## 2. AMINO ACIDS, PEPTIDES AND PROTEINS

## amino acids

functional groups: NH<sub>2</sub> COOH

-C-NH-O

amino acids bound by amide (peptide) bond

#### peptides

2-100 amino acids

#### proteins

> 100 amino acids

## AMINO ACIDS

~ 700 amino acids

- free compounds
- structural units of peptides, proteins and other compounds

## structure

amino group	$NH_2$	free, substituted
<ul> <li>carboxylic group</li> </ul>		-COOH
<ul> <li>additional functional g</li> </ul>	groups	
hydroxyl		-OH
thiol		-SH
sulfide		-S-R
		-NH·C-NH <sub>2</sub>
guanidyl		ŇН
phenyl etc.		
1 5		

#### classification

#### according to distance of amino group from carboxylic group

# R-CH-[CH<sub>2</sub>]<sub>n</sub>-COOH

	NH <sub>2</sub>	]		
2-amino acids	α-amino acids	0	—	
3-amino acids	β-amino acids	1		
4-amino acids	γ-amino acids	2		
5-amino acids	δ-amino acids	3		
6-amino acids	ε-amino acids	4		

#### according to their occurrence

found in all organisms (invariable), basic (proteinogenic), 21 amino acids found in only some organisms (variable), many amino acids

#### basic amino acids

**20** α-amino acids with primary amino group -NH<sub>2</sub>



1  $\alpha$ -amino acids with secondary amino group -NH-

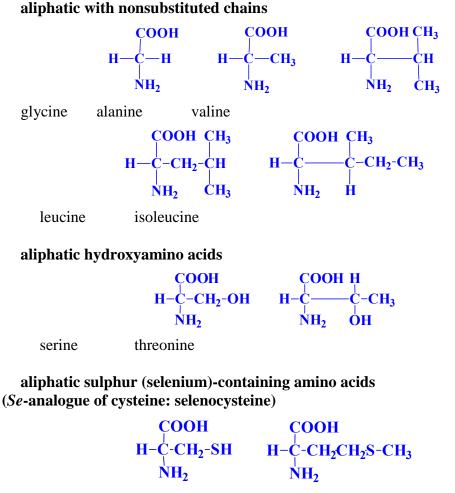
$$\begin{array}{cccc} H_2C & & H_2C & (CH_2)n \\ H_2C & & & H_2C & (CH_2)n \\ H_2C & & & H_2C & (CH_2)n \\ & & & H_2C & +\alpha| \\ H_2C & & & H_2C & +\alpha| \\ H_2C & & & H_2C & +\alpha| \\ H_2C & & & H_2C & (CH_2)n \\ H_2C & & &$$

n=0, pyrrolidine

20 amino acids = chiral compounds groups, L-amino acids

trivial names systematic names, symbols (tree letters, one letter), (book 1, table 2.1.)

classification of basic amino acids according the structure of side-chain and functional groups



cysteine

methionine

with another carboxyl group in the side-chain (monoaminodicarboxylic, acidic)

aspartic acid

glutamic acid

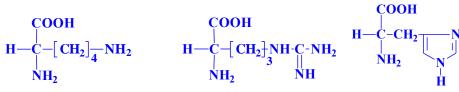
their monoamides (with carboxamides group in the side-chain)



asparagine glutamine

#### with basic groups in the side-chain

- amino group
- guanidylic group
- imidazole cycle

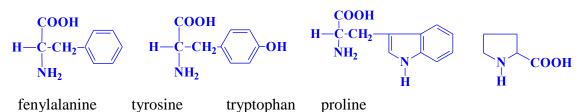




histidine

### with aromatic (heterocyclic) side-chain

arginine



## according to polarity of the side-chain and its ionic forms (in neutral medium)

- nonpolar, hydrophobic
   Val, Leu, Ile, Phe, Tyr, Met, Pro; to some extent Gly, Ala, Trp
  - **polar, hydrophilic** Ser, Thr, Cys, Asp, Glu, Asn, Gln, Lys, Arg, His

hydrophilic (according ionic form of side chain in neutral medium)

- neutral (without electric charge): most amino acids
- acidic (negative electric charge): Asp, Glu
- basic (positive electric charge): Lys, Arg, His

#### according to importance in human nutrition

- essential: Val, Leu, Ile, Thr, Met, Lys, Phe, Trp
- semiessential : Arg, His
- nonessential: others

