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FOOD CHEMISTRY

Basic Textbook

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The content of the textbook corresponds to the curriculum of the discipline "Food Chemistry". The textbook will be useful for students, postgraduates and teachers of higher education institutions.

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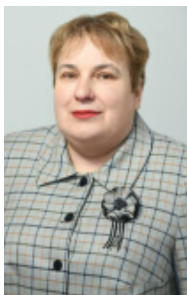
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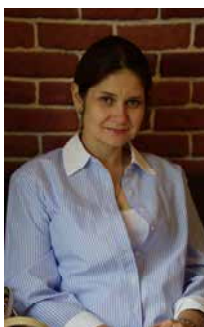
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INTRODUCTION

Food chemistry is the science of the chemical composition of food systems (raw materials, semi-finished products, ready-to-eat food products), its changes during the technological process under the influence of various factors (physical, chemical, biochemical, etc.).

Food chemistry studies the interaction of the structure and properties of food substances and its effect on properties and nutritional value of food products.

The purpose of studying the academic discipline "Food Chemistry" is to provide students with the necessary knowledge about the composition, nature, structure and transformation of inorganic and organic compounds, the composition of food raw materials, products of its processing and chemical transformations that occur during production, storage, and familiarization with modern methods of research.

Studying the course "Food Chemistry" will make it possible to prepare future specialists in the field of food technology, who must have knowledge about the chemical composition of food raw materials, as well as about the chemical and biochemical transformations that occur during the storage and use of food products, to solve the main task - providing the population corresponding products according to the composition, the body's needs in food substances and protective components.

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SECTION 1. WATER, PROTEINS, CARBOHYDRATES: CHARACTERISTICS, COMPOSITION, PROPERTIES AND THEIR CHANGES DURING THE TECHNOLOGICAL PROCESS

Topic 1.1. Water: structure, properties, importance in food systems

1.1.1. Characteristics and chemical structure of water

The water molecule has the chemical formula H_2O . It consists of one oxygen atom and two hydrogen atoms, which are connected by strong covalent bonds. It is these bonds that provide a stable structure of the molecule and determine its chemical properties (Fig. 1.1).

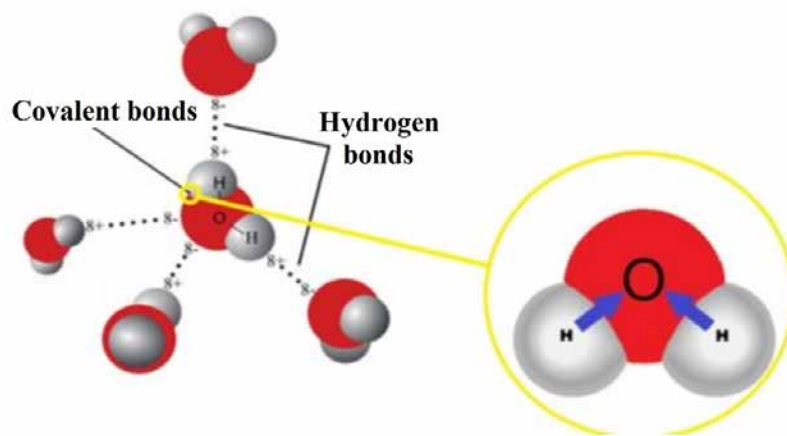


Fig. 1.1. Covalent and hydrogen bonds in water molecules

Oxygen can be considered a center with a bond angle of 105° between two hydrogen atoms in liquid water and a larger angle of 109° between hydrogens in ice (Fig. 1.2).

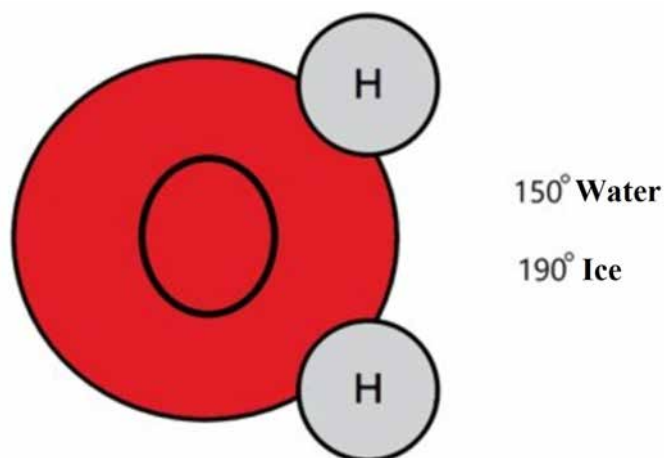


Fig. 1.2. Water and ice contact angle

The bonds between oxygen and each hydrogen atom are polar, having 40 % ionic character. This means that the electrons of the outer shell are unevenly distributed between oxygen and hydrogen atoms, the oxygen atom attracts them more strongly than each hydrogen atom.

As a result, each hydrogen atom is positively charged, and each oxygen atom is negatively charged. Therefore, they are able to form hydrogen bonds.

A hydrogen bond is a weak bond between polar compounds where a hydrogen atom of one molecule is attracted to an electronegative atom of another molecule.

The unique properties of water are due to its ability to form four hydrogen bonds between molecules and one hydrophobic interaction, resulting in strong intermolecular bonds that lead to the formation of associations (Fig. 1.3).

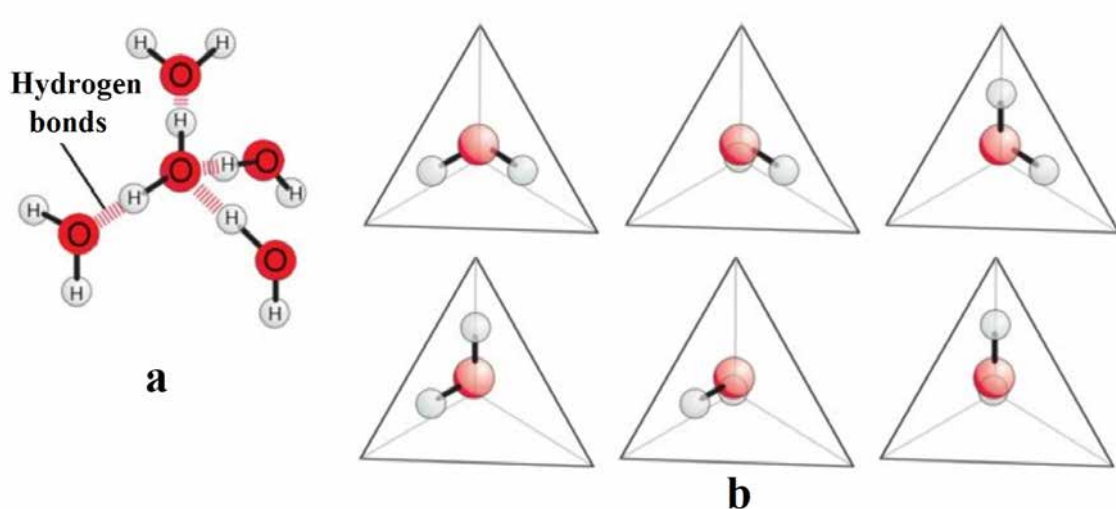


Fig. 1.3. Model of the hydrophobic effect

a: is a model of possible orientations of water molecules in a tetrahedral mesh.

b: is a different location of the water molecule, which allows it to form hydrogen bonds with neighboring water molecules.

Hydrogen bonds are located in the directions of the vertices, which are not occupied by hydrogen atoms in the figure

At the same time, two hydrogen bonds include two hydrogen atoms of a water molecule, and the other two – unpaired oxygen electrons and two hydrogen atoms of neighboring molecules, so they can simultaneously act as an electron donor and acceptor in the process of hydrogen bond formation.

In this case, one of the interacting molecules receives an excess positive charge, acquiring "acidic properties", and the other – a negative charge and "alkaline" properties. As a result, hydrogen-bonded molecules are able to form stronger bonds with other molecules.

A hydrogen bond is weak compared to chemical bonds such as covalent or ionic, but it is important because it has a significant cumulative effect on the properties of the substance in which it is located.

Water can form four hydrogen bonds, whereas oxygen can form two.

Hydrogen bonds between hydrogen and oxygen are common not only between water molecules, but also between many other types of molecules that are important in raw materials and foods, such as sugars, starches, pectins, and proteins.

Each hydrogen atom can form one hydrogen bond, but an oxygen atom can form two, which leads to a three-dimensional network of ice (Fig. 1.4).

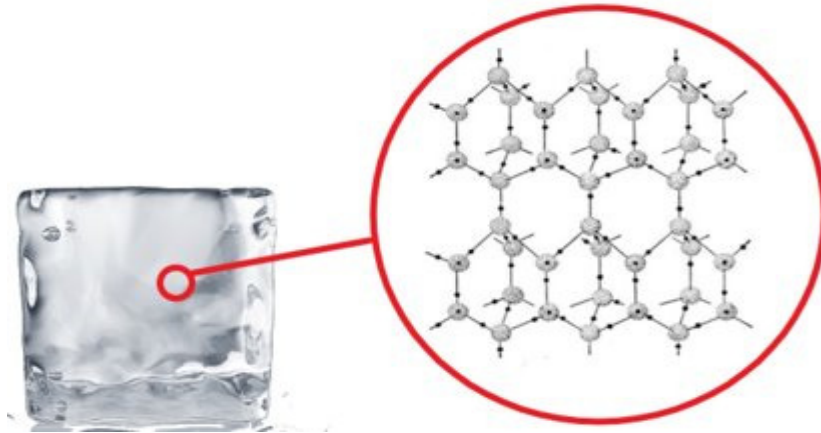


Fig. 1.4. Three-dimensional grid of ice

The structure of ice is dynamic, and hydrogen bonds are constantly being broken, with subsequent transformations between different water molecules.

Liquid water also contains hydrogen bonds and therefore has a variety of ordered structures that are constantly changing as hydrogen bonds break and reform.

In liquid water, about 80 % of the water molecules are involved in hydrogen bonding at 100 °C, while 90 % are involved in liquid water at 0 °C.

Because liquid water has a smaller bond angle than ice, the molecules can be packed more closely together, and so the average number of nearest neighbors is higher for water than for ice.

The average distance between water molecules is also affected by temperature. The distance increases with increasing temperature because molecules have more kinetic energy and can move faster and further at higher temperatures (Fig. 1.5).

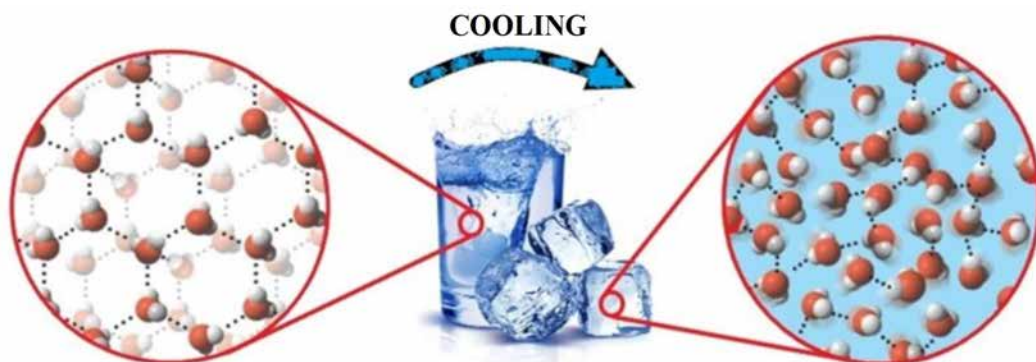


Fig. 1.5. Arrangement of water molecules

This affects the density of water, but the coordination number has a much larger effect. Ice has a less dense structure than water because the molecules are less ordered and cannot be packed together as tightly as water.

As water freezes, its density decreases and its volume increases by about 9 %. This phenomenon should be taken into account when freezing products with a high water content. Containers and equipment must be selected taking into account the increase in the volume of the frozen product. This increase in volume also contributes to damage to the soft fruit structure during freezing.

When water is heated above 4 °C, the average distance between molecules increases and the density decreases slightly. When ice is subjected to a vacuum and then heated, it turns into vapor without passing through the liquid phase. This phenomenon is known as sublimation and is the basis for a food processing method known as freeze drying.

Coffee is an example of a food product that is freeze-dried. The coffee beans are frozen and then vacuumed to remove almost all of the water.

Water is a component of all raw materials and food products. Technological properties, integral quality index and shelf life of food products largely depend on the properties, amount and state (form and bond energy, activity) of water.

Water is contained in almost all food products. Water affects the structure of food products, as can be seen when comparing grapes and raisins (dried grapes), or fresh and wilted lettuce. Water gives a clear texture to fruits and vegetables, and also affects the perception of tenderness of meat. For some food products, such as snacks, salt or sugar, the lack of water is an important aspect of their quality and the water content of these products is important to maintain quality.

Almost all methods of food processing involve the use of water: freezing, drying, emulsifying, bread making, starch thickening and making pectin gels, etc.

Also, since bacteria cannot grow without water, water content has a significant impact on maintaining food quality. This explains why freezing, dehydrating or concentrating foods increases shelf life and inhibits bacterial growth.

Water is important as a solvent or dispersing medium. Acids and alkali ionize in water; water is also necessary for bio- and chemical reactions, reactions with the participation of enzymes, for example, hydrolysis of carbohydrates. Water serves as a heating and cooling medium in food production technologies.

Because water has many functions that are important to you as food technology professionals. When modifying the water content of food, it is necessary to understand these functions in order, as it is possible to predict changes that may occur during technological operations.

1.1.2. Forms of water connection in food products

Water is a unique liquid, the properties of which differ sharply from the properties of all known substances on Earth.

The classification of water bond forms in materials, which takes into account the nature of bond formation and interaction energy, was proposed by P. A. Rebinder.

All forms of communication are divided into three groups:

- chemical;
- physical and chemical,
- physical and mechanical.

According to this classification, the following types of bound water are distinguished:

- chemically bound
- adsorption knitted,
- water of macro- and microcapillaries;
- osmotically bound water,
- freely held by the body frame (immobilization).

This classification was significantly supplemented and expanded by E. D. Kozakov, taking into account the role of water in biological and biochemical processes.

Thus, water in the product can be in a free and bound state.

Free water is close to ordinary (liquid) water in terms of its properties. It is easily removed from the product during drying, wringing, pressing, and freezes at a temperature of about 0 °C.

Free water is available for biochemical, chemical and microbiological reactions.

Properties of bound water:

- it is impossible to remove from the product by mechanical influence;
- the freezing point is greater than (-40) °C;
- does not act as a solvent.

Chemically bound water has a very strong bond and is not removed during drying, it is part of the molecules.

