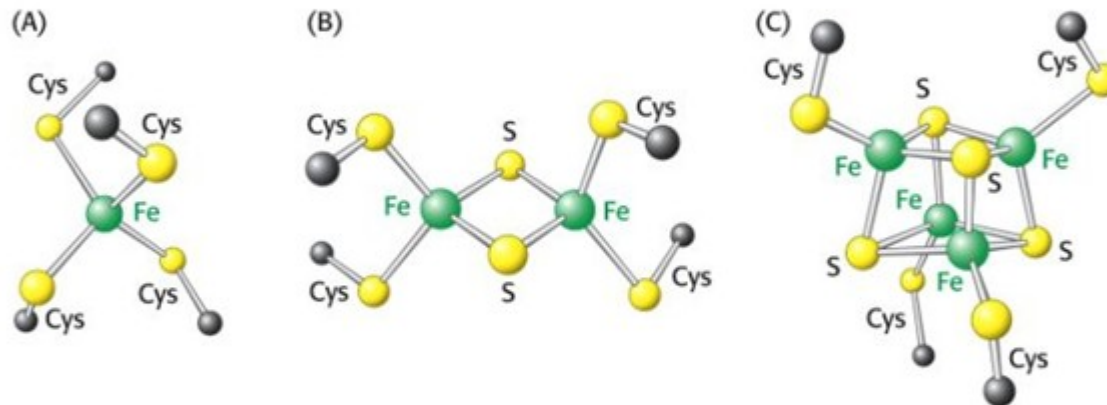
- Plastochinon
  - Obdoba UQ u fotosyntézy
  - Redukce 2 x 1e<sup>-</sup>





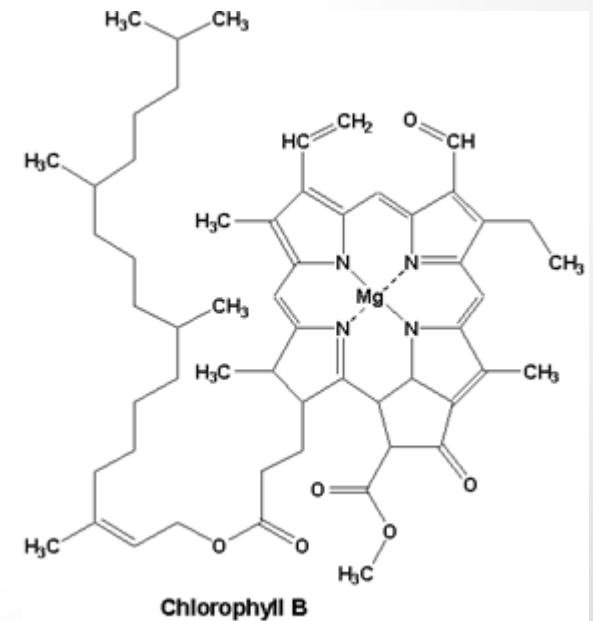
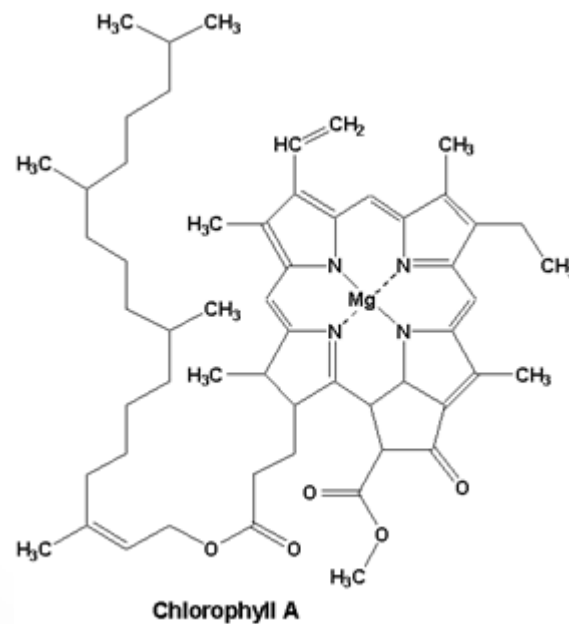
# Kofaktory oxidoreduktas

- Fe-S klastry, příklady prostetických skupin bílkovin feredoxinového typu



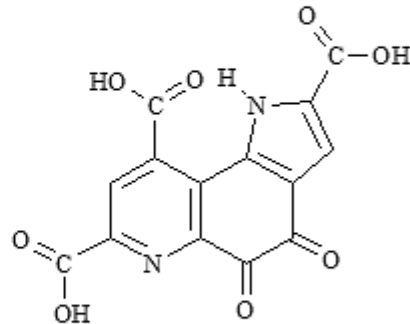
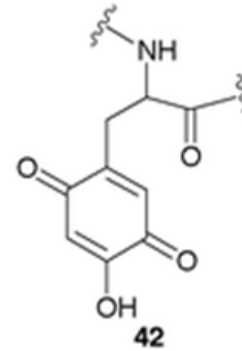
# Kofaktory oxidoreduktas

- Chlorofyly
  - Porfyrinová struktura, lipofilní substituent
  - $Mg^{2+}$
  - Fotosyntéza – transport  $e^-$