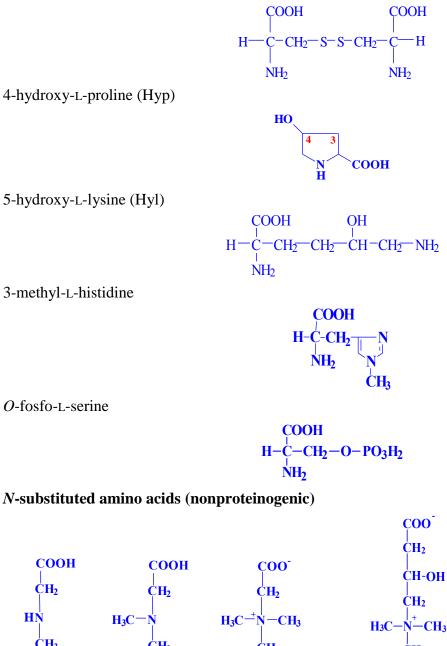
#### limiting amino acids

## DERIVATIVES OF PROTEINOGENIC AMINO ACIDS (formed by posttranslational modifications)

L-cystine (CySSCy)

ΗŃ

ĊH3



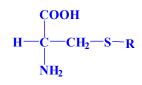
*N*-methylglycine *N*,*N*-dimethylglycine *N*,*N*,*N*-trimethylglycine L-carnitine (sarkosine) (3-hydroxy-4-trimethylaminobutyrate, vitamin B<sub>t</sub>)

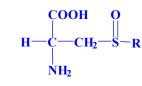
ĊH3

СООН	СООН
CH <sub>2</sub>	CH <sub>2</sub>
ĊH <sub>2</sub>	CH <sub>2</sub>
$\mathbf{NH}_{2}$	CH <sub>2</sub>
	NH <sub>2</sub>

 $\beta$ -alanine (3-aminopropionic acid)  $\gamma$ -aminobutyric (4-aminobutyric) acid (GABA)

#### sulphur-containing amino acids





S-alk(en)yl-L-cysteines

S-alk(en)yl-L-cysteine sulfoxides

basic amino acids and related compounds

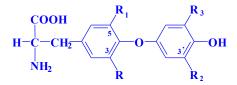
$$H - C - [CH_2]_{\overline{n}} - CH_2 - NH_2$$
  
NH2  
L-ornithine (n = 2)

$$\begin{array}{c} COOH \\ H - C - [CH_2]_n - CH_2 - NH - C - NH_2 \\ NH_2 \\ O \end{array}$$

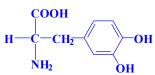
L-citrulline (n = 2, carbamoylderivative of ornithine) COOH CH<sub>2</sub> OH CH<sub>3</sub>N-C-NH-P-OH NH O

creatine-phosphate

aromatic amino acids



tetrajodthyronine (thyroxine),  $\mathbf{R} = \mathbf{R}^1 = \mathbf{R}^2 = \mathbf{R}^3 = \mathbf{I}$ 



3,4-dihydroxy-L-fenylalanine (DOPA)

essential amino acids

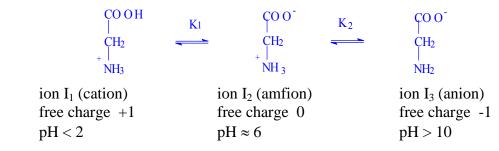
foods with limiting amino acids

- Lys cereals (generally vegetable proteins)
- Met milk, meat
- Thr wheat, ray
- Trp casein, corn, rice

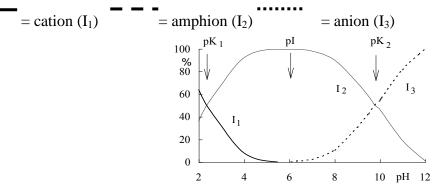
### physical-chemical properties of amino acids

- acidobasic properties (pK a pI) (book 1 table 2.3).
- optical activity
- sensory properties

## acidobasic properties (Gly)



Gly ionic forms dependence on pH



#### optical properties

- Gly = exception
- majority = chiral atom  $C_{\alpha}$

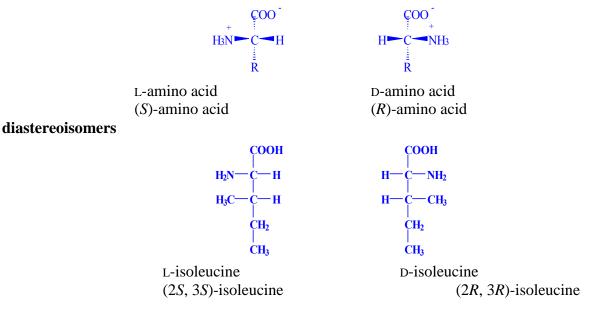
2 optical isomers (enantiomers)