It can be removed only as a result of reactions accompanied by the release of water (melanoid formation, caramelization, etc.).

Chemically bound water is divided into water bound by mono- and polymolecular adsorption. Moisture at the level of monomolecular adsorption (3...6 %) has sublimation drying products – instant coffee, vegetable and fruit powders.

The input bound by monomolecular adsorption is not a solvent and does not participate in chemical reactions, does not freeze at temperatures close to absolute zero. Moisture at the level of polymolecular adsorption (6...14 %) is typical for many dry products (food concentrates, flour, cereals, etc.).

In products with moisture at the level of polymolecular adsorption, microbiological growth is impossible, but enzymatic processes and reactions of melanoid fermentation (darkening, change of smell, etc.) can occur.

The osmotic relationship of water is due to the fact that the vapor pressure above the solution is lower than above the solvent (free water).

Osmotically bound water diffuses as a liquid through the semipermeable membranes of living cells due to the difference in concentration inside and outside the cell.

Osmotically bound water includes swelling water and structural water retained during the formation of gels.

Physically and mechanically bound water includes water of micro- and microcapillaries. Capillary-bound water is retained due to the formation of an

adsorption bond of a monomolecular layer under the walls of the capillary and a decrease in the vapor pressure above the concave meniscus in the capillary compared to the vapor pressure above the flat surface of free water.

When this system is mechanically damaged in products, for example, when cutting meat, fish, vegetables, their cell juice is partially lost.

Capillary and osmotically bound water in fresh fruits and vegetables makes up to 95 %, in the muscles of animals and fish there is 45...55 % of osmotically bound water, 40...45 % – capillary and 6.7...7.5 % – adsorption.

Some food products absorb well from the environment or emit water vapor and volatile substances. This process is called sorption. Special cases: absorption of substances from solutions or gases by the surface of a solid body; absorption of substances from a mixture of gases by a liquid in its entire volume; desorption is the reverse process of the transition of substances from the surface layer to the environment.

1.1.3. Properties of water

Thermal properties of water. Liquid water has the highest heat capacity (4.18 kJ (kg/°K)). The high heat capacity of water makes water an excellent energy carrier. Water transfers heat and softens the effects of heat.

For example, vegetable semi-finished products heated in a pan can burn, but if they are surrounded by water, even distribution of heat is guaranteed.

Water also transfers heat more efficiently, so, for example, potatoes heat up faster in boiling water than, for example, in an oven.

Since water has a higher specific heat than other substances, it neutralizes temperature changes. It takes more energy to raise the temperature of 1 gram of water than 1 gram of fat.

For example, oil heats up twice as fast as water for the same amount of heat.

Thus, most methods are based on the use of water for heat transfer:

- boiling;
- stewing;
- steam cooking.

Dry heating methods use heat in the form of radiation and include:

- baking;
- frying

Dry and moist heat methods are used in the microwave oven. Microwaves are a form of radiation that heats the water molecules in food and then heats the food itself.

Heat treatment of products in the flow of electromagnetic radiation of the infrared spectrum is based on the fact that free water contained in semi-finished products intensively absorbs IR radiation with a wavelength of 0.75...2.5 μm , heating the surface layer of the product.

Cooking the product with moist saturated steam is based on the condensation of steam on the surface of the product and the transfer of latent heat of vaporization to the product.

The duration of cooking products with steam at atmospheric pressure is approximately 50 % longer compared to cooking in water.

Boiling and freezing point. Water may not be brought to a boil, but individual water molecules gain enough energy to escape from the liquid as vapor. If the liquid is in a closed container, in equilibrium, some molecules always evaporate, and vapor molecules condense, so there are no general changes in the system.

The vapor (gaseous molecules) released from the liquid state exerts a pressure on the surface of the liquid, known as vapor pressure.

In the case of high vapor pressure, the liquid evaporates easily and most of the molecules exist in the vapor state, while the boiling point is low.

Also, at low vapor pressure, the liquid does not evaporate intensively, while there are few molecules in the vapor state.

The boiling point for this liquid is higher. Water boils when the vapor pressure reaches the external pressure.

Vapor pressure increases with temperature. At higher temperatures, the molecules have more energy and it is easier for them to overcome the forces that keep them in the liquid and evaporate.

The vapor pressure decreases with the addition of soluble substances such as salt or sugars. In fact, the solutes dilute the water, so there are fewer water molecules available for evaporation.

Gravity of dissolved substances also limits evaporation. A decrease in vapor pressure (the pressure of a gas above a liquid) increases the boiling point.

This is due to the fact that the vapor pressure decreases at a certain temperature. The external pressure does not change with the content of salt or sugar in the water, since it is more difficult for the molecules to evaporate.

Therefore, the temperature at which the vapor pressure is the same as the external pressure (boiling point) will be higher.

One mol of sucrose raises the boiling point by 0.52 °C and 1 mol of salt raises the boiling point to 104 °C. Salt has twice the effect on water as sucrose because it is ionized, and for every mole of salt there are 1 mole of sodium ions and 1 mole of chloride ions.

Similarly, salts and sugars lower the freezing point of water. For example, the external pressure increases when heating in a pressure cooker or retort packages, the boiling temperature increases.

Water as a solvent. Water can act as a solvent and structure macromolecules through internal bonding and hydrophilic and hydrophobic interactions.

Consumers perceive the taste of finished products, which depends on the type of dissolved substances such as sugar, salts, acids and other aromatic compounds, and, as a result, on their increased ability to affect taste receptors.

Soft water has a higher solubility than hard water.

This is due to the fact that hard water has already dissolved a certain amount of substances and, therefore, will dissolve less food substances and flavorings.

Water may exhibit temporary hardness due to iron content or calcium and magnesium bicarbonate ions. Water can be softened by boiling (soluble bicarbonates precipitate on boiling and leave scale) and insoluble carbonates can be removed from the water.

Hard water cannot be softened by prolonged boiling because it also contains calcium or magnesium sulfates (CaSO_4 or MgSO_4) and other salts that do not settle.

For example, the organoleptic quality indicators of such drinks as tea and coffee, legumes, cereals, and meat deteriorate due to the use of hard water for their preparation.

For example, the duration of cooking vegetables in hard water is longer compared to the duration of cooking in soft water (Tab. 1.1).

Table 1.1. Duration of cooking certain vegetables in hard and soft water

Characteristics of water	Duration of cooking, min.	
	carrot	beet
Water: soft	40	90
hard	46	95

Losses of vitamins (B_1 B_2 , PP) when soaking legumes in soft water are greater than in hard water.

The duration of cooking vegetables also depends on the pH values of the water (Tab. 1.2).

Table 1.2. Duration of cooking vegetables at different pH values of water (environment)

Beet		Carrot		Cabbage	
pH water	Duration of cooking, min	pH water	Duration of cooking, min	pH water	Duration of cooking, min
5.70	23	6.0	15	6.1	18
4.15	60	3.7	37	3.8	40
3.60	25	2.1	17	2.2	20

Water as a solvent participates in the mechanism of formation of meat broths. A certain role in the formation of broth belongs to the diffusion of water-soluble substances from meat into water during cooking of meat.

There is a violation of the connection between water and protein as a result of the denaturation of muscle proteins, the compaction of the formed protein jellies at an increase in the cooking temperature leads to the fact that the water released into the intercellular space is partially bound in the process of collagen welding, and a significant part of it is released into the external environment.

The amount of water released increases as the temperature inside the product increases.

The transition of soluble substances from meat to broth as a result of diffusion can be enhanced by increasing the hydromodulus (ratio of water and meat)

In the process of defrosting fish in water, the following mass exchange processes take place: the weight of the fish increases by 5...10 % as a result of water absorption, and about 0.25 % of organic and 0.1 % of mineral substances pass from the fish to the water due to diffusion.

To inhibit the diffusion process when defrosting fish, it is recommended to add table salt to the water in the amount of 0.8 %.

Water also forms solutions with minerals and water-soluble vitamins. This increases the probability that minerals and vitamins can get from the raw materials into the water, causing the loss of nutrients in the manufactured products.

For example, about 10% of soluble substances and vitamin C pass from sliced potatoes into water, so it is not recommended to store peeled and even more so sliced potatoes in water for a long time.

In addition, a significant part of soluble substances contained in cells, as well as soluble products of the destruction of starch, protopectin, hemicellulose, passes from vegetables and fruits into water during cooking.

Also, in the process of washing cereals, proteins, starch, sugars and other food substances are partially transferred to the water. When soaking legumes for 10 hours, 12% of nitrogen is extracted.

Water can be a solvent for caffeine and other aromatic compounds from tea leaves and coffee beans. As the temperature increases, the amount of solute that dissolves in water increases, which explains why hot water is used for making coffee and tea – the temperature is from 80 °C.

Water dissolves small molecules such as salts, sugars, or water-soluble vitamins to form unsaturated, saturated, and supersaturated solutions. Combining a solvent and water results in true, colloidal solutions, suspensions, or emulsions.

These mixtures differ from each other in the size or solubility of dissolved substances. In true solutions, the solute molecules are so small that they dissolve completely and do not precipitate. They cannot be separated by filtering.

An ionic solution is formed by dissolving substances that ionize in water, such as salts, acids, or bases.

Taking sodium chloride as an example, the solid contains sodium (Na^+) and chloride (Cl^-) ions held together by ionic bonds (Fig. 1.6).

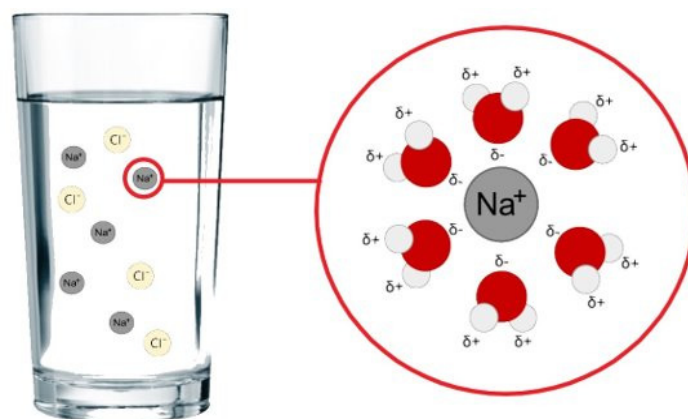


Fig. 1.6. Interaction of the Na^+ ion with water molecules

Once in water, water molecules reduce the forces of attraction between oppositely charged ions, ionic bonds are broken, and individual ions become surrounded by water molecules or hydrated.

Each ion is usually surrounded by six water molecules; ions move independently of each other.

Polar molecules such as sugars that are hydrogen bonded dissolve to form molecular solutions. When the sugar crystal dissolves, the hydrogen bonds interact and the hydrogen bonds between the polar hydroxyl groups on the sugar molecules are broken and replaced by hydrogen bonds between water and sugar molecules.

Thus, the sugar crystal gradually hydrates; each sugar molecule is surrounded by water molecules. Water molecules are hydrogen bonded to polar groups on sugar molecules. Sugar molecules are released from the sugar crystal and hydrate, so water molecules surround them and bond with them through hydrogen bonds. When hydrogen bonding occurs, solubility increases with increasing temperature.

Therefore, sucrose dissolves faster in hot water than in cold water. Dissolved substances increase the boiling point of water and a sharp increase in the solubility of sucrose at temperatures above 100 °C (the boiling point of pure water), allows you to determine the concentration of sucrose by measuring the boiling point of the sucrose solution. This feature is used in confectionery technologies.

An increase in temperature allows more of the solute to dissolve in the water, forming a saturated solution.

Increasing the temperature even higher leads to obtaining a supersaturated solution, which is unstable and its cooling must occur gradually to avoid precipitation or crystallization of the dissolved substance. Confectionery technologies, in particular lipsticks, are based on the creation of supersaturated solutions.

Colloidal solutions. Molecules that are too large to form true solutions can disperse in water. Those with a particle size of 1...100 nm are dispersed, forming colloids or sols.

Examples can be molecules of cellulose, starch, pectin substances, proteins. Colloidal solutions are usually unstable.

They are particularly unstable to factors such as heating, freezing or pH changes.

A change in conditions in a stable dispersion may cause precipitation or gelation. However, these processes are desirable in some cases, for example, in the production of pectin jellies.

Examples of different types of these dispersed systems include solids in a liquid or liquid in another liquid (salad dressing) or solid (jam, jelly, cheese, butter) and gas that can be incorporated into a liquid (egg foam protein, marshmallow or whipped products).

Suspensions. Particles of substances larger than 100 nm are too large to form colloidal solutions. They form a suspension when mixed with water. Particles in suspension separate over a period of time compared to colloidal solutions.

Mixing starch and water results in a suspension in which starch grains are distributed in the liquid.

Emulsion. Water and fat phase (oil, margarine, butter, etc.) do not dissolve in each other, but they can disperse in each other, forming an emulsion (Fig. 1.7 and 1.8).

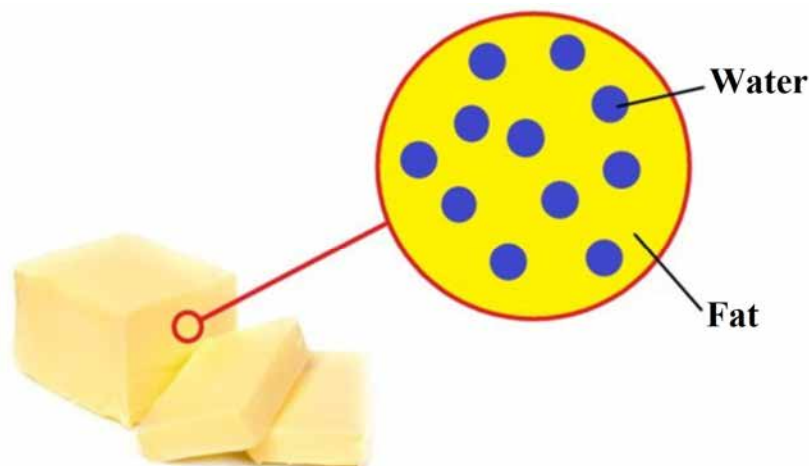


Fig. 1.7. Schematic representation of the distribution of the aqueous phase in butter

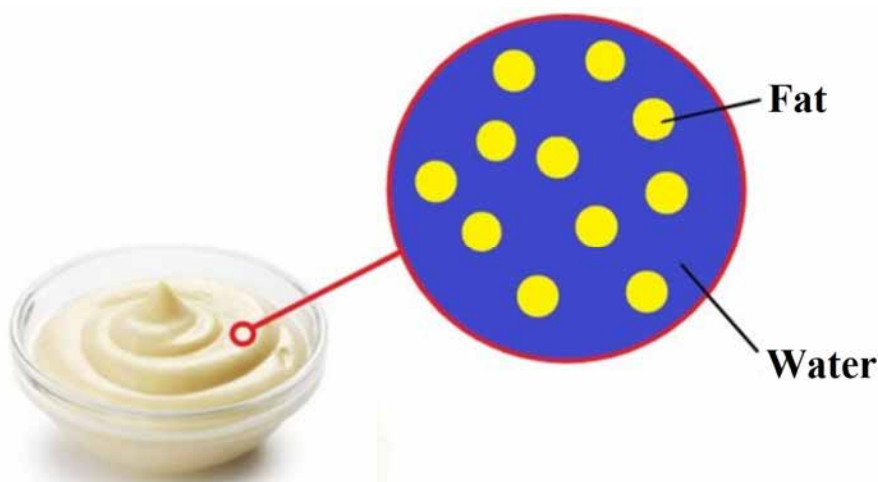


Fig. 1.8. Schematic representation of the distribution of the aqueous phase in mayonnaise

Examples of food emulsions can be mayonnaise, sauces and salad dressings.