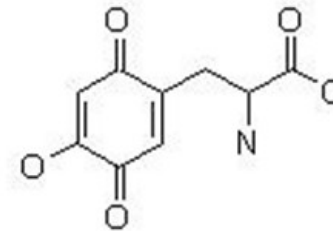


# Kofaktory oxidoreduktas

- Přeměněné AK
  - Prostetické skupiny
  - Bílkovinný původ



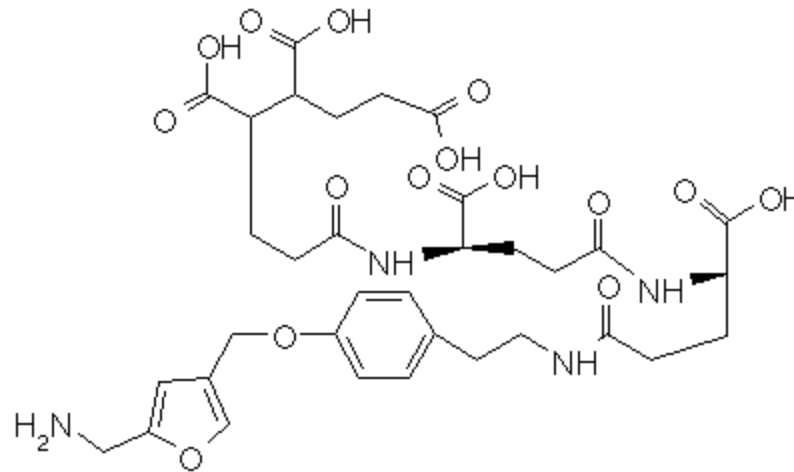
Pyrolochinolichinon  
PQQ



TOPAchinon  
TrihydrOxyPhenylAlanin

# Kofaktory oxidoreduktas

- Kofaktory metanogeneze



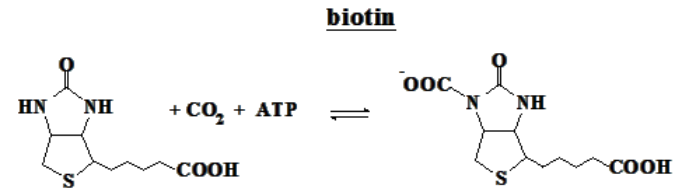
Metanofuran



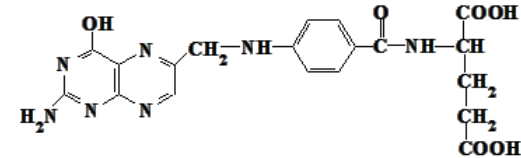


# Koenzymy transferas

- Biotin
  - Vitamin B
  - Vázán na Lys enzymu
  - Aktivní karboxyl
- THF – tetrahydrofolát
  - Z folátu
  - Disociabilní
  - Aktivní 1C metabolity
  - Syntézy nukleotidů - bazí
- TPP – tiamindifosfát
  - Aktivní aldehydy (2C)
  - Prostetická skupina

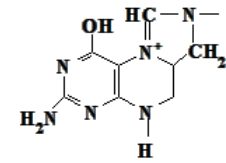
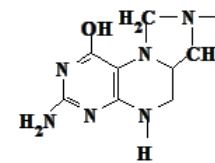


Kys. listová

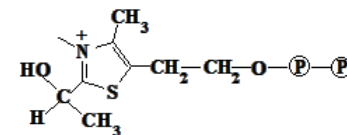
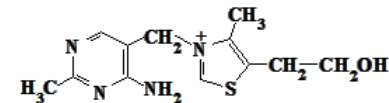


**methylenetetrahydrolistová k.**

**methenyltetrahydrolistová k.**



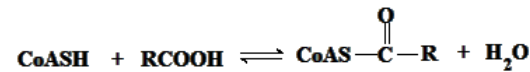
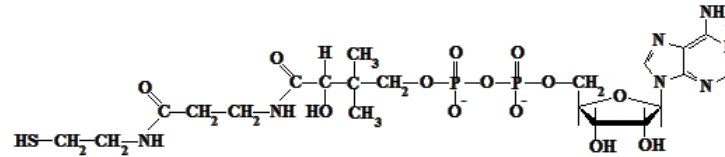
**thiamin**



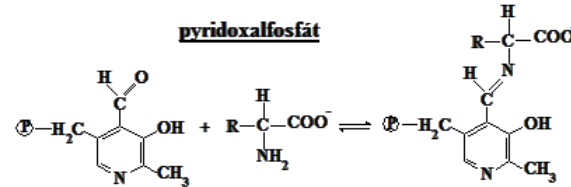
# Koenzymy transferas

- Koenzym A
  - Z pantotenátu
  - Aktivní acyly
  - Spřaženo ATP = AMP + PP
- PALPO
  - Z pyridoxinu
  - Metabolismus aminů, AK
  - Tvorba Schiffovy báze
  - Úloha apoenzymu – typ reakce
- CDP – netřeba vitamin
- UDP - dtto
  - Aktivní monosacharidy
  - UTP + Glc-1-P = UDP-Glc + PP

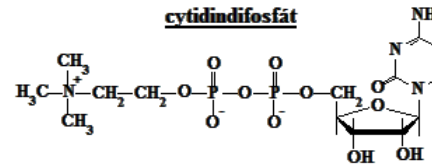
koenzym A - CoA - CoASH



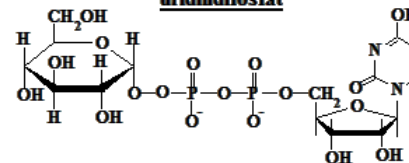
pyridoxalfosfát



cytidindifosfát

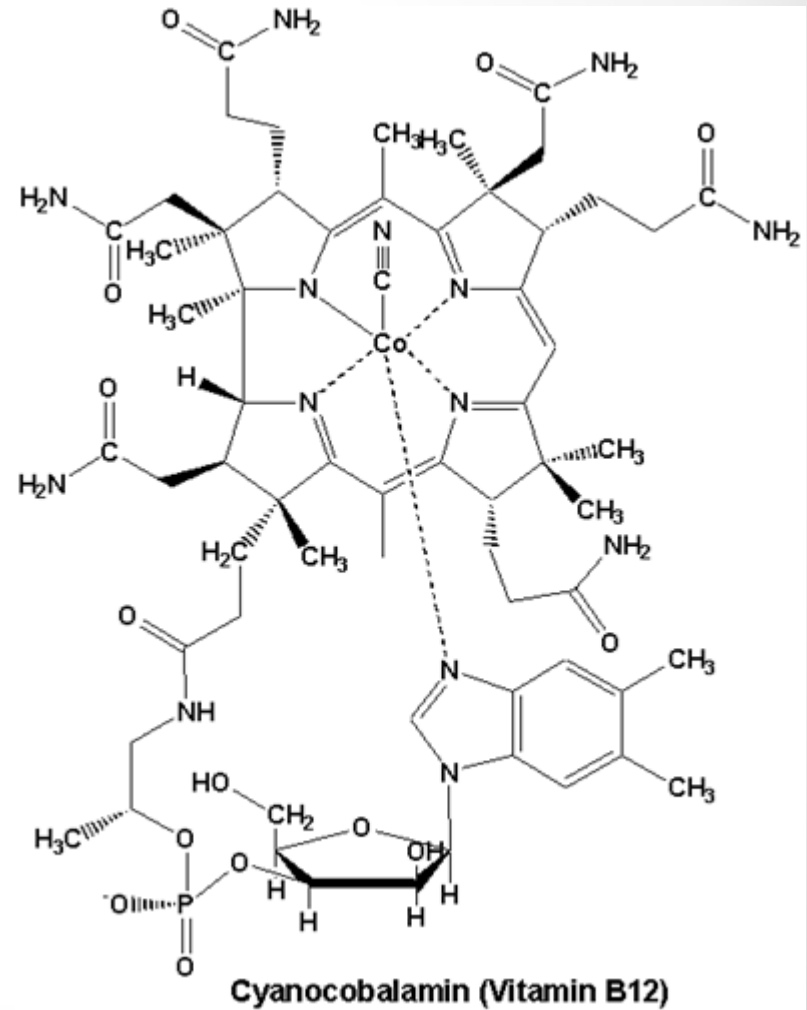


uridindifosfát



# Koenzymy isomeras

- Vitamin B<sub>12</sub>
  - Kobalamin
    - Korinoid + nukleotid
  - Ligandy
    - CN neúčinnější
  - Transkarboxylace
  - Krvetvorba
    - Perniciósní anemie
  - Aplikace
    - Perorální nespolehlivá
    - Vnitřní faktor pro vstřebávání
  - Biotechnologická produkce
    - Výkaly přežvýkavců
    - Aktivovaný kal