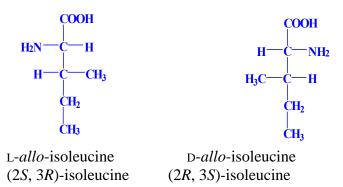
some = two 2 chiral centres (Ile, Thr, Hyp, CySSCy)

## L- and D-amino acids

L-amino acids = (S)-stereoisomers, exception: L-cysteine = (R)-stereoisomer D-amino acids = (R)-stereoisomers

content (book 1, table 2.25)





## sensory properties

- sweet Gly, Ala, Thr, Pro
- sour Asp, Glu
- bitter Leu, Ile, Phe, Tyr, Trp
- indifferent all the other

special properties = **umami** taste

**ÇOON**a  $H = C = CH_2 = CH_2 = COO^{-1}$ 

natrium-hydrogen-glutamate

## PEPTIDES

#### structure

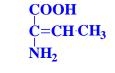
condensation of 2 amino acids (linear and cyclic dipetides)

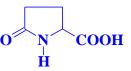
- uncommon binding of some amino acids
  - distal COOH group of  $Glu = \gamma$ -peptide bond
- biding of D-amino acids
- biding of uncommon amino acids

СООН	СООН	СООН	ŞO₃H
CH <sub>2</sub>	CH-NH <sub>2</sub>	CH <sub>2</sub>	ĊH <sub>2</sub>
ĊH <sub>2</sub>	$CH_2$	CH <sub>2</sub>	ĊH <sub>2</sub>
NH <sub>2</sub>	ĊH <sub>3</sub>	CH <sub>2</sub>	NH <sub>2</sub>
		NH <sub>2</sub>	

 $\begin{array}{lll} \beta \mbox{-aminobutanoic acid} & \gamma \mbox{-aminobutanoic acid} & taurine \\ (3\mbox{-aminopropionic acid}) & 2\mbox{-aminobutanoic acid} & 4\mbox{-aminobutanoic acid}) \end{array}$ 

ÇOOH
C=CH <sub>2</sub>
NH <sub>2</sub>





2-aminoacrylic acid (dehydroalanine) (*E*)-2-aminocrotonic acid (dehydrobutyrine)

pyroglutamic acid

### classification

#### number of bound monomers (amino acids)

- oligopeptides (2-10 amino acid)
- polypeptides (11-100 amino acid)

#### chain character

- linear
- cyclic

#### bond type

- homodetic (peptide bonds only)
- heterodetic (peptide bonds and other bonds) disulfide -S-Sesters (depsipeptides) -CO-O-R

#### bound components

- homomeric amino acids only
- heteromeric amino acids and other compounds

nucleopeptides	phosphopeptides
lipopeptides	chromopeptides
glycopeptides	metalopeptides

#### occurrence

- product of metabolism, natural peptides
- product of proteolysis, enzymatic and nonenzymatic

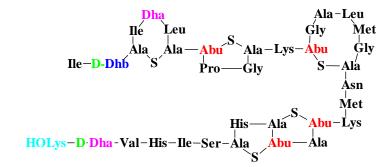
• synthetic peptides, artificial sweeteners etc.

## properties

- biological activities
- sensory activities

## products of lactic acid fermentation =bacteriocines

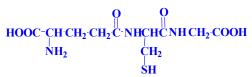
**nisine** *Streptococcus cremoris*, syn. *Lactococcus lactis* ssp. *lactis* antibiotic properties, preservation agent, stabilisation of lactic acid fermentation products



Abu = 2-aminobutanoic $\leftarrow$  GluDha = 2-aminoacrylic (dehydroalanine) $\leftarrow$  Ser, CysDhb = 2-aminocrotonic (dehydrobutyrine) $\leftarrow$  ThrHoLys = 5-hydroxylysine, D = D-isomer

## other important peptides

glutathione (G-SH or G-S-S-G)



γ-L-glutamyl-L-cysteinylglycine (γ-amidic bond)

occurrence microorganisms, plants, animals

wheat flour	10-15 mg/kg
meat	300-1500 mg/kg

## functions

- detoxification of toxic forms of O<sub>2</sub>
- transportation of amino acids into cells
- metabolic processes (biosyntheses of leucotriens)
- stabilisation of oxidation state of SH-proteins (peroxidases, glutathione reductases)
- technology (white bread production)