Emulsions can be separated by freezing, high temperatures. Hydrophobic and hydrophilic interactions lead to the formation of structures in which the properties of water differ from bulk water. Thus, part of the water can be so strongly associated with food ingredients that it is not able to form ice crystals during freezing. It is impossible to freeze water with egg white in the amount of 0.55 g/g, with corn starch in the amount of 0.35 g/g and with cellulose in the amount of 0.16 g/g. This is due to the interaction of water with proteins, which affects crystallization of ice.

Since water is a very good solvent, however, the properties of the solvent depend on the solute and the molecular interaction between them, for example, the mixing energy of hydrated wheat flour increases with a water content of more than 28%.

This is due to the interaction between water and protein molecules. When the water content is above 28%, the protein chains become mobile, the appropriate structure of the dough is formed and the energy of mixing increases.

Starch and gluten, the two main components of wheat flour, interact with water to different degrees. In starch with a water content of 2 %, nuclear magnetic resonance does not show the presence of water protons.

In gluten, this effect occurs at a water content of 7.5 % water. Protein mobility begins at a water content of 0.1...0.2 g/g.

The influence of water on the rheological properties of food products. Water affects the rheological properties of food products both in liquid and solid state. Water is a Newtonian liquid and its viscosity depends on temperature.

Increased temperature reduces the number of hydrogen bonds and increases the vibration of molecules. This leads to a decrease in the influence of small molecules and ions on the viscosity of water. An increased concentration of solute increases the viscosity of the solution.

Water affects the mechanical properties of plant tissues. Hydrating hydrophilic compounds, it plasticizes the structure of the walls and middle plates. This property ensures a fairly high turgor pressure in tissues. Turgor is a state of tension resulting from the pressure of the contents of cells on their elastic membranes and the pressure of the membranes on the contents of cells.

1.4. The concept of water activity

To assess the degree of water participation in various chemical, biochemical and microbiological reactions, the water activity indicator (a_w) is widely used, which is defined as the ratio of the partial pressure of water vapor above the product to the partial pressure of vapor above pure water.

A schematic representation of the determination of water activity is shown in Fig. 1.9.

The indicator "water activity" was proposed by W. Scott in 1953 and is currently widely used in practice.

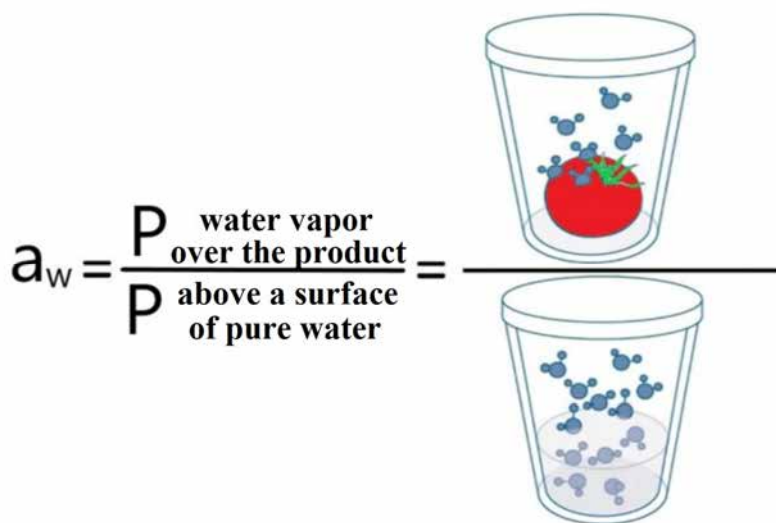


Fig. 1.9. Schematic representation of determination of water activity

The "water activity" indicator determines the microbiological situation, the nature and direction of mass exchange, the intensity of biological, physicochemical and chemical processes occurring in food products, and thereby characterizes their quality, stability and safety.

Given the importance and high informativeness of the a_w indicator, it is included in the ISO 9000 system of standards, and is also used in risk analysis for critical control points.

In the countries of the European Union, its definition, along with the "moisture" (W) and "hydrogen ion concentration" (pH) indicators, is mandatory during the examination of a number of products, and in the United States, the definition of a_w is included in the instructions for quality control of food products and medicinal products.

In domestic scientific practice, the term "equilibrium humidity" is often used, however, the relative humidity of the environment is taken as the water activity of the product.

Since the gradient of the water activity values of the product and the relative humidity of the environment serves as the driving force of mass exchange during various thermal and hydrothermal processes, as well as during storage, data on the activity of water in the technological process of obtaining products are necessary to substantiate the optimal modes of this process.

Another definition of thermodynamic activity was proposed by H. Lewis and M. Randall: "activity is the ratio at a given temperature of fugacity f of a substance in a specific state to its fugacity f_0 in a normal state, which for convenience is taken as standard", while fugacity is considered as the ability of a substance to volatility and is characteristic of materials whose vapor pressure to one degree or another deviates from the ideal. Provided that this ideality is not too great, the fugacity can be replaced by the measured value of the vapor pressure. This is the case with water, because at normal temperatures, water vapor approaches an ideal gas. The fugacity of the solvent (water) is taken as the standard state of aqueous solutions.

In the ideal case, Raoult's law applies to solutions:

$$a_w = n_1 / (n_1 + n_2) = p_1 / p_0 = p_{p.B.B.} / 100, \quad (1.1)$$

where n_1 i n_2 – the number of moles of solute and solvent in an ideal solution;

p_1 i p_0 – partial vapor pressure above the solution and solvent (water);

$p_{p.B.B.}$ – equilibrium relative humidity, %.

According to Raoult's law, the activity of water must be equal to the molar fraction of water in the solution. However, in practice, significant deviations from the ideal case are observed.

According to M. Karel, these deviations are caused by several reasons:

- not all water in the product is a solvent (for example, water in a monomolecular layer);

- not all dissolved substances are in the real solution (part of it may be associated with other components, for example, proteins may be associated with salts or sugars);

– interactions between molecules of a dissolved substance can cause deviations from the ideal situation.

Energy of connection of water with material (kJ / mol):

$$E = -RT \ln a_w, \quad (1.2)$$

R – universal gas constant, equal to 8.3144 kJ / (kmol·K);

T – temperature, K

It is assumed that the activity of free water is equal to one, and that of absolutely dry matter is zero (chemically bound water is not taken into account).

The movement of water in colloidal capillary-porous materials is caused by the presence of a transfer potential gradient, which is the difference between the activity values of water and the product.

The magnitude of the potential is directly related to the binding energy of water in the product.

Thus, adsorption bound water moves in the product in the form of steam and the transfer potential is the partial pressure of the steam.

Water in micro- and macrocapillaries moves in the form of liquid (molecular transport) or steam.

In the first case, the transfer potential is the capillary potential, in the second - the partial pressure of water vapor.

Osmotically bound water moves as a liquid (diffusive transfer), and the potential is the osmotic pressure, which is related to the activity of the solution water.

Various methods are used to determine the water activity of food products: manometric (direct measurement of water vapor pressure in a vacuum), hygrometric, tensometric, etc.

The graph of the dependence of humidity on water activity at a given temperature is called a sorption isotherm.

For most food products, isotherms have the so-called S-shaped character (Fig. 1.10).

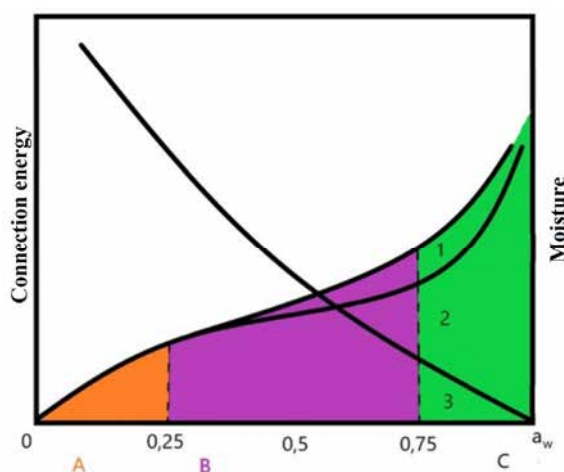


Fig. 1.10. Hypothetical curve of the isotherm of water vapor sorption by the product:
1 – desorption; 2 – adsorption; 3 – bond energy

In Fig. 1.10 **zone A** characterizes the area in which water is strongly bound by monomolecular adsorption, it is characteristic of products with low moisture content, such as freeze-dried products.

Zone B characterizes the area where water is less tightly bound (polymolecular adsorption) and enzymatic reactions can already occur, albeit very slowly.

Zone C is an area of weakly bound water, in which microbiological and other types of product spoilage reactions can occur, the intensity of which depends on the level of water activity.

Using the isotherm, it is possible to predict the behavior of the material or product when the relative humidity of the environment changes, the intensity of various chemical and biochemical reactions, the structural and structural-mechanical properties of the product itself, etc.

In Fig. 1.11 shows graphs of the dependence of the intensity of the vital activity of microorganisms, the rate of oxidation reactions, non-enzymatic darkening, enzymatic processes, structural and structural-mechanical properties of the product itself on the level of water activity.

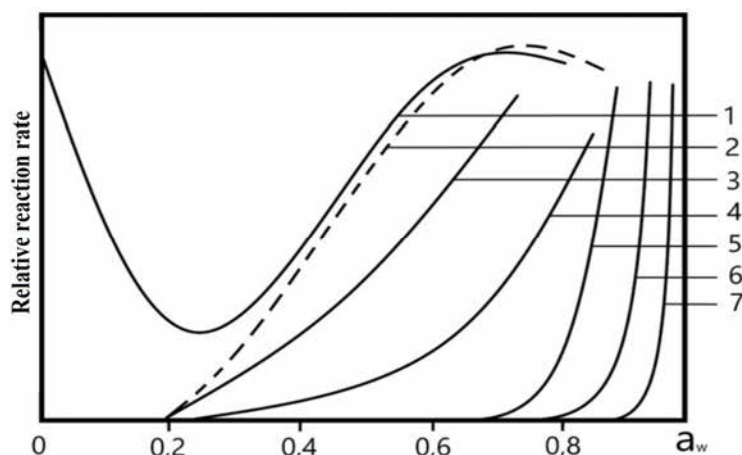


Fig. 1.11. The influence of water activity on the intensity of processes that cause spoilage of products (according to T. Labuza): 1 – lipid oxidation; 2 – non-enzymatic darkening; 3 – hydrolytic reactions; 4 – enzymatic activity; 5 – mold development; 6 – development of yeast; 7- development of bacteria.

There are generally accepted marginal areas of the value of water activity, which characterize the intensity of certain reactions of spoilage of food products.

Thus, the process of lipid oxidation accelerates at low values of water activity (up to 0.2), at 0.3 it reaches a minimum, at a_w values greater than 0.5 it gradually accelerates.

The maximum development of non-enzymatic darkening reactions occurs in the interval 0.5...0.7, and enzymatic processes begin to develop and accelerate at water activity values of more than 0.7.

For freeze-dried food products, the water content is considered optimal at the level of a monomolecular layer, since the water in it is so tightly bound that it cannot move, it is not a solvent and is not capable of reactions.

Removal of monomolecular adsorption water during drying in some cases accelerates spoilage reactions, such as lipid oxidation. This is due to a change in the activity of the catalysts of this reaction, which is lower in water than in fat.

One of the reasons is considered to be the removal of the hydrate shell from metals that catalyze the oxidation process.

An increase in the moisture content of freeze-dried products above the monomolecular layer leads to the formation of polymolecular layers, whose water is already capable of participating in chemical reactions involving non-enzymatic browning.

Of particular interest are the data on the vital activity of microorganisms at different levels of a_w (Tab. 1.3).

For a significant number of bacteria, mold, and yeast, a_w values have been established below which they do not develop.

In a generalized form, they can be presented in the following form: the development of bacteria stops at a_w below 0.9, mold – at a_w below 0.7, yeast – at a_w below 0.6.

Water activity plays an important role in the survival of microorganisms during sterilization and pasteurization of food products.

A decrease in the water activity of the product leads to an increase in the resistance of microorganisms to thermal effects, which must be taken into account when developing sterilization modes.

A study of the influence of different levels of water activity and disinfectant concentration on the destruction of *E. coli* showed that water activity significantly affects the disinfection efficiency: when a_w is reduced from 0.995 to 0.874, a tenfold increase in the concentration of the drug is necessary to ensure the same efficiency.

An increase in the activity of water in products by 0.01 leads to a 2-fold reduction in their storage time, which is associated with an increase in the speed of microbiological processes.

In recent years, technologies for food products with a reduced content of table salt and sugar have been developed, with the use of non-traditional types of raw materials and various food additives, which leads to a change in the water activity of the product.

In practice, changing the composition of food products, for example, reducing the proportion of sugar, leads to a reduction in shelf life and the need to introduce preservatives.

Thus, reducing the share of sugar in the recipe of dough products by 20 % leads to an increase in water activity and, as a result, a reduction in the shelf life from nine to three days.

The indicator "water activity" is of great importance in the development of technologies for so-called food products with intermediate moisture, the a_w of which is 0.6...0.8, at a humidity of up to 40%, and in which reactions that cause spoilage of the product do not occur for a long time.

In connection with the need to develop a new generation of products with intermediate moisture, interest arose in studying the activity of water solutions and sorption isotherms of various food substances, so-called "moisturizers".