# Vitaminy

- Vitaminy jako prekurzory kofaktorů
  - Většinou, některé nepotřebují
  - Některé jsou spíše metabolity (askorbát)
- Fyziologická role – zde druhořadé
- Výskyt – vlastnosti (polarita)
  - Rozpustné ve vodě – polární
  - Rozpustné v tucích – nepolární
  - Hledisko dietetické
- Následující přehled
  - Korelace struktur s kofaktory

Podrobnější přehled [cs.wikipedia.org/wiki/Vitamín](https://cs.wikipedia.org/wiki/Vitamín)

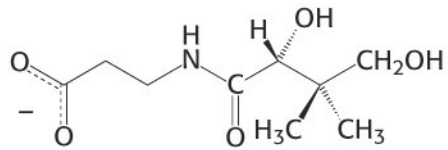
**TABLE 8.9 Water-Soluble Vitamins**

Vitamin	Coenzyme	Typical reaction type	Consequences of deficiency
Thiamine (B <sub>1</sub> )	Thiamine pyrophosphate	Aldehyde transfer	Beriberi (weight loss, heart problems, neurological dysfunction)
Riboflavin (B <sub>2</sub> )	Flavin adenine dinucleotide (FAD)	Oxidation–reduction	Cheliosis and angular stomatitis (lesions of the mouth), dermatitis
Pyridoxine (B <sub>6</sub> )	Pyridoxal phosphate	Group transfer to or from amino acids	Depression, confusion, convulsions
Nicotinic acid (niacin)	Nicotinamide adenine dinucleotide (NAD <sup>+</sup> )	Oxidation–reduction	Pellagra (dermatitis, depression, diarrhea)
Pantothenic acid	Coenzyme A	Acyl–group transfer	Hypertension
Biotin	Biotin–lysine complexes (biocytin)	ATP-dependent carboxylation and carboxyl-group transfer	Rash about the eyebrows, muscle pain, fatigue (rare)
Folic acid	Tetrahydrofolate	Transfer of one-carbon components; thymine synthesis	Anemia, neural-tube defects in development
B <sub>12</sub>	5'-Deoxyadenosyl cobalamin	Transfer of methyl groups; intramolecular rearrangements	Anemia, pernicious anemia, methylmalonic acidosis
C (ascorbic acid)		Antioxidant	Scurvy (swollen and bleeding gums, subdermal hemorrhages)

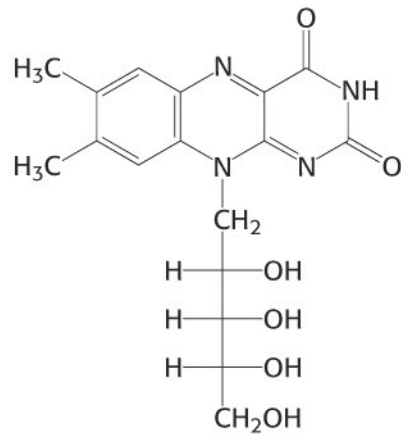
**TABLE 8.10 Fat-soluble vitamins**

Vitamin	Function	Deficiency
A	Antioxidant	Inhibition of sperm production; lesions in muscles and nerves (rare)
D	Regulation of calcium and phosphate metabolism	Rickets (children): skeletal deformities, impaired growth Osteomalacia (adults): soft, bending bones
E	Roles in vision, growth, reproduction	Night blindness, cornea damage, damage to respiratory and gastrointestinal tract
K	Blood coagulation	Subdermal hemorrhaging

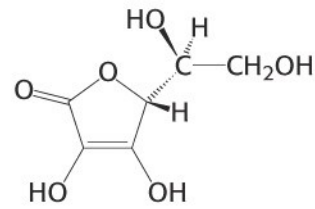
Chyba – A a E!?



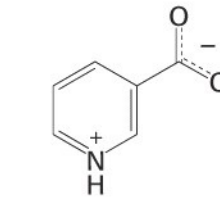
**Vitamin B<sub>5</sub>**  
**(Pantothenate)**



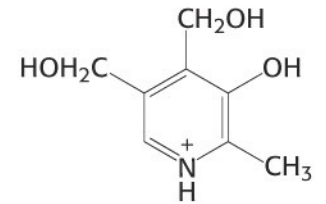
**Vitamin B<sub>2</sub>**  
**(Riboflavin)**