Chorleywood process of white bread production using ascorbic acid

 $H_2A + \frac{1}{2}O_2 \rightarrow A + H_2O$  (ascorbate oxidase)

 $A + 2 \text{ G-SH} \rightarrow H_2A + \text{G-S-S-G}$  (glutathione dehydrogenase)

G-S-S-G without influence on rheological properties of dough

 $P\text{-}S\text{-}S\text{-}P + G\text{-}SH \rightarrow P\text{-}S\text{-}S\text{-}G + P\text{-}SH$ 

## β-alanylhistidine dipeptides

**content in meat** (book 1, table 2.5.)

balenine (n = 1), R = 
$$-CH_2 \underbrace{\bigcup_{\substack{N \\ CH_3}}^{N}}_{l}$$

## function

- participation on muscle contraction
- buffering capacity of muscle
- sensory properties

#### analysis

• meat origin in meat products

## proteolysis

## • autolysis

desirable meat maturation (consistency, aroma), production of yeast autolyzates (additives) undesirable

## • intentional proteolysis

cheese production (desirable consistence, aroma) malt production (stabilisation of beer foam) protein hydrolyzates production enzymatic protein hydrolyzates: soya sauce acid protein hydrolyzates (hydrolysed vegetable protein)

## bitter peptides of enzymatic hydrolyzates

hydrophobic amino acids Val, Leu, Ile, Phe, Tyr, Trp (MW < 6000 Da)

## synthetic peptides

artificial sweetner Aspartam (Asp-Phe-methylester)

 $\begin{array}{c} \mathbf{O} \\ \mathbf{-} \mathbf{CH}_{2}\mathbf{CH} - \mathbf{NH} - \mathbf{C} - \mathbf{CH} - \mathbf{CH}_{2} - \mathbf{COO}^{-} \\ \mathbf{COOCH}_{3} & \mathbf{NH}_{3}^{+} \end{array}$ 

## PROTEINS

polymers of amino acids

>100 amino acids,  $M_r \thicksim 10.000$  - milions Da

organized structures

constitution and conformation optimal for their functions

main nutrients

peptide bonds

other bonds

- disulfide -S-S-
- ester
- amide

other compound besides amino acids

- water
- inorganic ions
- lipids, saccharides, nucleic acids, colour compounds (pigments)

### classification according to origin

- animal (meat, milk eggs, 60% proteins of protein nutrients)
- vegetables (cereals, pulse, fruits, vegetables), 30% proteins of protein nutrients)
- nontraditional (algae, microbs)

### classification according to function

- structural (components of cells, e.g. collagen)
- catalytic (enzymes, hormones)
- transport (tranport of compounds, e.g. myoglobin)
- motoric (muscle proteins, e.g. actin, myosin)
- defensive (imunoglobulins, lectines)
- storage (ferritin)
- sensory (rhodopsin)
- regulatory (histones, hormones)
- nutritional (source of essential amino acids, source of nitrogen, material for tissues)

#### according to structure (presence of nonprotein components)

simple

- globular spheroproteins(albumins, globulins)
- fibrilar (fibrous), scleroproteins, stromatic proteins (collagens, keratins, elastins)

#### conjugated

- nucleoproteins (nucleic acids)
- lipoproteins (neutral lipids, phospholipids, sterols)
- glycoproteins (saccharides)
- phosphoproteins (phosphoric acid)
- chromoproteins (porphyrins, flavins)
- methaloproteins (bound metals)

## according to solubility

soluble

- albumins milk: lactalbumin egg white: ovoalbumin, conalbumin wheat: leucosin
- globulins meat: myosin, actin milk: laktoglobulin egg: ovoglobulin
- gliadins (prolamins) wheat: gliadin barley: hordein corn: zein
- glutelins wheat: glutelin rice: oryzenin
- protamins fish: cyprimin, salmin, clupein, scombrin
- histones
   blood: haemoglobin and myoglobin

insoluble

collagen, elastin, keratin

#### according to origin

- native (natural, they have various biological functions)
- denaturated
- modified (additives)