Table 1.3. Minimum water activity values necessary for the development of microorganisms (according to J. Troller)

Microorganisms	Water activity, a_w	Microorganisms	Water activity, a_w
Mildew		Yeast	
<i>Monascus (Xeromyces) bisporus</i>	0.61	<i>Saccharomyces rouxii</i>	0.62
<i>Eurotium echinulatum</i>	0.62	<i>Saccharomyces builii</i>	0.80
<i>Chrysosporium fostidium</i>	0.69	<i>Debaryomyces hansenii</i>	0.83
<i>Aspergillus conicus</i>	0.70	<i>Saccharomyces cerevisiae</i>	0.90
<i>Eremascus albus</i>	0.70	Bacteria	
<i>Eurotium (Aspergillus) amstelodami</i>	0.70	<i>Halobacterium halobium</i>	0.75
<i>Eurotium rubrum</i>	0.70	<i>Micrococcus halodenitrificans</i>	0.86
<i>Chrysosporium xerophilum</i>	0.71	<i>Slaphylococcus aureus</i>	0.86
<i>Eurotium chevalieri</i>	0.71	<i>Vibrio costicolus</i>	0.86
<i>Eurotium repens</i>	0.71	<i>Bacillus subliu</i>	0.90
<i>Eurotium carnoyi</i>	0.74	<i>Bacillus stearothermophilus</i>	0.93
<i>Eurotium herbariorum</i>	0.74	<i>Micrococcus lysodeikticus</i>	0.93
<i>Aspergillus candidus</i>	0.75	<i>Clostridium botulinum type B</i>	0.94
<i>Aspergillus restrictus</i>	0.75	<i>Microbacterium spp.</i>	0.94
<i>Wallemia sebi (Sporendonema epizoum)</i>	0.75	<i>Vibrio parahaemolyticus</i>	0.94
<i>Aspergillus niger</i>	0.77	<i>Aerobacter aerogenes</i>	0.94
<i>Aspergillus ochraceous</i>	0.77	<i>Bacillus cereus</i>	0.95
<i>Eremascus fertilis</i>	0.78	<i>Bacillus megaterium</i>	0.95
<i>Aspergillus flavus</i>	0.78	<i>Clostridium botulinum type A</i>	0.95
<i>Aspergillus sydowii</i>	0.78	<i>Clostridium perfringens</i>	0.95
<i>Aspergillus tamarii</i>	0.78	<i>Escherichia coli</i>	0.95
<i>Aspergillus terreus</i>	0.78	<i>Lactobacillus viridescens</i>	0.95
<i>Aspergillus versicolor</i>	0.78	<i>Salmonella spp.</i>	0.95
<i>Emericella (Aspergillus) nidulans</i>	0.79	<i>Clostridium botulinum type E</i>	0.97
<i>Penicillium chrysogenum</i>	0.79	<i>Pseudomonas fluorescens</i>	0.97
<i>Penicillium martensii</i>	0.80		
<i>Penicillium citrinum</i>	0.80		
<i>Penicillium fellutanum</i>	0.80		
<i>Penicillium spinulosum</i>	0.81		
<i>Penicillium brevicompactum</i>	0.81		
<i>Penicillium cyclopium</i>	0.81		
<i>Penicillium frequentans</i>	0.81		
<i>Penicillium patulum</i>	0.81		
<i>Penicillium puberulum</i>	0.81		
<i>Penicillium viridicatum</i>	0.82		
<i>Aspergillus fumigatus</i>	0.83		
<i>Penicillium expansum</i>	0.83		
<i>Penicillium islandicum</i>	0.83		
<i>Penicillium palitans</i>	0.84		
<i>Alternaria citri</i>	0.84		
<i>Aspergillus wentii</i>	0.84		
<i>Paecilomyces variotii</i>	0.93		
<i>Batrytis cinerea</i>	0.93		
<i>Mucor plumbeus</i>	0.93		
<i>Rhizopus nigricans</i>	0.94		
<i>Stuchybotrys atra</i>	0.96		
<i>Rhizoctonia solani</i>			

You can change the a_w of the product in different ways:

- adding soluble salts, sugars and other components;
- dehydration;
- increase in osmotic pressure;
- by turning part of the water into ice during freezing, etc.

Sugar and table salt are traditionally used as substances that reduce the activity of water in food production technologies.

In a saturated solution of sugar at 20 °C, the activity of water is 0.864, and that of table salt is 0.753.

In recent years, the range of moisture-binding food additives has been constantly expanding and is presented in:

- salts;
- polysaccharides;
- amino acids;
- proteins;
- polyhydric alcohols, etc.

When studying the relative effectiveness of several moisturizers capable of reducing the activity of water in a concentration of 5...10%, the following order of effectiveness of the agents was established: sodium chloride and salts of organic acids, amino acids and protein hydrolyzate, glycerin, sorbitol, sucrose and molasses, polysaccharides, egg albumin.

However, it is necessary to pay attention not only to the sorption characteristics of the product, but also to the aggregate state of its components.

Most components of food products (low molecular weight carbohydrates and salts, proteins, polysaccharides) can be in one of several phase states: solid crystalline, solid amorphous (vitreous) and in the form of a solution.

An unwanted increase in humidity and water activity can occur when dry products are stored in unfavorable conditions as a result of absorption of water vapor from the surrounding air.

The rate of absorption of water from the environment is proportional to the square of the amount of water that must be absorbed before reaching equilibrium.

Water activity also affects the organoleptic indicators of product quality. For example, for snacks there is a certain range of water activity values (0.35...0.50), in which there is a decrease in fragility, crumbliness and, as a result, a deterioration in taste properties.

Water activity of food products.

The activity of water in certain food products and raw materials is shown in the Tab. 1.4.

In raw cleaned vegetables, the water activity is high, but carrots and beets have lower a_w values, which is caused by the content of a fairly large amount of sugars in these root crops compared to other vegetables (Tab. 1.5).

Table 1.4. Water activity in certain food products and raw materials

Product	Humidity, %	a_w
fruits	90-95	0.97
bread	35-50	0.95
cake	20-28	0.83
jam	30-35	0.82-0.94
honey	10-15	0.75
meat	65-75	0.69-0.99
boiled sausages	62-72	0.96-0.98
boiled and smoked sausages	40-43	0.90-0.93
eggs	70-80	0.97
flour	12-15	0.80
cookies	6-9	0.60
chocolate	5-7	0.40
sugar	0-0.015	0.10
caramel	7-8	0.65
semi-smoked sausages	40-55	0.94-0.97
raw smoked sausages	24-30	0.78-0.85

Table 1.5. Water activity of semi-finished products from vegetables and potatoes

Semi-finished product	Humidity, %	a_w
Peeled raw potatoes	81.4	0.993
Peeled raw carrots	87.1	0.987
Peeled raw beet	86.3	0.985
Raw, peeled onions	86.7	0.992
Boiled potatoes	82.6	0.987
Cooked carrots	81.3	0.985
Steamed carrots	78.7	0.982
Boiled beets	80.2	0.983
Steamed beets	76.8	0.982
Sautéed carrots	44.8	0.933
Sauteed onions	39.2	0.901
<i>fried potatoes:</i> predominantly bars	73.2	0.963
<i>deep fried:</i> bars	46.7	0.895
stripes	21.5	0.796
crispy	4.5	0.327

The effect of heat treatment on the water activity of the product on the example of semi-finished products and vegetable products shows that cooking vegetables in water practically does not affect their water activity, while cooking with hot steam leads to a more noticeable decrease in a_w , which is associated with a greater loss of water as a result of evaporation.

When vegetables are sautéed, the activity of water is noticeably reduced due to significant dehydration of the product.

The effect of the frying process on the water activity of potato products shows that the degree of reduction in water activity is proportional to the dehydration of the product.

Boiling and frying meat semi-finished products do not have a significant effect on the change in the water activity values of the finished product, despite rather large mass losses (mainly due to the water contained in the product).

For example, the water activity of semi-finished "entrecote" is 0.991, and after frying – 0.982, which indicates the presence of a certain amount of loosely bound water with high fugacity in the finished product.

The water activity of semi-finished products and meatball products is lower than that of natural products, which is explained by the grinding of the product, the partial yield of soluble proteins, the addition of salt, bread. Thus, the water activity of the semi-finished product "homemade meatballs" is 0.984, and that of fried products is 0.977.

The water activity of natural chopped products also does not change significantly in the process of heat treatment - the water activity of the semi-finished "beefsteak natural cut" is 0.989, the finished product is 0.981.

In soups – borschts, mashed soups, etc. the activity of water is high and can be compared with the activity of salt solutions of low concentration.

Sauces are characterized by high values of water activity, which indicates the presence of a significant amount of loosely bound and free water in this group of products.

Thus, it is not always possible to judge the stability of a product by its moisture content.

Semi-finished products from biscuit and custard dough have fairly high values of water activity, which are determined by the humidity and amount of sugar provided in the recipe.

Shortbread and puff pastry have water activity at a level typical of products with intermediate moisture.

The water activity of baked semi-finished products is much lower than in dough and is at the level of products with intermediate moisture.

The decrease in water activity of baked semi-finished products is mainly explained by the loss of water during baking, as well as structural changes in proteins and starch.

The amount of sugar in the product plays an important role in reducing water activity. Thus, the water activity of the biscuit semi-finished product is 0.803, and that of the custard - 0.950 at a humidity of 22.8 and 23.7 %, respectively.

It should be noted that the main importance is not only the quantitative content of sugars, but also their qualitative composition. For example, apple jam with a moisture content of 32.59 % has a lower value of water activity ($a_w=0.825$) than cream with a moisture content of 15.2 % ($a_w = 0.851$).

The presence of reducing sugars in the fondant mass leads to a significant decrease in the level of water activity ($a_w = 0.837$).

The vast majority of bacteria do not develop at a water activity below 0.95, the exception being *Staphylococcus aureus* and *Micrococcus*, which have a minimum $a_w = 0.86$, therefore decorative semi-finished products and especially creams represent a potential danger due to the possible development of these microorganisms.

There is a classification of products according to water activity levels (Tab. 1.6).

Table 1.6. Classification of some food products according to the level of water activity

Approximate value of water activity and humidity limits (%)	Product name	Most likely causes of product spoilage during storage
Very high: $a_w > 0.95$, $W = 60...95$	Vegetables, meat, fish. Soups, sauces, side dishes from boiled and fried vegetables. Meat and fish products	Development of bacteria, mold and yeast, enzymatic processes.
High: $a_w = 0.90...0.95$, $W = 40...60$	Semi-hard cheeses, ham; products with 55 % sucrose or 12 % NaCl (wt.)	Development of mold and yeast
Average: $a_w = 0.50...0.90$, $W = 15...40$	Fermented sausages (salami), biscuits; hard cheeses; margarine; products containing 65% sucrose or 15% (w/w) NaCl. Most fruit juice concentrates; condensed milk with sugar; flour; rice; legumes with a moisture content of 15-17 %; fruit pies; Jam fondants; marmalade; glazed fruit marzipan. Oat flakes; raisins; nuts, molasses; jelly; soft prune. Dried fruits, caramels, honey (<20 % water) toffee. Pasta spices (12 % water), Egg powder (5 % water)	Reactions of melanoid formation, development of yeast and osmophilic mold, enzymatic processes
Low: $a_w = 0.20...0.50$, $W = 5...0.5$	Dried vegetables, milk powder, crackers, chips, puff pastry and shortbread products, food concentrates, cereals, flour, freeze-dried products	Reactions of lipid oxidation and non-enzymatic browning

The classification is based on experimentally obtained water activity data of various product groups and generally accepted limits of water activity values, which determine the intensity of the development of undesirable chemical, biochemical and microbiological reactions.

Questions for discussion and self-examination

1. *The distance between water molecules when it is heated and frozen.*
2. *Describe the forms of water bonding.*
3. *Features of water as a solvent.*
4. *Interaction of Na⁺ ions with water molecules.*
5. *Concept of water activity.*
6. *The activity of water as an inhibitor of the development of pathogenic microflora.*

Topic 1.2. Dispersed systems of food products

1.2.1. The concept of dispersed systems

All raw materials and semi-finished products and finished food products produced from them are characterized by a multiphase structure and are dispersed systems.

Dispersed systems are heterogeneous systems that consist of two phases (components) or more, one of the phases exists in the form of particles distributed in the medium between which there is an interface (Fig. 1.12).

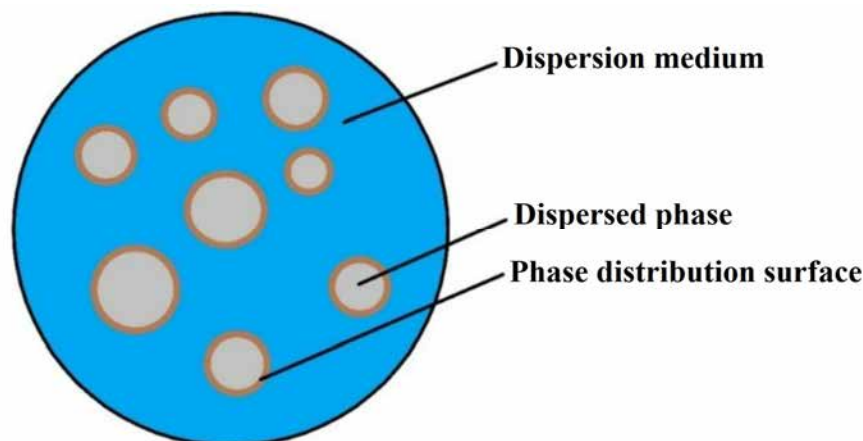


Fig. 1.12. Schematic representation of a dispersed system

A phase is a set of homogeneous parts of the system, which are limited from each other by physical interfaces.

Dispersion medium (first phase) – water, alcohol, etc.

The dispersed phase (second phase) is a collection of colloidal particles that are evenly distributed in the dispersion medium (proteins, fat, sugar, etc.).

The most important characteristic of dispersed systems is the degree of grinding or its dispersion.

1.2.2. Classification of dispersed systems of food products

Disperse systems are classified according to the following characteristics:

- by the nature of the dispersion medium and the dispersed phase;
- by the degree of dispersion;
- by the interaction between the dispersed phase and the dispersion medium;
- by the interaction between particles of the dispersed phase.

The most famous classification, proposed by V. Osvald (Tab. 1.7), is based on the difference in the aggregate state of the dispersed phase and the dispersed medium.