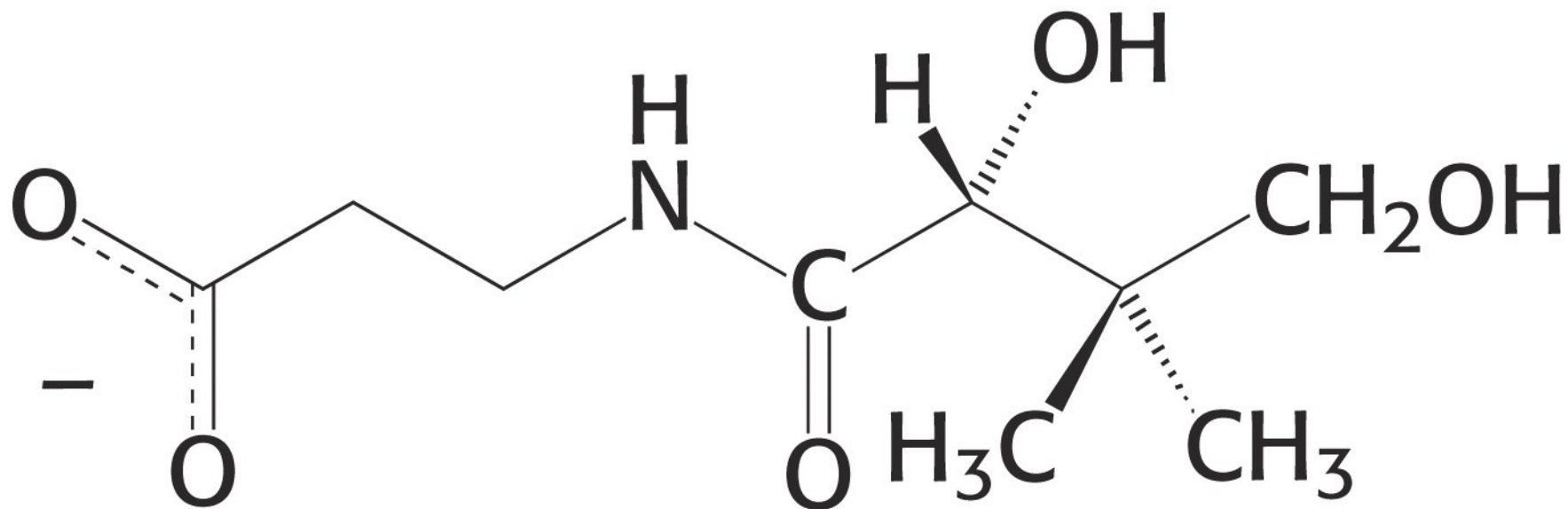
**Vitamin C**  
**(Ascorbic acid)**



**Vitamin B<sub>3</sub>**  
**(Niacin)**

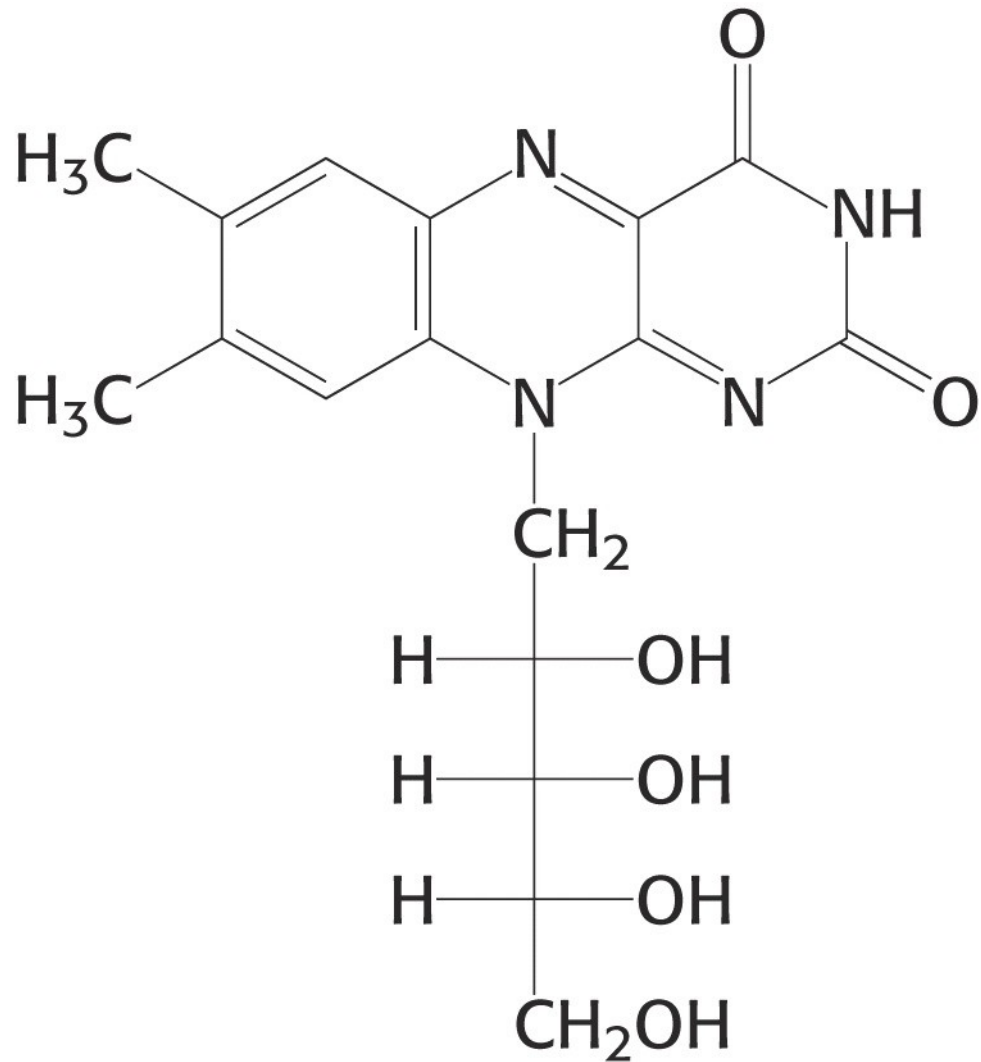


**Vitamin B<sub>6</sub>**  
**(Pyridoxine)**