## according to nutritive value

- nutritionally balanced (essential amino acids in optimal amount) egg and milk
- almost nutritionally balanced (shortage of some essential amino acids) muscle proteins of animals
- nutritionally disbalanced (some amino acids in shortage) all vegetables from animals connective tissues,

foods with shortage of some essential amino acids

Lys	cereals (generally plant proteins)
Met	milk, meat
Thr	wheat, rye
Trp	casein, corn, rice

content in foods (book 1, tables 2.9 and 2.10)

protein (P) content generally 0-100% (in dry matter) animal proteins > plant proteins pulses, oilseed plants > fruit, vegetables

eggs	75% H <sub>2</sub> O 13% P (whole) 52% P in dry matter	pulses	12% H <sub>2</sub> O 24% P (soya 32-45 %) 27% in dry matter
meat (beef)	69% H <sub>2</sub> O 21% P 68% in dry matter	bread	38% H <sub>2</sub> O 7% P 11% in dry matter
milk (3.5 % fat)	87-90% H <sub>2</sub> O 3.4% P 28% in dry matter	potatoes	78% H <sub>2</sub> O 2% P 9% in dry matter

#### structure see biochemistry books

#### physiology and nutrition

coverage of total requirement of energy: ~ 10% ratio of nutrients: proteins : lipids : saccharides mass = 1 : 1 : 4 energy = < 14 : < 14 : <56% minimum need of nutritionally balanced proteins: 0.5-0.6 g.kg<sup>-1</sup> advisable need of nutritionally balanced proteins : 1.0-1.2 g.kg<sup>-1</sup> (not digested optimally) ~2.4 g.kg<sup>-1</sup> during growth, reconvalescents etc.

#### nutrition value (biological)

- total intake
- •
- composition of amino acids (book 1, tables 2.12 a 2. 13)
- availability of peptides bound by digestive enzymes
- other factors

#### formerly

- BV (Biological Value, g of P retained by body / 100 g P in food)
- NPU (Net Protein Utilization)
- PER (*Protein Efficiency Ratio*) etc.

depends on:

absolute content of essential amino acids relative relations nonessential amino acids digestibility

#### today

AAS (*Amino Acid Score*) EAAI (*Essential Amino Acid Index*), better results

$$AAS(\%) = \frac{100 A_i}{A_{si}}$$

 $A_i$  = content of essential amino acid in protein

 $A_{si}$  = content of the same amino acids in standard (reference) protein

Standard protein = fictional protein, optimal composition of essential amino acids (AAS=100%)

$$EAAI = \sqrt[n]{\frac{100A_{1}}{A_{S1}} \cdot \frac{100A_{2}}{A_{S2}}} \cdot \frac{100A_{n}}{A_{Sn}}$$

#### physical-chemical properties

- solubility, hydratation, swelling
- dissociation
- optical activity
- gel formation
- emulsion formation
- foam stabilisation
- denaturation

physical factors: temperature, pressure, ultrasound, irradiation chemical factors: salts, pH , surface active compounds

consequences

better access of digestive enzymes

denaturation of antinutritive factors, toxic compounds (inhibitors of proteases, amylases, lectins, decomposition of toxic compounds)

inhibition of undesirable enzymes and microorganisms

#### meat, meat products, poultry, fish

4 main types of tissue (another one is blood)

- epithels
- connective tissue
- muscle tissue
- neural

## definition

parts of warm-blooded animals in natural or processed state

mainly skeletal muscle tissue

components

- free amino acids 0.1–0.3%
- vitamins
- taurine (0.02-0.1%)

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

## CH2-SO3H

• quaternary ammonium compounds choline 0.02-0.06%, phospholipids, transmethylation reactions, acetylcholine, sinapine

carnitine 0,05-0,2%, transport of fatty acids

## COOH CH2 CH-OH CH2-N(CH3)3

• creatine phosphate, creatine, creatinine)

#### COOH CH<sub>2</sub> OH CH<sub>3</sub>N-C-NH-P-OH NH O

- glycogen
- sugar phosphates and free sugars
- lactic acid and other acids
- purines and pyrimidines

## myofibrillar proteins

muscle fibrilles myofibrilles (contractible fibrilles) microfilaments (microfibrilles) myosine actine other proteins

reactions in vivo

reactions post mortem

- ATP by anaerobic glycolysis from glycogen
- lactic acid  $\rightarrow$  decrease of pH from 6.8 to < 5.8