Table 1.9. Types of food dispersion systems

Dispersion medium	Dispersed phase	Conventional designation	The name of the dispersion system	Product (including raw materials, semi-finished products)
Gas	Liquid	G/L	Liquid aerosol	Milk dispersion in a spray dryer, coffee or tea extract during spray drying
	Solid	G/S	Solid aerosol	Flour during pneumatic transportation
Liquid	Gas	L/G	Foam	Protein foam, cream, whipped cream
	Liquid	L/L	Emulsion	Milk, mayonnaise, cream
Liquid	Solid	L/S	Solid foam, porous solid	Ice cream, meringue, crackers
Solid	Liquid	S/L	Solid emulsion, a porous solid filled with liquid	Fruits, vegetables, native muscle tissue, butter
	Solid	S/S	Solid suspension	Pasta, chocolate, caramel

When determining the rheological behavior of the product, the data given in Table 1.7 allow the food product to be classified as:

- loose;
- liquid- and solid-forming (depending on the concentration of the dispersed phase) or solid.

Food products, which are presented in Table 1.8, are assigned to one or another system according to the most important features.

Examples:

1. minced meat is subjected to cauterization, it is saturated with air and is a suspension saturated with air bubbles, that is, a three-phase system;

2. cream, depending on its temperature and mechanical impact (stirring, whipping) with the formation of butter, according to the transition from one type of dispersion to another, can be attributed to different systems.

Therefore, the above classification allows you to cover almost all dispersed food products as raw materials in the technologies of food products of a wide range (meat, dairy, fat, vegetable, semi-finished products) at all intermediate stages of its production, with the exception of one G/G system, since gas in under normal conditions form a homogeneous system.

There are also complex dispersed systems of food products

Table 1.8. Complex dispersed systems of food products

Dispersion medium	Dispersed phase	Foodstuff
Crystalline aqueous phase	Protein macromolecules, air bubbles, fat balls	Milk, cream, ice cream and sherbet
Crystalline form of cocoa butter	Sugar crystals, solid cocoa particles, air bubbles	Chocolate
Starch and protein gel	Air bubbles, partially crystalline starch molecules, bran particles	Crumb of bread
Protein macromolecules	Particles of liquid, bones, fat droplets	Meat
Cellulose, protein shell	Particles of liquid, air bubbles, starch grains	Vegetables, fruits, grains, seeds

According to the degree of dispersion (Fig. 1.13), the systems are divided into:

- ion- and molecular-disperse;
- colloidal;
- microheterogeneous;
- coarsely dispersed.

By dispersion (by the size of the particles of the dispersed phase), the systems are divided into:

- molecularly dispersed or true solutions ($a < 10^{-9}$ m);
- colloidally dispersed or ultramicroheterogeneous ($a = 10^{-9} \dots 10^{-7}$ m);
- coarsely dispersed or micro-heterogeneous systems ($a = 10^{-7} \dots 10^{-5}$ m).

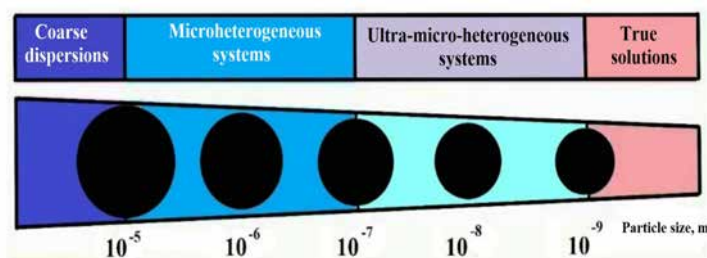


Fig. 1.13. Classification of dispersed systems by the size of particles of the dispersed phase

Dispersed systems have properties (Tab. 1.9).

Solutions are divided into three types according to the degree of dispersion (Fig. 1.14).

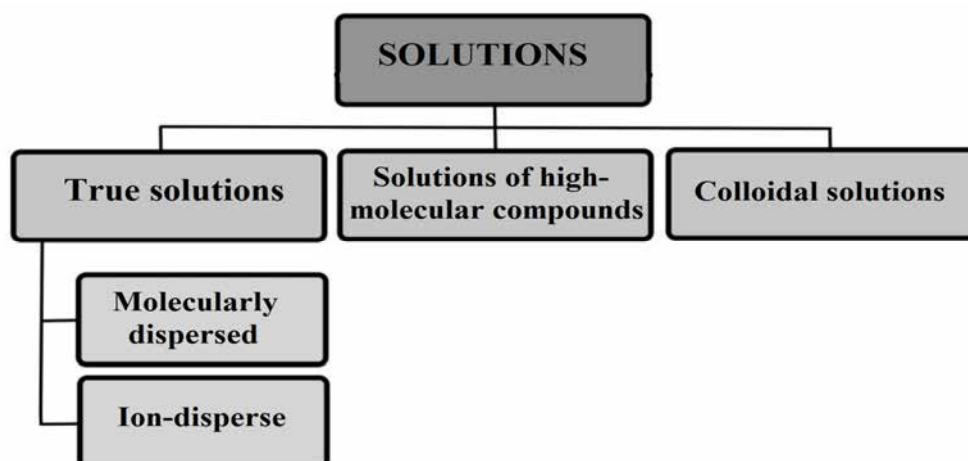


Fig. 1.14. Classification of solutions according to the degree of dispersion

Table 1.9. Properties of dispersed systems

Molecularly dispersed	Colloidally dispersed	Coarsely dispersed
1. Transparent, homogeneous, stable	1. Transparent, heterogeneous, relatively unstable	1. Opaque, heterogeneous, unstable
2. Pass through the pores of a paper filter and an ultrafilter*	2. Pass through the pores of the paper filter, but are retained by the pores of the ultrafilter	2. They do not pass through the pores of a paper filter and an ultrafilter
3. Invisible in the ordinary and ultramicroscope; the largest molecules are visible in an electron microscope	3. Invisible in an ordinary microscope; are detected in an ultramicroscope; visible in an electron microscope	3. Visible in an ordinary microscope, an ultramicroscope and an electron microscope
4. Easily diffused and dialyzed	4. They diffuse poorly and do not dialyze	4. Do not diffuse or dialyze
5. Disintegrate into separate molecules or ions	5. A collection of molecules in the form of aggregates	5. A collection of molecules, but the particles are large
6. Ordinary solutions (solution of sugar, salt in water)	6. Ashes, gels, jelly, gelatin, plant juice	6. Emulsions (milk), suspensions (coffee)

Note* – the pores of the ultrafilter have the size of colloidal particles.

True solutions include two categories of dispersed systems:

- molecularly dispersed, in which the particle size is less than 1 nm;
- ion-dispersed, in which the particle size is about 0.1 nm.

Non-electrolyte solutions, such as sucrose, alcohol, belong to molecularly dispersed solutions.

The dissolved substance disperses in the form of kinetically independent molecules.

Solutions of electrolytes, such as sodium chloride, belong to truly dispersed systems.

The dissolved substance is in the form of individual hydrated ions.

Solutions of high molecular weight compounds (HMWC) are molecularly dispersed systems formed by diphilic macromolecules and are single-phase homogeneous systems.

Colloidal solutions are dispersed systems with a particle size of 1...100 nm. Unlike true ones, they are heterogeneous systems that consist of two phases and are capable of sedimentation (deposition of particles in a gravitational field) under certain conditions.

Colloidal solutions have molecular kinetic properties.

Brownian motion, which was discovered by R. Brown in 1828 while observing the movement of flower pollen suspended in water.

Chaotic motion is also characteristic of colloidal solutions. When colloidal particles collide with solvent molecules, they acquire kinetic motion (particles can change position up to 10²⁰ times per second).

Diffusion is the process of arbitrary leveling of the concentration of a dispersed substance under the influence of the thermal movement of solvent particles. Diffusion in colloidal solutions is slower than in true solutions. If the duration of diffusion in true solutions takes place over the course of hours, then in colloidal solutions – over the course of days. An example of diffusion is the production of fruit and vegetable preserves, where sucrose or fructose diffuses from the bay to the vegetable and fruit part.

Osmotic pressure. This phenomenon is typical for systems with semipermeable membranes. Colloidal solutions, which have large particles, create a lower osmotic pressure than ionic or molecular solutions. For example, osmotic pressure exists in milk due to the content of salts and lactose (milk sugar). Also, osmotic pressure occurs in condensed milk with sugar.

Sedimentation is the deposition of particles (dispersed phase) under the action of the earth's gravity. This process is the opposite of diffusion and leads to the formation of a concentration gradient, while diffusion leads to concentration equalization.

However, an equilibrium is established between sedimentation and diffusion over time, with smaller particles that diffuse better being placed mainly in the upper layers of the solution, and larger particles mainly in the lower layers of the solution.

Viscosity is the internal friction between layers of solution that move relative to each other. Colloidal solutions, in comparison with true ones, have a higher viscosity, which is due to a larger particle size.

The stability of dispersed systems is characterized by the fact that its main characteristics do not change over time, in particular, such as the size and uniformity of the distribution of particles (dispersed phase) in the volume of the solvent (dispersion medium).

A distinction is made between kinetic and aggregative stability of colloidal solutions.

Kinetic stability consists in the ability of a dispersed system to be in a colloidal state and not to settle. It largely depends on the surface charge and the size of the diffusion adsorption layer.

Aggregative stability consists in the ability of a dispersed system to keep the particle size unchanged (dispersed phase). Loss of aggregative stability occurs due to flocculation (gluing) of particles and their joining into aggregates. As a result, precipitation of the dispersion phase and coagulation of the colloid occurs. Most colloidal solutions are kinetically and aggregatively unstable. However, their stability increases under the following conditions:

- in the presence of the same charge on the particles, which leads to mutual repulsion, preventing aggregation;
- in the presence of a hydrate shell around the counterion, which prevents particles from sticking together.

Unlike molecular (ion)-dispersed systems, colloidal systems have relatively low stability. This is due to the fact that the dispersed phase of colloidal systems has a developed surface and has a significant excess of free surface energy. Such systems tend to reduce the reserve of free energy to a certain minimum. In colloidal systems, the reduction of free surface energy is achieved as a result of the increase of particles by sticking together (coagulation).

Coagulation is the sticking together of particles of colloidal systems with the formation of more or less large aggregates, which leads to the formation of flakes that settle (or float), as a result of which the number of suspended particles in the system becomes insignificant. During coagulation, a continuous spatial structure can also be formed in the volume – the coagulation structure of the gel.

Coagulation of the colloid system can be caused by the following factors:

- increase or decrease in temperature;
- mixing of the solution;
- addition of alkaloids, dyes to the solution;
- change in the pH of the environment;
- addition of ions that have the same charge as the counter ion, that is, the charge is opposite to the charge of the granule.

The coagulating effect of ions is characterized by the coagulation threshold, i.e. the lowest electrolyte concentration at which coagulation of the colloidal solution occurs. Coagulating action of electrolytes depends on the amount of ion charge and concentration. The Schulze-Hardy rule - the coagulating effect of ions increases with an increase in their valence.

Protection of colloidal solutions is achieved by adding small amounts of high molecular weight substances that are adsorbed on the surface of the particles and prevent them from sticking together (when proteins and polysaccharides are added).

Colloidal protection by proteins is of great importance for biological fluids.

All biological fluids are colloidal solutions, since poorly soluble substances present in them (cholesterol, triglycerides, higher fatty acids, and others) can be maintained in a soluble state only due to stabilization.

An example can be the production of sour milk cheese obtained by coagulation of milk under the influence of temperature and acids.

All dispersed systems with a colloidal degree of dispersion are called **sols**:

- with a gas dispersion medium – aerosols;
- with a liquid dispersion medium with the designation - lyosol.

Depending on the nature of the dispersion medium, lyosols are divided into:

- hydrosols (their dispersion medium is water);
- alcosols (alcohol);
- ethersols (ether);
- benzols (benzene);
- organosols (organic liquid).

Disperse systems are divided into two main groups based on the "interaction between the dispersed phase and the dispersed medium":

- lyophilic (true lyophilic and surface lyophilic);
- lyophobic.

Lyophilic systems – in which dispersed particles strongly interact with the solvent (dispersion medium). In the case when the solvent is water, they can be called hydrophilic systems. Examples of hydrophilic systems are solutions of proteins or polysaccharides in water.

In truly lyophilic systems, the dispersed phase is completely permeated by the dispersion medium, that is, the system is supposedly single-phase (solutions of protein substances, for example, gelatin).

In surface lyophilic systems, the particles of the dispersed phase are mosaic-built from lyophilic and lyophobic areas and interact with the dispersion medium only on the surface.

Lyophobic systems – in which the dispersed particles interact weakly with the solvent (dispersion medium). In the case when the solvent is water, these systems are called hydrophobic, since the surface of the particles is weakly wetted by water.

Lyophobic systems are unstable over time, as they are gradually destroyed as a result of the increase of its particles under the influence of molecular forces of cohesion (for example, oil in water).

Dispersed systems are divided into two classes based on the "**interaction between the particles of the dispersed phase**":

- freely dispersed – structureless systems, the particles of which are not connected to each other in one continuous network (lyosols, suspensions, emulsions, aerosols);
- bound-dispersed – particles of these systems are connected to each other due to intermolecular forces, form spatial grids or frameworks (gels, concentrated suspensions (pastes), concentrated emulsions, solid foams and powders).

1.2.3. Obtaining dispersed systems

Dispersed systems are obtained in two ways (Fig. 1.15):

- dispersive;
- condensing.

Dispersion methods for obtaining dispersed systems include methods of mechanical grinding.

Due to the external mechanical influence, intermolecular forces are overcome with the accumulation of free surface energy.

An example of mechanical impact is the process of grinding grain to obtain flour. Grinding is carried out in crushers, mills and mills of different designs and different principles of action and other devices with a similar principle of action.

At the same time, solid bodies are crushed, ground, squeezed or split, and liquid bodies are shaken, vigorously mixed or precipitated with subsequent removal into a dispersion medium under the influence of high pressure.

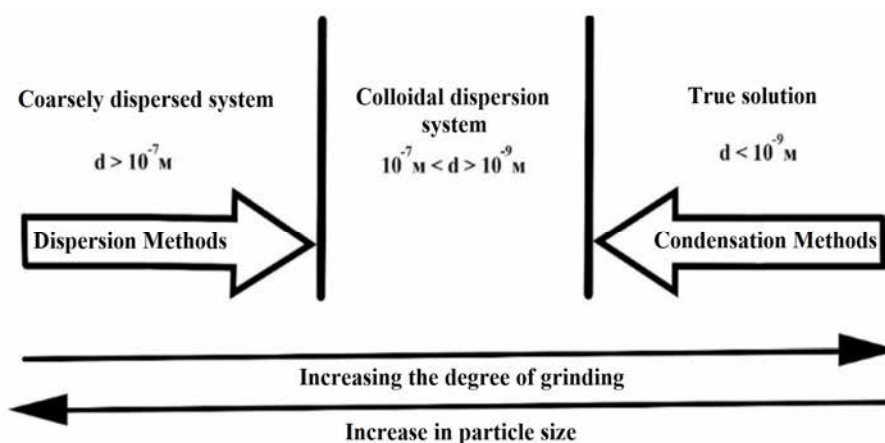


Fig. 1.15. Scheme of the formation of dispersed systems

The most common machining equipment is ball mills. Food systems to be ground are loaded into hollow cylinders that are partially filled with metal or porcelain balls. As the mill cylinder rotates, the balls roll and fall onto the food systems, thereby grinding them.