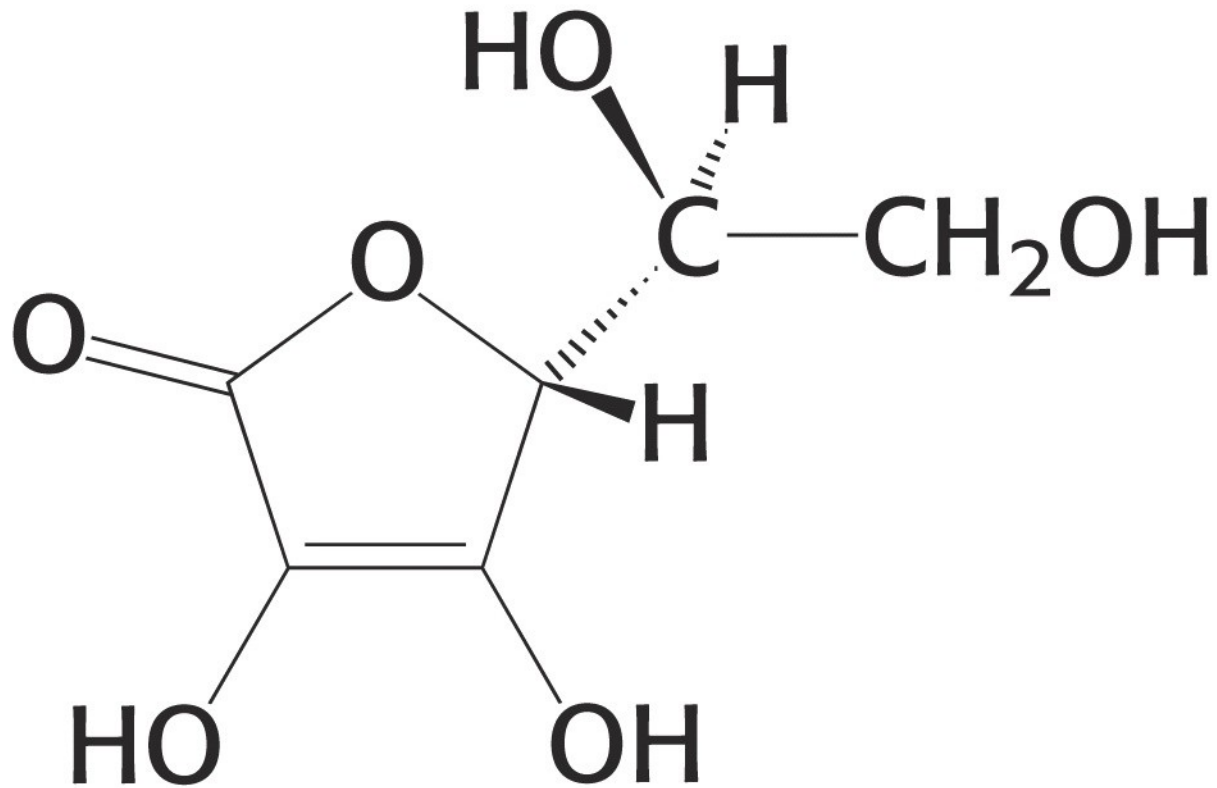


**Vitamin B<sub>5</sub>**  
**(Pantothenate)**

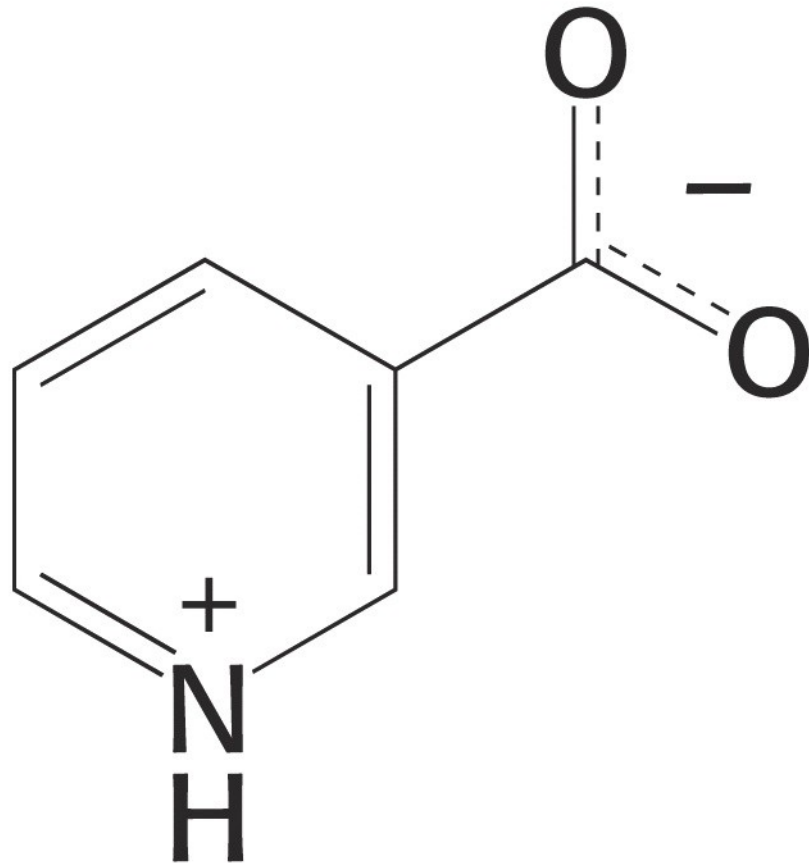




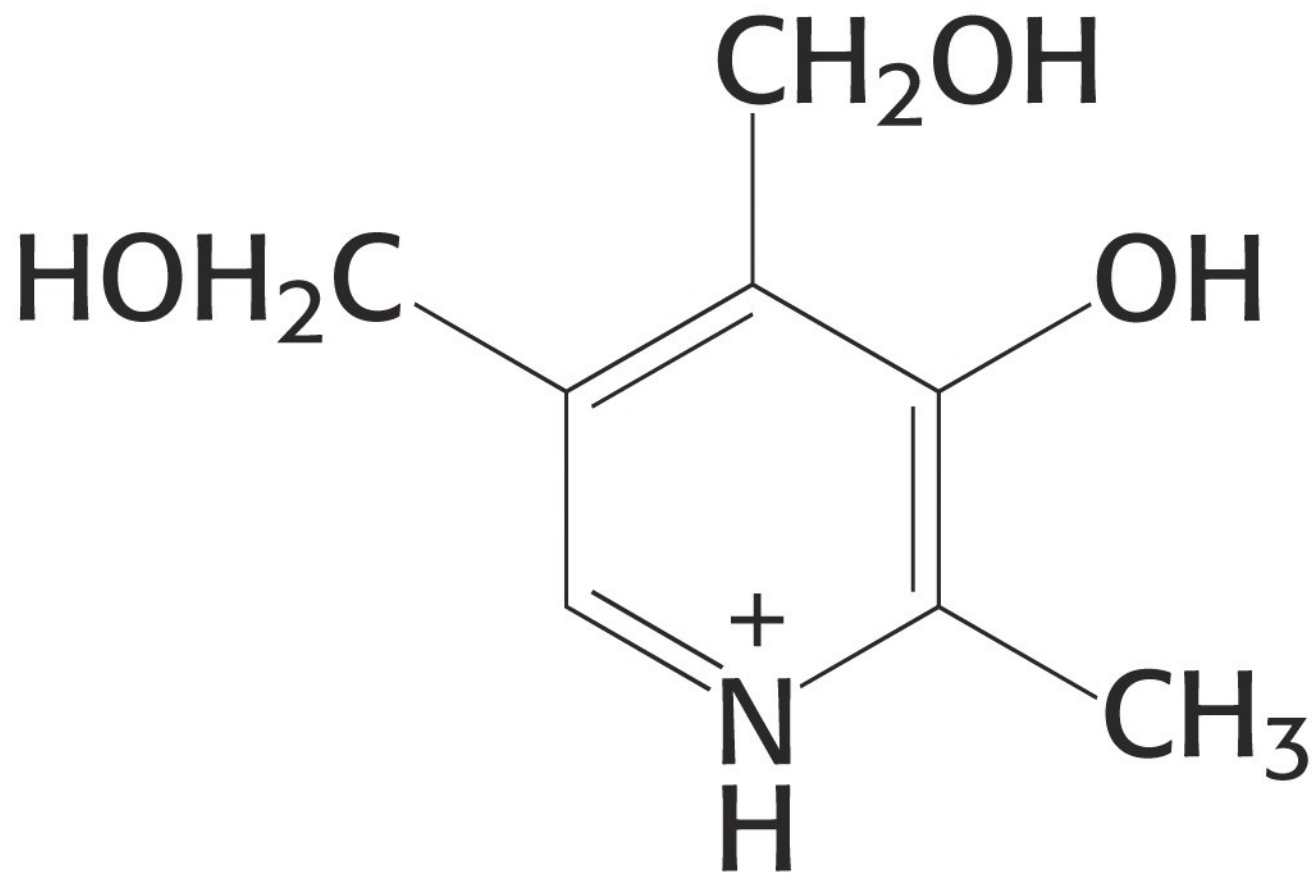
**Vitamin B<sub>2</sub>**  
**(Riboflavin)**