- inhibition of glycolytic enzymes
- $Ca^{2+}$  / reaction of actine with myosine, ATP is missing  $\rightarrow$  (*rigor mortis*)

influence on meat quality

ripening of meat

- splitting of actomyosin by endogenous proteases (mostly cathepsins)
- splitting of collagen (collagenases)

defects of meat

- DFD (*dry-firm-dark*) a DCB (dry-cutting-beef) dark, high water holding capacity, low stability, remotion of lactic acid during blooding, pH~ 6
- PSE (*pale-soft-exudative*) pale, low water holding capacity, grey-green surface, increased glycolysis stimulated by hormones, pH~ 5.6

changing during processing

~35°C association of sarcoplasmatic proteins, decrease of water holding capac	
increase of firmness	
~45°C visible changes, shrinkage =denaturation of myosin	
~50-55°C denaturation of actomyosin	
~55-65°C denaturation of sarcoplasmatic proteins, association, gel structure	
~60-65°C changes of collagen conformation (shrinkage by 1/3-1/4)	
~80°C oxidation SH-groups	
~90°C gelatinisation of collagen (loosening of tropocollagenic fibres, sol, gelat	ine)
~100°C elimination $NH_3$ , $H_2S$ , other compounds, aroma formation, changes in $C$	colour

## milk and milk products

content of nutrients in milk (book 1, table 2.14)

water according to type of milk: 63-88%

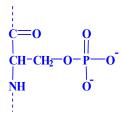
complex disperse system

- globular whey proteins: colloidal disperse
- casein molecules: micellar disperse
- fat: fat globules (microsomes,  $\phi 0.1$ -10 µm): emulsion
- particles of lipoproteins: colloidal suspension
- low molecular weight compounds (lactose, amino acids, minerals, vitamins: solution
- colour

composition of cow milk proteins (book 1, table 2.16) content of amino acids in milk (book 1, table 2.15)

## caseins and whey proteins

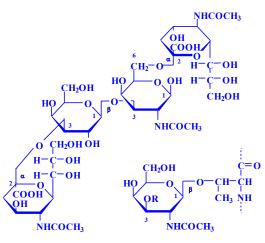
 $\alpha$ -case ins = phosphoproteins,  $\alpha_{S1}$ ,  $\alpha_{S2}$ , phosphose rine



 $\beta$ -case ins = phosphoproteins

 $\gamma$ -case ins =  $\beta$ -case ins degradation products

 $\kappa$ -caseins = glycoproteins (2 genetic variants, B), sugar = tetra-, tri-, di-, mono-, GalNAc, Gal, NeuAc, binding on Thr 133)



main components of k- caseins

 $\alpha_{S}$ -,  $\beta$ -,  $\kappa$ -caseins: aggregation into submicells and micells

### changes during storage and heat processing

- agglomeration of fat globules in fresh milk, ~ makroglobulin
- whey proteins thermolabile, denaturation, caseins thermostable, practically do not denaturate

denatured appr. 50-90% whey proteins
most of enzymes are inhibited
reduction of disufide bonds
$H_2S$ elimination ( $\beta$ -lactoglobulin)
sulfide, disulfide, taste changes (Met)
thiamine degradation
lactones and methylketones formation
100% proteins denatured
reaction of lactose with whey proteins, Lys losses (Maillard
reaction), aroma compounds, fresh and pasteurised milk ~ 400 aroma compounds (1-100 mg/kg)

#### precipitation and proteolysis of caseins

fresh milk:pH 6,5-6,75precipitation of caseins :pH 4,6 (due to microorganisms)

#### hard cheese

- microorganisms (lactic acid), (pH 5,5)
- proteolytic enzyme rennin (chymosin,), specific hydrolysis of  $\kappa$ -casein: *para*- $\kappa$ -casein = hydrophobic part, component of micells,  $\kappa$ -casein makropeptid = hydrophilic part,
- coagulation (storage  $\rightarrow$  firmness, whey centrifugation, addition of NaCl, ripening (at Emmental cheese conversion of lactic acid  $\rightarrow$  propionic acid + CO<sub>2</sub>), proteolysis, lipolysis  $\rightarrow$  hard cheese

soft cheese, youghurt

• precipitation, low pH (fermentation of lactose, lactic acid), partial coagulation of caseins, micells association (gel structure)

other products

- unsoluble acid casein
- sweet casein (precipitated by enzymes)
- caseinates (soluble:Na, K, NH<sub>4</sub>; dispersable: Ca, Mg)
- soluble coprecipitates
- whey

## eggs

white egg protein 53 %, yolk 47 % content of nutrients in eggs (book 1, table 2.17) composition of egg white protein and egg yolk protein (book 1, tables 2.18 and 2.19)