Colloid mills are used to achieve finer grinding.

At the same time, the suspension or emulsion is passed through a narrow opening between the rotor and the stator. Particles of the dispersed phase are destroyed under the action of centrifugal force.

Ultrasonic and electrical dispersion are used to achieve higher dispersion.

The dispersive effect of ultrasound is associated with cavitation - the formation and closing of cavities in the liquid.

In order to obtain stable systems by dispersion methods, it is necessary to add a third component – a stabilizer – to the food dispersion system.

Stabilizers are solutions of high-molecular compounds or surface-active substances, the introduction of which into the system leads to the formation of ionic or molecular adsorption layers at the phase separation boundary, which prevent the aggregation of crushed particles and/or their sedimentation.

Dispersion methods also include peptization.

Peptization is a chemical dispersion.

The fresh sediment formed during coagulation of the colloidal solution is converted into a sol by processing it with a peptizer: a solvent, acid solution, or surfactant solution.

When washing the sediment with a solvent, substances that contributed to the aggregation of particles are removed, so the latter pass into the solution.

Dispersion is used in the homogenization of fruit and berry purees, production of flour, cocoa powder, powdered sugar, etc.

Condensation methods combine processes based on the emergence of a new phase by joining molecules, atoms or ions in a homogeneous medium.

There is **physical** and **chemical** condensation.

Physical condensation includes: condensation from steam and replacement of the solvent.

During condensation from steam, the following occurs: when the vapor of a substance passes into a liquid, a stable lyosol is formed as a result of condensation. Aerosols are obtained by condensation of vapors of various substances in a gaseous environment. Hydro- and organosols of many substances were obtained by joint condensation of a pair of substances forming a dispersed phase and a dispersion medium on a cooled surface.

The method of replacing the solvent consists in the fact that the solution of the substance is added in small portions to the liquid, which is mixed with the solvent, but in which the substance dissolves so little that it is practically separated in the form of a highly dispersed phase, that is, a lyosol is formed.

Sulfur, cholesterol, and rosin hydrosols are obtained by adding alcohol solutions of these substances to water.

Chemical condensation is based on the condensation separation of a new phase, which is formed as a result of a chemical reaction, from a supersaturated solution.

Therefore, the concentration of the substance in the solution must exceed the solubility. However, this condition is common both for the formation of sol and the usual sediment of the solid phase. According to Weimarn's theory, in order to obtain a highly dispersed system, it is necessary that the rate of formation of dispersed phase nuclei far exceeds the rate of crystal growth. Practically, this is achieved by adding a concentrated solution of one component to a very dilute solution of the second with intensive mixing. The accumulation of free surface energy during the formation of a dispersed system increases the probability of the particle aggregation process. In this way, it is necessary not only to achieve the desired dispersion, but also to stabilize it with the help of a stabilizer.

Various reactions lead to the formation of a dispersed system: double exchange, hydrolysis, reduction, oxidation.

Condensation methods take place in rectification devices during the production of alcohol, crystallization of sugar, evaporation of solutions, etc.

1.2.4. Characteristics and properties of aerosols, suspensions, emulsions

Aerosols are systems in which gas acts as a dispersion medium.

Since in most cases the dispersion of aerosols is lower than that of colloids, they are called aerodisperse systems.

Aerosols have a high dispersion of particles and are aggregatively unstable, since the process of coagulation and sedimentation always takes place in them.

The coagulation process occurs due to Brownian motion, which results in the collision of finely dispersed particles of the system.

Sedimentation occurs due to the deposition of coarse particles of the system.

Powders – aerosols with a gas dispersion medium, which are obtained by dispersion using crushers, mills, rollers, etc., are of particular importance in food production technologies.

Technological and organoleptic properties of powders depend on their dispersion.

The dispersion of powders and powdered products varies widely and they are all micro-heterogeneous systems (dust), so the size of powder particles can be determined microscopically (Fig. 1.16).

Powders are characterized by the following properties:

- bulk density;
- the ability to stick together (adhesion);
- fluidity (fluidity);
- hygroscopicity (wetting);
- abrasiveness.

Bulk density is the mass of a unit volume of powder. In coarse powders, the bulk density does not depend on the size of the particles, but with an increase in the dispersion of the powder, intermolecular forces begin to act, which increase the friction between the particles and subsequently contribute to the formation of a looser structure with a decrease in the bulk density.

Adhesion binds to the surface of solid powder particles or when these particles interact with the container walls.

Cohesiveness is the ability of powder particles to form aggregates. This property is due to the cohesive interaction of powder particles with each other.

Flowability is the mobility of powder particles relative to each other and the ability to move under the influence of external forces. The flowability of powders depends on the size of their particles, humidity and the degree of compaction.

Also similar to flowability is the fluidity of the powder, which depends on the nature of the contact between the particles.

Hygroscopicity is the ability of the powder to absorb moisture from the environment. Absorption of moisture by powders leads to changes in many of their properties. This property is caused by the solubility of the powder in water.

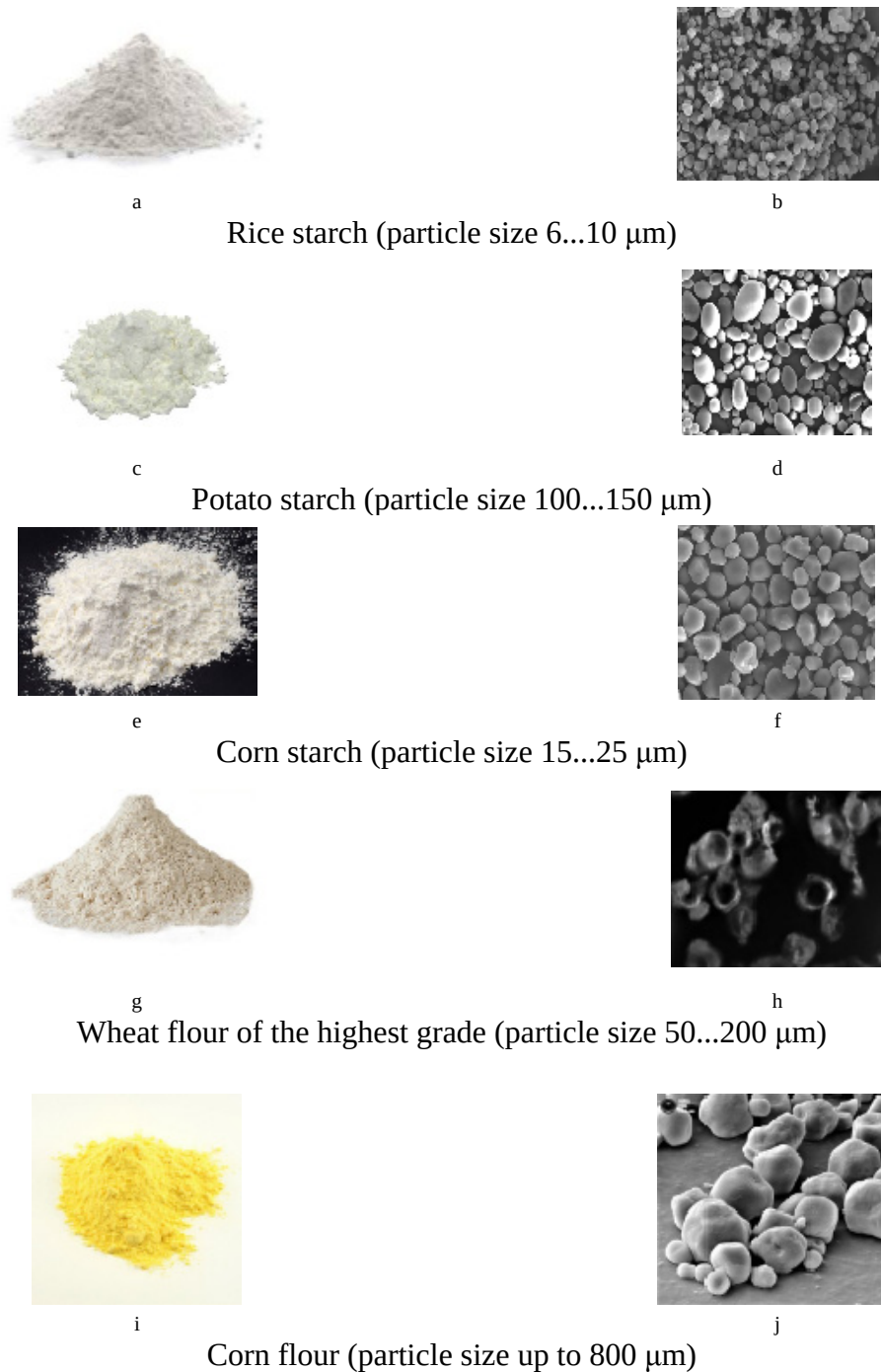


Fig. 1.16. Appearance (a, c, e, g, i) and photomicrographs (b, d, f, h, j) individual types of powders

The mechanism of moisture absorption occurs as follows. Water molecules are adsorbed on the surface of the particles followed by capillary condensation in solid porous bodies. The condition of this process is the hydrophilic surface of the powder particles.

The hygroscopicity of powders can be reduced or increased by treating them with surfactants.

Abrasive properties of powders are characterized by hardness and particle shape, size and density.

In food production, aerosols (powders) are formed during the operation of crushers, mills, rollers, sifters, etc.

The released dust pollutes the production, getting between the parts of the machines that are exposed to friction, accelerates their wear, and creates unsanitary conditions for human work.

In the production workshop, where dust is generated (mills, flour sifting department, etc.) are classified as fire and explosive. This should be taken into account when designing and organizing production processes.

Suspensions are microheterogeneous systems with a solid dispersed phase and a liquid dispersion medium. Suspensions include (Fig. 1.17).



the dough is thin



sauces



cream soup



juice with pulp

Fig. 1.17. Appearance of food suspensions

The properties of colloidal solutions are typical for suspensions:

- light scattering - turbidity, not opalescence, because light rays are refracted and reflected by particles of the suspension, and not scattered;
- aggregate instability;
- coagulation in the presence of electrolytes (electrophoresis).

The difference from colloidal solutions is as follows. Particles of suspensions are usually larger in size than colloidal particles (more than 10 μm) and settle under the influence of gravity. This quantitative difference determines their peculiarity. In most suspensions, particles of the dispersion phase do not participate in Brownian motion.

Therefore, they are considered as an independent type of dispersed systems.

In dilute suspensions, each particle is kinetically independent and moves freely in the liquid.

In concentrated suspensions (pastes), there are forces between particles that lead to a spatial grid as a certain structure.

Therefore, suspensions are sedimentationally unstable and prone to phase separation. This phenomenon leads to deterioration of the appearance and consistency of food systems that are suspensions.

To improve their properties, it is necessary to use special stabilizers or thickeners, in the role of which polymers act:

- in mashed soups – flour and egg-milk mixture;
- in sauces – flour, starch, pectin substances, etc.

Most often, natural thickeners are used - gums (carob, guar, xanthan) and slimes (carrageenans), pectin, gelatinizers, starch, etc.

Emulsions are dispersed systems that consist of two mutually insoluble phases, one of which is inside the other and is presented in the form of crushed particles.

Emulsions are widespread in food products (milk, sour cream, cream, butter, margarine, mayonnaise, butter creams, etc.).

Emulsions are classified as:

1. By the polarity of the dispersed phase and dispersion medium (Fig. 1.18).
2. According to the concentration of the dispersed phase in the system:
 - diluted (up to 0.1% by volume of the dispersed phase);
 - concentrated (up to 74% by volume of dispersed phase);
 - highly concentrated (more than 74% by volume of the dispersed phase).

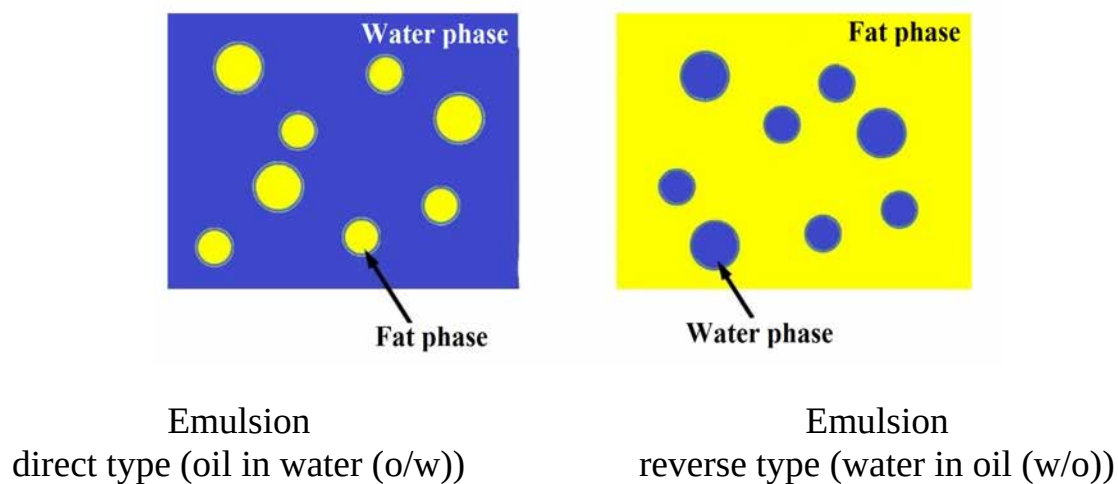


Fig. 1.18. Schematic representation of emulsion types

Concentrated emulsions can be monodisperse and polydisperse. Monodisperse emulsions (Fig. 1.19, a) – o/w have fat globules of the same size (high-fat cream for the production of butter).

For polydisperse emulsions (Fig. 1.19, b) containing fat globules of different sizes, this limit (5 times the content of the dispersed phase) is higher, so smaller fat globules can be placed between large ones.

In highly concentrated emulsions (Fig. 1.19, c), the particles of the dispersed phase are mutually deformed and take the form of polyhedra (polyhedra). As a result, the particles are not capable of sedimentation and have mechanical strength (similar to the properties of gels).