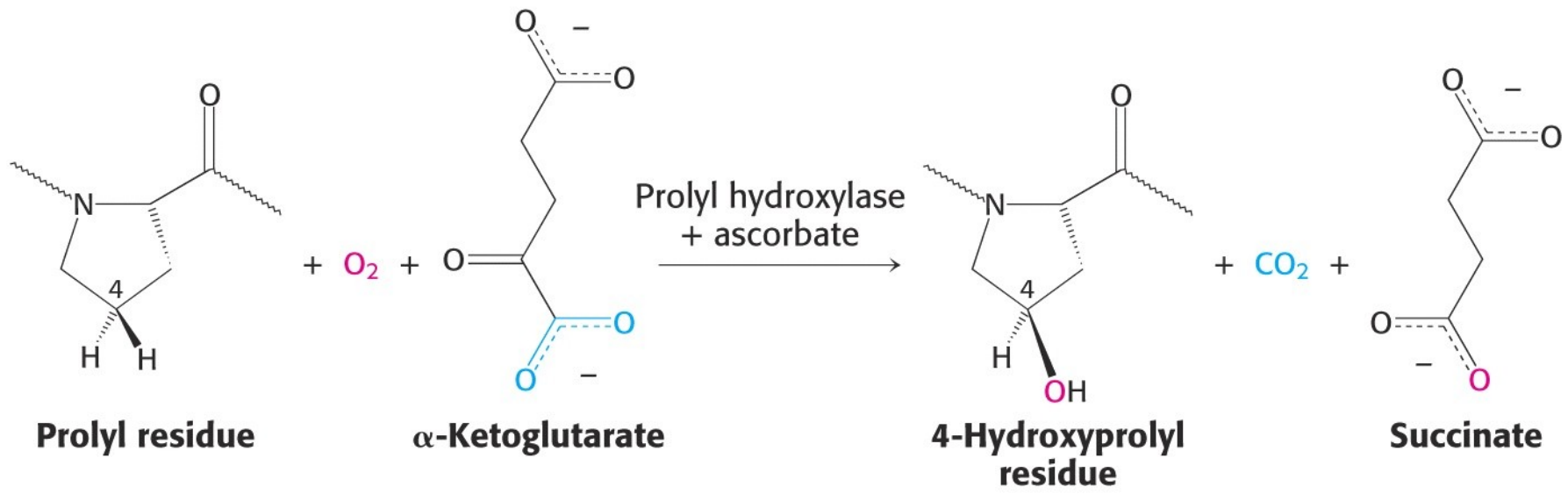
**Vitamin C**  
**(Ascorbic acid)**

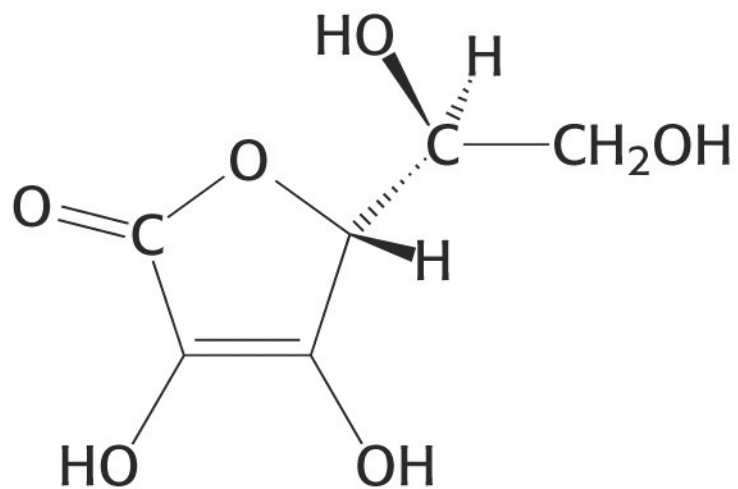


**Vitamin B<sub>3</sub>**  
**(Niacin)**

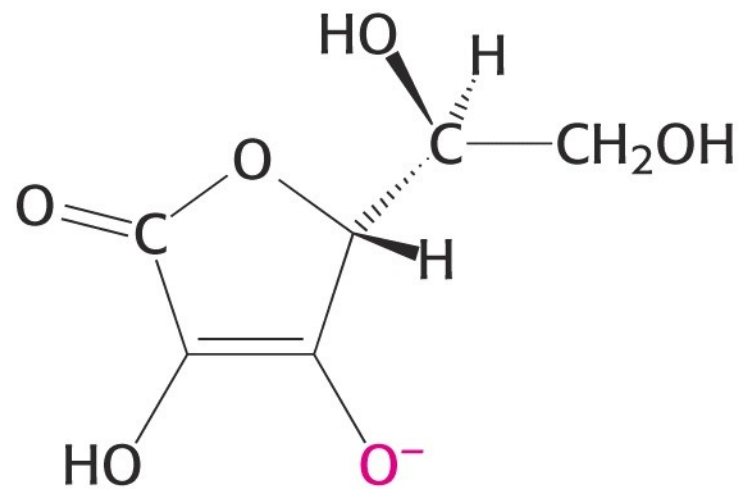


**Vitamin B<sub>6</sub>**  
**(Pyridoxine)**

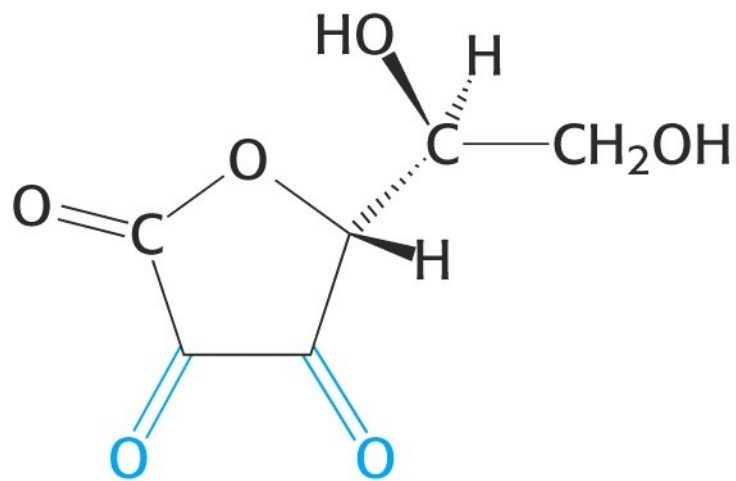