## white egg poroteins

~ 40 proteins (globulins, glycoproteins and phosphoproteins)

- enzymes (lysozyme, activity of *N*-acetylmuramides, murein, cell walls of bacteria)
- protein components of enzymes (flavoprotein/riboflavin, avidin/biotin)
- proteases inhibitors (ovomucoid, ovoinhibitor)

consequences

- viscosity and gel consistence of egg white: ovomucoid a ovomucin
- foam stabilisation of whipped egg white: ovoglobulins G<sub>2</sub> a G<sub>3</sub>
- antimicrobial effects: lysozyme (ovoglobulin G<sub>1</sub>)
- antinutritive effect: avidin

egg yolk proteins (emulsion of fat in weater)

1/3 = proteins, 2/3 = lipidsglyko-, lipo-, glycophospho- a glycophospholipoproteinsgranules: lipovitellin a fosvitinplasma: lipovitellenin a livetin

## changes during storage and processing

- partial denaturation of egg white protein during whipping
- heat denaturation
   57°C: beginning
   60-65°C most of proteins denaturate (ovomucoid does not)
   65-70°C most of yolk proteins denaturate (phosvitin not)

## cereals and pseudocereals

basic cereals chemical composition (book 1, table 2.21) cereals proteins and their composition (book 1, tables 2.22 and 2. 23)

wheat protein

flour proteins: 7-13% (to 15%)

- 15% albumins (soluble in water) leukosin
- 7% globulins (0.4 M-NaCl) edestin

- 33% prolamins (70% ethanol) gliadin
- 46 % glutelins (rest) glutenin

ratio: prolamins / glutelins = 2:3

strong flour = bread flour (12-14%, dough elastic, firm, essential intensive mixing during preparation, hinder  $CO_2$ , air, voluminous products)

week flour = crackers production (< 10 %)

## dough

gluten = viscoelastic matter, 2/3 water, 1/3 hydrated glutelins (viscosity), gliadins (elasticity), dry matter of gluten = 90 % proteins, 8 % lipids, 2 % sugars

products without gluten

alergenic celiac disease (~ 0,05 % children in Europe)

changes of epithelial gut cells, improper resorption of nutrients, responsible: prolamine fraction of wheat, rye, barley, sequences: Pro-Ser-Gln-Gln and Gln-Gln-Pro, limits < 100 mg gliadins/kg (dry matter)

rye proteins

- gluten is not present
- backer's properties: pentosans, some proteins, (swell in acidic medium)
- acid formation due to activity of S. cerevisiae, S. minor, L. plantarum, L. brevis

## legumes and oil seeds proteins

high content of globulins, function during germination content of amino acids (book 1, tab. 2.24)

## utilisation of nontraditional protein sources

texturised plant proteins, protein rich products

## Reactions

elimination, isomeration, addition, oxidation reaction

influence of food composition, reaction conditions: temperature, pH, O<sub>2</sub>, other compounds

#### consequences

- decrease of nutritive value decomposition of essential amino acids formation of unmetabolised products decrease of digestibility formation of antinutritive and toxic compounds
- formation of flavour compounds mostly Cys, Met, Orn, Pro (amines, aldehydes, alcohols, *S*-compounds)

# elimination reactions

decarboxylation (elimination of CO<sub>2</sub>)

$$\begin{array}{c} R - CH - COOH \\ \downarrow \\ NH_2 \end{array} \xrightarrow{\phantom{aaaa}} R - CH_2 - NH_2 \end{array}$$

flavour compounds biologically active compounds (biogenic amines)

$$\begin{array}{c} CH_2-CH_2-NH_2\\ NH_2\\ H \end{array}$$

#### elimination of ammonia and water

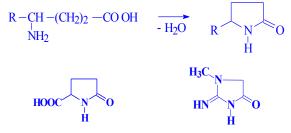
formation of 2,5-dioxopiperazines (cyclic dipeptides)

...

formation of alk-2-enic acids

$$\begin{array}{ccc} R - CH - CH_2 - CO OH & & \\ & & \\ NH_2 \end{array} \qquad R - CH = CH - COOH \end{array}$$

$$\beta$$
-amino acid (Asp) alk-2-enon acids  
formation of γ-lactams z γ-amino acids, γ-amino acid Glu, creatine