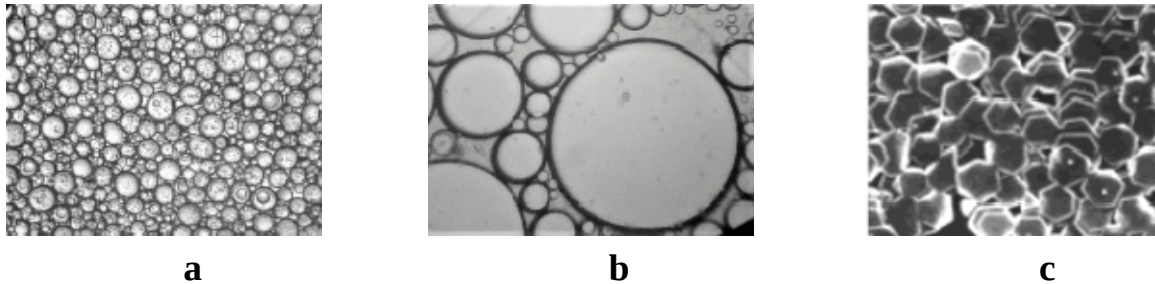


Fig. 1.19. Micrographs of monodisperse (a), polydisperse (b) and highly concentrated (c) emulsion

Emulsion is a thermodynamically unstable system, as the liquids forming it differ in polarity.

The main reasons for the instability of emulsions are (Fig. 1.20):

- layering;
- flocculation;
- coalescence;
- phase reversal.

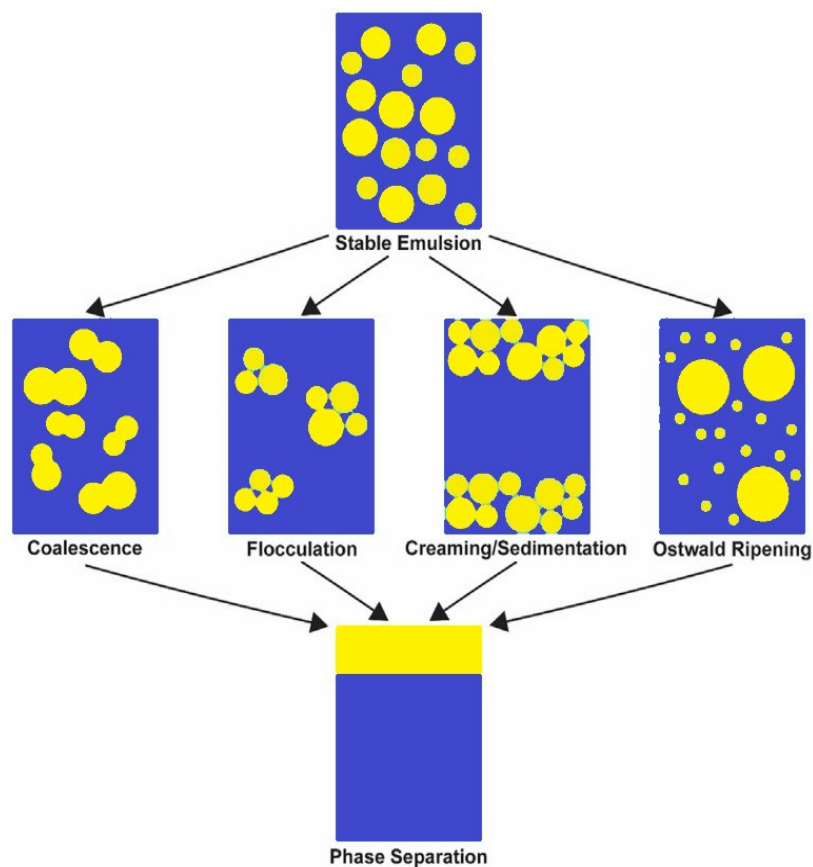


Fig. 1.20. Schematic representation of the causes of instability of emulsions direct type

Under these phenomena, the emulsion ultimately divides into two macrophases with different polarities (Fig. 1.21).

Stratification of the emulsion over time occurs due to differences in the density of the dispersed phase and the dispersion medium, which leads to the volumetric separation of systems under the influence of gravity.

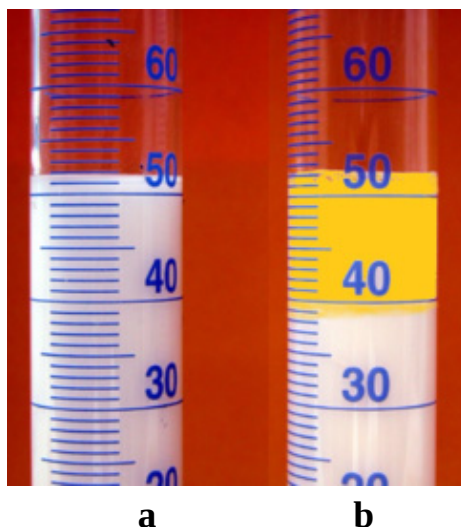


Fig. 1.21. Appearance of stable emulsion (a) and emulsion separated into microphases (b)

Deposition of particles of the dispersed phase occurs if its density is higher than the density of the dispersion medium. Most often, delamination occurs with the upward movement of the dispersed phase, since in most cases in oil-in-water emulsions, the density of the fat phase is lower than the density of the aqueous phase.

Flocculation can occur in an emulsion when the Vander Waals energy exceeds the energy of the repulsive forces. When disproportionation is broken, small droplets settle on the surface of larger droplets. The reason is the large curvature of the surface of small droplets, as a result of which the solubility near the surface of these droplets is higher than the solubility in the volume or near the surface of large droplets.

Aggregate instability of emulsions manifests itself in the spontaneous formation of aggregates of droplets with subsequent merging (coalescence) of individual droplets with each other. As a result, the emulsion separates into two layers (phases).

Surface-active substances – emulsifiers are used to obtain aggregation-resistant emulsions.

Due to the use of emulsifiers, it is possible to obtain emulsions of both the direct type (fat in water) and the reverse type (water in fat).

Stabilization of the resulting emulsions is due to the fact that the emulsifier concentrates on the surface of the phase separation and reduces the interfacial surface tension.

Emulsifiers have a diphilic structure, contain hydrophilic (polar) and hydrophobic (nonpolar) groups:

- hydrophilic groups ensure the solubility of the emulsifier in the aqueous phase;
- hydrophobic groups ensure the solubility of the emulsifier in non-polar solvents (alcohol, ether, etc.).

The emulsifier, being adsorbed on the surface of fat globules, orients its hydrophobic radicals in the direction of fat, and hydrophilic radicals in the direction of water.

The stabilizing effect of emulsifiers is explained by the creation of mechanically strong, electrically charged and hydrated (surrounded by water molecules) films on the surface of fat droplets (Fig. 1.22).

The ratio of the sizes of the polar and nonpolar groups of the emulsifier molecule is expressed in the value of the hydrophilic-lipophilic balance (HLB).

Hydrophilic-lipophilic balance (HLB) is a value that characterizes the effectiveness of the emulsifier and allows you to evaluate the relative importance of individual constituent parts of its molecule, namely hydrophilic groups and a non-polar hydrocarbon chain) in the manifestation of the entire molecule as a whole to water and organic solvents.

The larger the value of HLB, the higher the hydrophilicity of the emulsifier, the smaller it is, the higher its hydrophobicity.

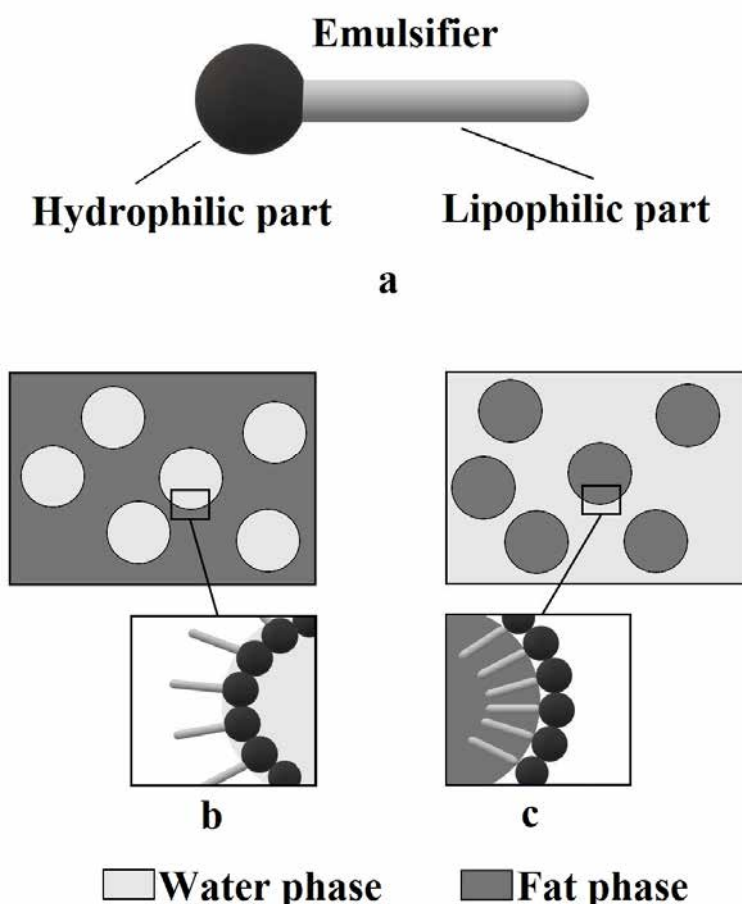


Fig. 1.22. The structure of the emulsifier molecule (a) and the mechanism of emulsion stabilization of direct (c) and reverse types (b)

Food emulsifiers used to stabilize emulsions are divided into natural and synthetic.

How natural emulsifiers are used (Fig.1.23, a):

- dry milk;
- egg yolk;
- phospholipids;
- lecithin.

As synthetic emulsifiers (Fig. 1.23, b):

- esters of monoatomic higher fatty alcohols;
- ethers of polyatomic alcohols;
- condensation products of oxyacids with higher fatty acids.

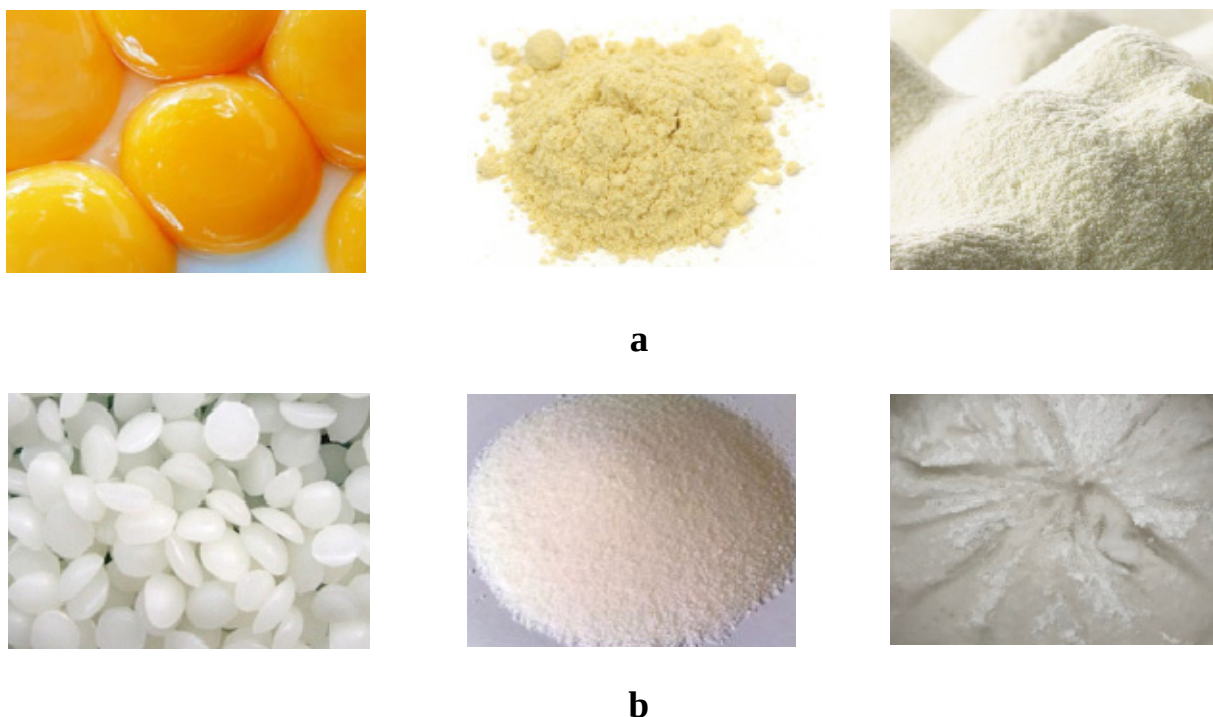


Fig. 1.23. Appearance of natural (a) and synthetic (b) emulsifiers used to obtain stable emulsions

Emulsifiers with high HLB values (6-10) stabilize emulsions of the direct type – "oil in water". Emulsifiers with low HLB values (1-5) stabilize emulsions of the reverse type – "water in oil".

1.2.5. Characteristics of gelling agents and the mechanism of gel formation

Gels are bound-dispersed colloidal systems in which particles of the dispersed phase form solid spatial structures – nets, frameworks.

Gels are biopolymer-solvent systems that are characterized by large inverse deformations in the almost complete absence of viscous flow.

The characteristics of the main gelling agents are presented in Table 1.10.

Gels are classified as follows:

- depending on the ability to retain water;

- according to the effective force of gel formation;
- by type in multicomponent food systems;
- in relation to temperature.

Table 1.10. Characteristics of gelling agents

Gem former	Source of receipt	Composition and features of the structure	Solubility
Agar	Red seaweed	D-galactose and 3,6-anhydro-L-galactose residues alternating and connected by β -1,4- and α -1,3-bonds	Solubility at room temperature
Agaroid		It has a structure similar to agar	Poorly soluble in cold water
κ -Carrageenan		D-galactose residues with a strict alternation of α -1,3 and β -1,4 bonds between them. 1 sulfate for 2 galactose	Dissolves only when heated
ι -Carrageenan		The same, but has 2 sulfates for 2 galactose	Partially dissolves at room temperature
Alginates	Brown seaweed	β -D-mannuronic and α -L-guluronic acids linked by 1,4-glycosidic bonds	Dissolves at room temperature
Pectins	Cell walls and intercellular tissue formations of higher plants	Galacturonic and polygalacturonic acids, partially esterified with methyl alcohol, and rhamnose	Dissolves at room temperature
Gelatin	Acid or alkaline extraction of collagen	Fibrillar protein	Partially swells in cold water depending on pH, dissolves only at temperatures above 40 °C

Gelatin. Gel is formed during cooling. Transition from coils of molecules to spirals followed by their aggregation.