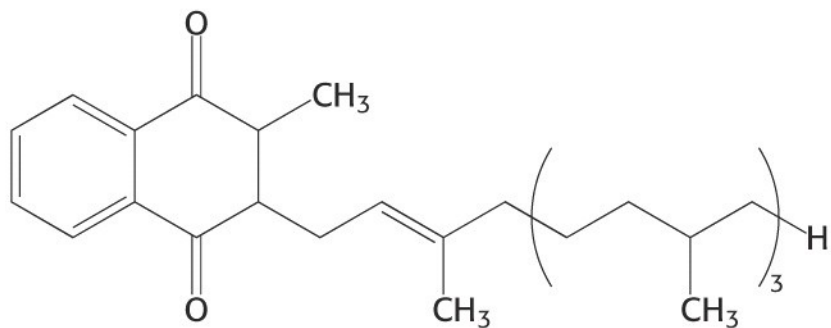
**Ascorbic acid**



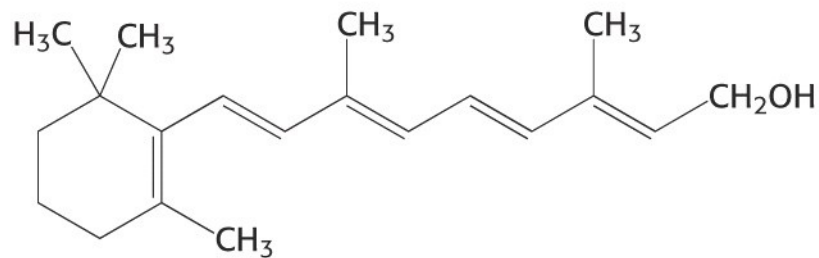
**Ascorbate**



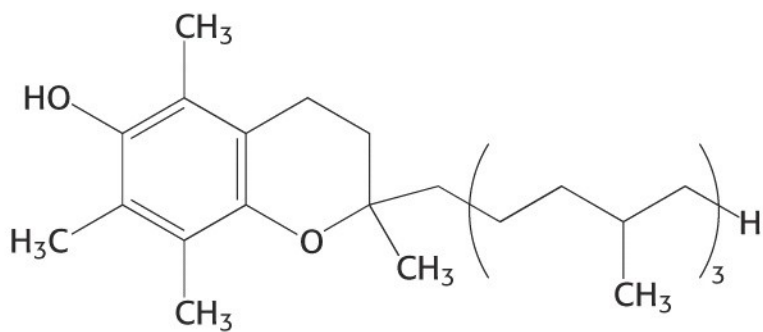
**Dehydroascorbic acid**



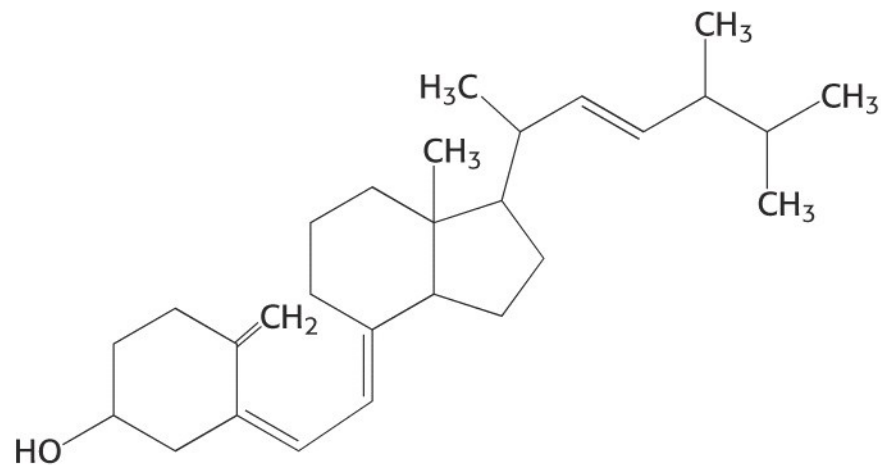
**Vitamin K<sub>1</sub>**



**Vitamin A (Retinol)**



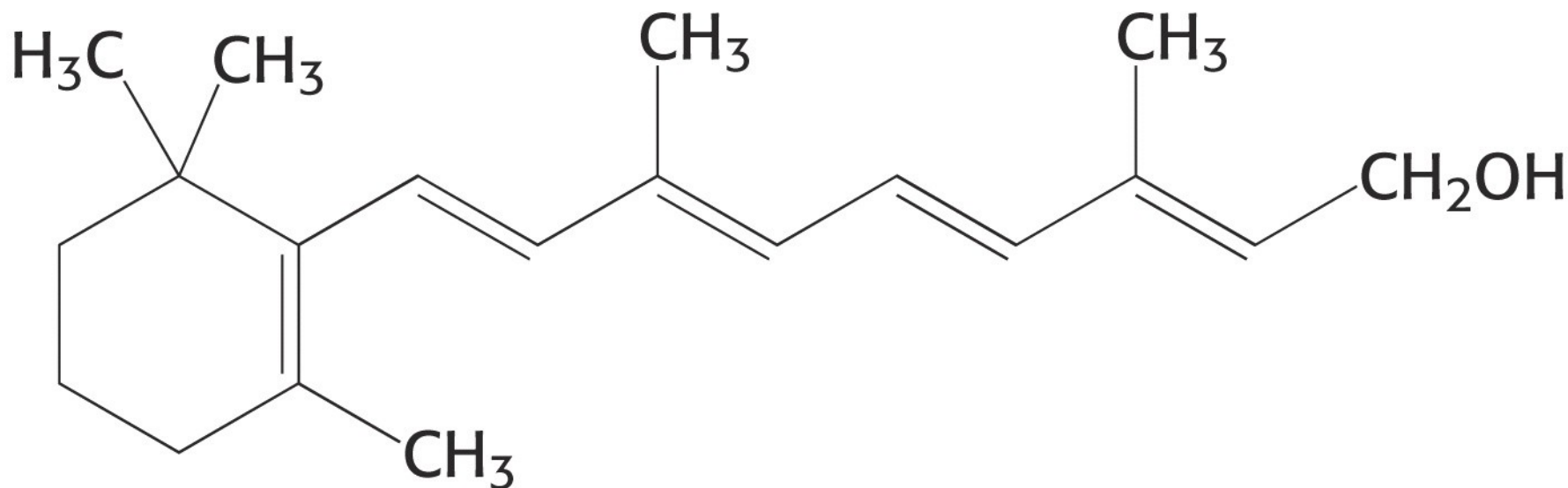