2-oxopyrrolidin-2-carboxylic acid

#### creatinine

## elimination of functional groups of side-chains

• reaction in acid medium or by thermal reaction

- deamidation of proteins, hydrolysis
- reaction in neutral medium or by thermal reaction
  - formation of unusual bounds
- reaction in alkaline medium or by thermal reaction
  - o formation of unusual bounds, unusual amino acids, D-amino acids (abiogenic acids)

### consequences

- decrease of digestibility
- decrease of nutritive value
- formation of potentially toxic amino acids
- formation of flavour compounds

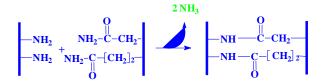
## acid medium

production of protein hydrolysates

- enzymes autolysis, yeast autolysates, soya souce
- acid protein hydrolysates

## neutral medium

formation of cross-binding and unusual amino acids ε-amino groups of Lys, carboxamide group of Asn, Gln



## alkaline medium

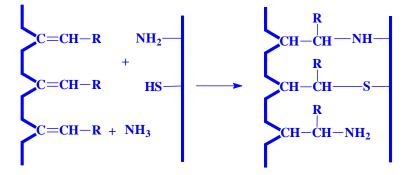
losses of Lys, Cys, Ser, Thr, Arg etc. 1,2-elimination of H-X (from Ser, Thr, Cys, SySSCy) and hydrolysis



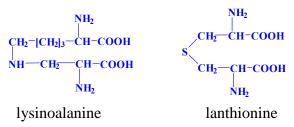
 $Cys, Ser \rightarrow 2 \text{-} aminoacrylic acid (dehydroalanine), Thr \rightarrow 2 \text{-} aminocrotonic acid (dehydrobutyrine)}$ 

$$\begin{array}{c} CH_2 = C - COOH \\ & \downarrow \\ NH_2 \end{array} \qquad \begin{array}{c} CH_3 - CH = C - COOH \\ & \downarrow \\ NH_2 \end{array}$$

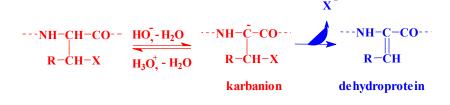
intra- and intermolecular crossbinding



• hydrolysis of cross-linked proteins and formation of unusual amino acids:

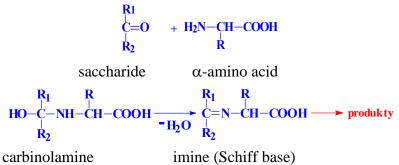


• isomerisation and formation of D-amino acids, decreased utility (book 1, table 2.25)



#### addition reaction

reaction with saccharides (aldehydes, ketones), Maillard reaction



• coloured products, flavour compounds, biologically active compounds

#### oxidation reactions

#### oxidative deamination and transamination

enzymatic reactions

deaminases or transaminases, hydrolases, decarboxylases, alcoholdehydrogenases

R-CH-COOH NH2	0, <b>-</b> H <sub>2</sub> O	R-CH-COOH II NH	H2O, <b>-</b> NH <sub>3</sub>	R – CH – COOH O	- CO <sub>2</sub>	R-CH=O	2 H	R−СН <sub>2</sub> −ОН
$\alpha$ -amino acid		$\alpha$ -imino ac	id	2-oxo acid		aldehyde		alcohol

• aldehydes: fruit and vegetable aroma

• alcohols: aroma of alcoholic drinks (fusel oil alcohols)

Strecker degradation (oxidative decarboxylation)

Formation of Strecker aldehydes (book 1, table 2.27) Nonenzymatic reaction

$$\begin{array}{c} R-CH-COOH \\ \downarrow \\ NH_2 \end{array} \xrightarrow{\text{oxidace}} R-CH=O + CO_2 + NH_3 \end{array}$$

 $\alpha$ -amino acid

aldehyde (Strecker aldehyd)

$$\begin{array}{ccc} R-CH-CH_2-COOH & \xrightarrow{\text{oxidace}} & R-C-CH_3 + CO_2 + NH_3 \\ NH_2 & 1/2O_2 & O \end{array}$$

β-amino acid

methylketone

oxidative agents

- dicarbonyl compounds
- saccharides
- chinones
- inorganic compounds (hypochlorite)

formation of other compounds, N- a S-heterocyclic compounds

### other oxidation reactions and reactions with food compounds

- cysteine, cystine, methionine
- reaction of amino acids with oxidised lipids (decrease digestibility or undigestible products)
- reaction of amino acids with oxidised phenols (dark colour of protein isolates, decrease of digestibility or undigestible products)