**Vitamin E (α-Tocopherol)**



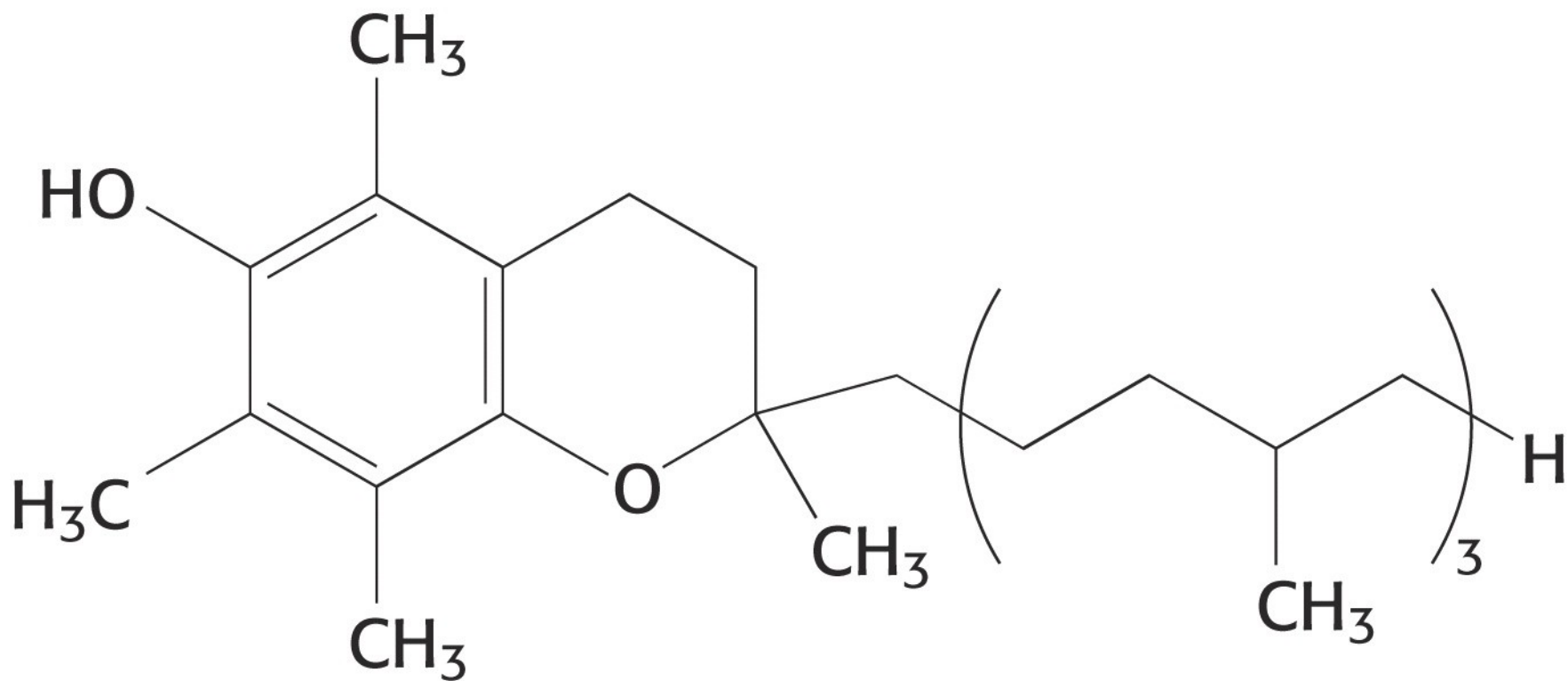
**Vitamin D<sub>2</sub> (Calciferol)**



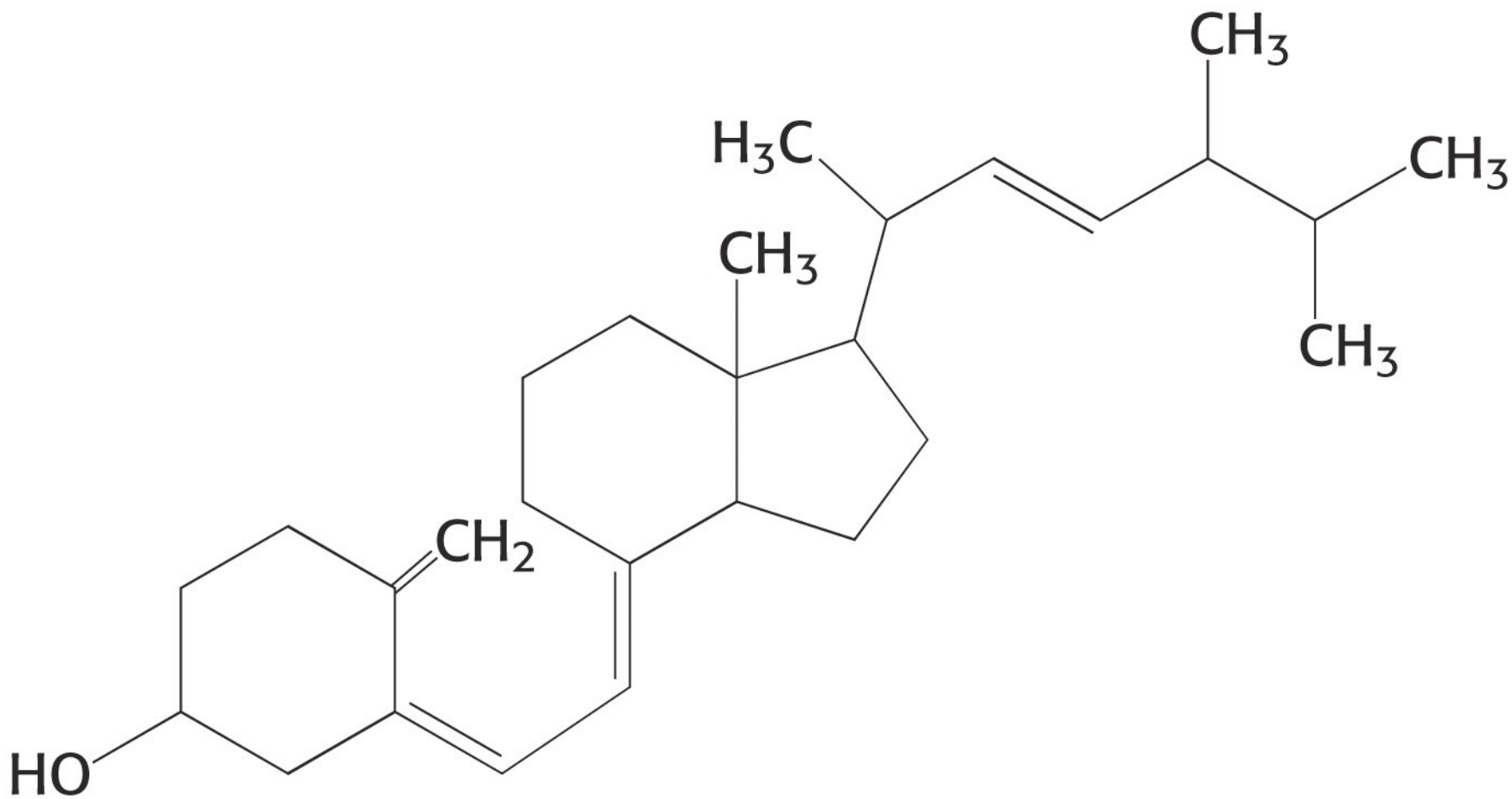




**Vitamin A (Retinol)**



**Vitamin E (α-Tocopherol)**



**Vitamin D<sub>2</sub> (Calciferol)**