Agar. A gel is formed during cooling. The transition from coils of molecules to spirals, followed by their aggregation.

Low esterified pectin. The gel is formed in the presence of calcium salts and low pH (3...4.5). Cations cause intermolecular cross-linking. Low pH values reduce intermolecular electrostatic repulsion.

Kappa-carrageenan. A gel is formed during cooling in the presence of potassium salts. The transition from tangles of molecules to spirals with their subsequent aggregation. Potassium ions bind to helices. Salts reduce electrostatic repulsion between chains, thereby promoting aggregation.

Iota-carrageenan. The gel is formed during cooling in the presence of calcium salts. Calcium ions bind to helices. Salts reduce electrostatic repulsion between chains, thereby promoting aggregation.

Sodium alginate. The gel is formed with the addition of polyvalent cations, especially calcium at low pH (4). Molecules are cross-linked by polyvalent ions. Residues of guluronic acid form a bent conformation, which ensures effective binding of cations (egg package model).

Highly esterified pectin. The gel is formed in the presence of easily soluble solids (for example, 50% sugar) and at low pH values (3.5).

Drangles are a spatial molecular framework immersed in an aqueous environment, which is formed by interconnected macromolecules.

Water as a solvent affects the nature and magnitude of intermolecular forces, thanks to which the integrity of the framework is maintained. A big role in the stabilization of the structure belongs to hydrogen bonds that arise between molecules. There is a significant force field around them, due to which the polar groups are bound by secondary valences.

A large number of technological factors affect the gel formation process (Fig. 1.24).



Fig. 1.24. Factors affecting the gelation process

In contrast to coagulation, the gel-formed stability is only partially lost, phase separation does not occur, the system acquires a certain structure, but remains a two-phase heterogeneous system. Gels are characterized by the phenomenon of thixotropy.

Thixotropy is the ability of gels to liquefy under mechanical influence (shaking, stirring), i.e. to change into a sol state, and after the phenomenon ceases, to

restore its structure. Thixotropic transformations are reversible and isothermal, that is, they occur at a constant temperature.

Gels do not have elasticity, when dehydrated they turn into fragile, porous and non-swollen bodies. They absorb any liquids that wet them, almost without changing their volume.

Gels are characterized by the phenomenon of syneresis.

Syneresis is the process of involuntary compaction of gels, accompanied by the separation of the dispersion medium from the cells of the structural mesh, the aging process of gels.

As a result of syneresis, the volume of the gel and its transparency decrease.

A slight increase in temperature, as a rule, promotes syneresis, as it facilitates the movement of molecules.

But a significant increase in temperature, on the contrary, leads to the formation of a solution of high-molecular compounds. An increase in the concentration of high molecular weight compounds also promotes syneresis.

If no chemical reactions occur during syneresis, then the process is reversed. Otherwise, the reversibility is lost and aging of the gels occurs.

Most often, syneresis is an undesirable process that causes stale bread, wetting of marmalade, jelly, jams, etc.

Syneresis plays a positive role in the technology of sour-milk cheese and in the ripening process of rennet, hard cheeses.

1.2.6. Types of foam, formation mechanism

Foams are dispersed systems consisting of a dispersed gas phase (usually air) in a dispersed liquid medium and are a lyophobic system.

The following definition is also possible: foams are dispersions of gas in a liquid.

In the theory of physico-chemistry of foams and foam films, the most important parameters characterizing them include:

- foaming ability;
- multiplicity;
- dispersion;
- stability;
- the shape of the bubbles.

The foaming capacity of a solution is the amount of foam, expressed by its column height (in mm) or volume (in ml), which is formed from a constant volume of solution in case of compliance with specified conditions for a certain time.

Multiplicity of foam (n) is the ratio of the volume of the foam to the volume V_f of the liquid V_s contained in it.

$$n = V_f/V_s = (V_g + V_s)/V_s = 1 + V_g/V_s, \quad (1.3)$$

V_f – volume of foam;

V_s – volume of the solution;

V_g – the volume of gas in the foam.

The dispersion of foam is characterized by the average size of gas bubbles and the average thickness of liquid films (the size of bubbles reaches $10^{-3} \dots 10^{-2}$ m), and the thickness of liquid foam can be different, but not less than 10^{-8} m, since the film collapses at a smaller thickness.

The stability of the foam is understood as its ability to keep the main parameters unchanged over time: dispersion, multiplicity and volume of the foam as a whole.

The gas-filled foam cells are separated by films of the dispersion medium, and the shape of the polyhedra continuously changes in the process of gas diffusion transfer and coalescence.

A tetrahedron or a pentagonal dodecahedron (Fig. 1.25) is used as a model cell to calculate the dispersion of the foam and the radius of the Plateau-Gibbs channels, since in real foam the average number of films surrounding the cell is close to 14.

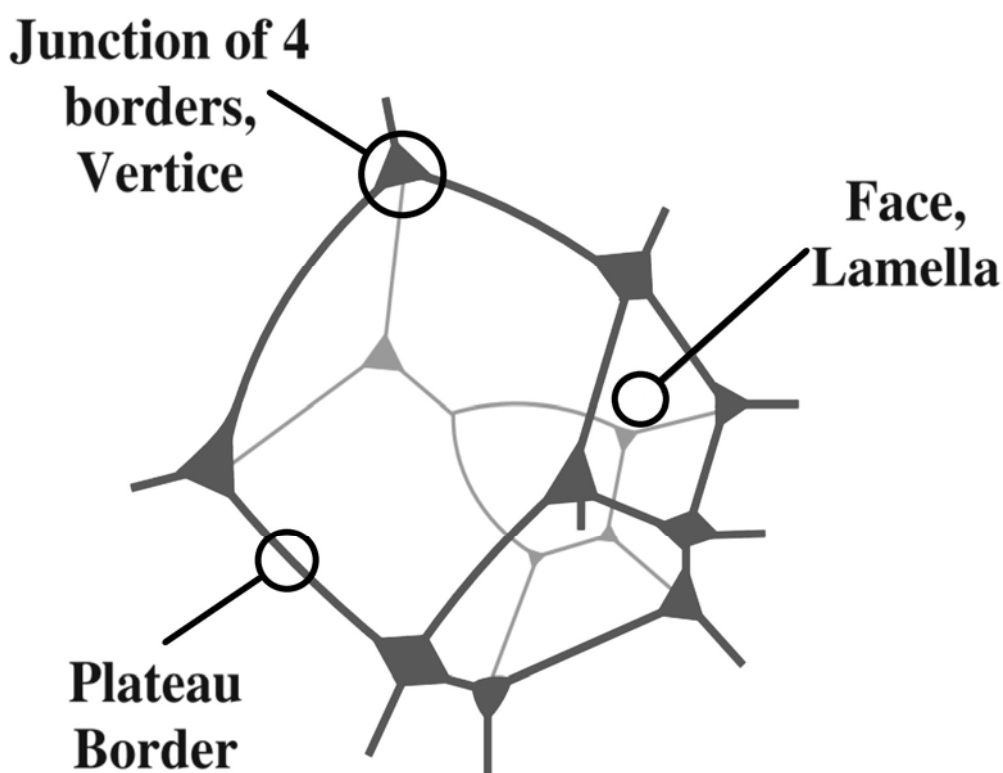


Fig. 1.25. The structure of the foam shell

The edges of the foam shell are Plateau-Gibbs channels filled with a dispersion medium.

According to the Plateau-Gibbs rule, the tension forces of films in one plane can be balanced only if the angles between them are equal to 120° . According to this rule, 3 films forming an angle of 120° always converge on one edge of the shell, and only 4 edges can converge at one point.

At the same time, the Plateau-Gibbs channel is created (Fig. 1.26, 1.27).

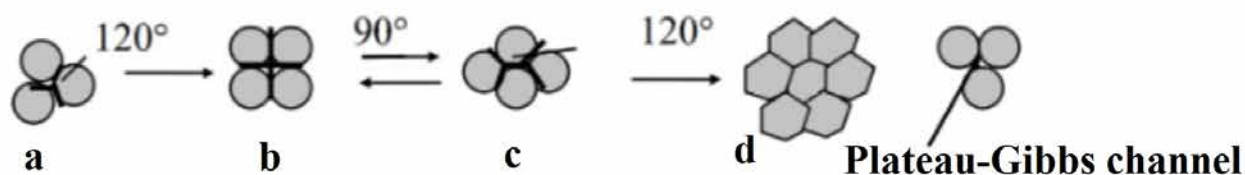
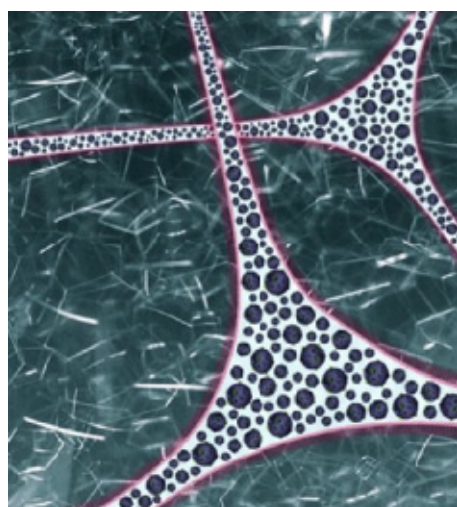
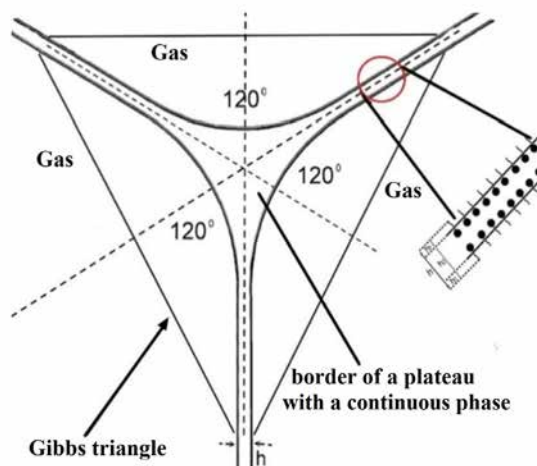


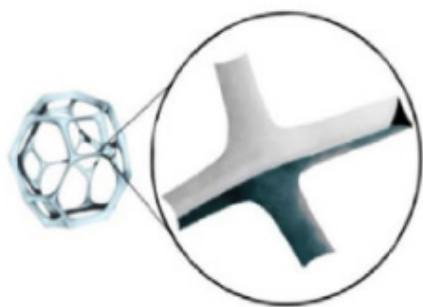
Fig. 1.26. The shape of the contact area of gas bubbles
 a – equilibrium state of three bubbles; b – unstable position of four bubbles; c – equilibrium state of four bubbles; d – a monolayer of polyhedral foam from identical bubbles.



a



b



c

Fig. 1.27. Scheme of the foam frame (a); the Plateau-Gibbs channel (b); water channels formed at the junction of neighboring bubbles (c)

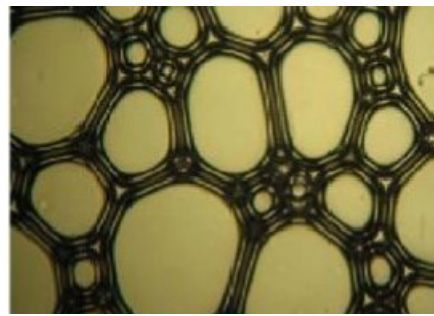
The surface of the channel has a complex concave shape. The capillary pressure under the concave surface causes the reduced pressure in the Plateau-Gibbs channel.

Vertices of adjacent pentagonal dodecahedrons form nodes in which four channels converge.

As an example, we can cite whipped proteins (Fig. 1.28).



a



b

Fig. 1.28. Appearance (a) of egg white foam and its photomicrograph (b) at a magnification of 300 times

Depending on the shape of the gas bubbles, foams are divided into two types:

- spherical;
- multifaceted.

Spherical foams are characterized by a high liquid content and, as a result, low stability, so they are classified as conditionally stable. In unstable foams, the Plateau effect is observed: the liquid phase leaves the channels under the influence of gravity and rapid coalescence (sticking) of gas bubbles occurs.

Foams with a low viscosity of the dispersed medium are short-lived. Due to the large difference in the density of gas and liquid, spherical foams quickly separate into a pure dispersion medium and a more concentrated foam (Fig. 1.29).



a



b



c

Fig. 1.29. Examples of foam-like structures of champagne (b), carbonated sweet water (b), beer (c)

Obtaining a stable (long-lasting) foam of a pure liquid (that is, without a foaming agent) is impossible.

A number of technological factors affect the foaming ability (Fig. 1.30, Table 1.11).

The structure of molecules of surfactants. The foaming ability of surfactant solutions depends on the location of the hydrophilic group in the molecule. The closer the hydrophilic group is to the middle of the molecule, the higher the foaming ability of solutions.

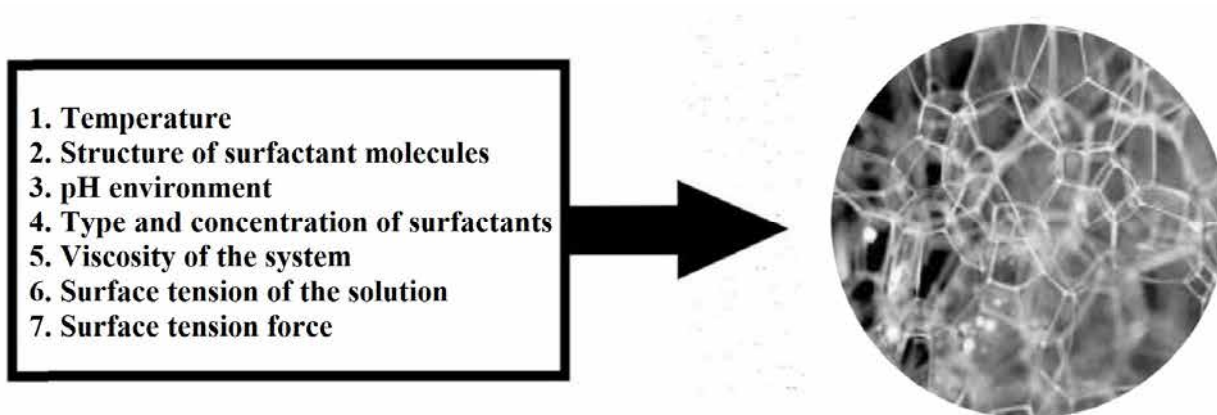


Fig. 1.30. Technological factors that affect foaming ability

Dependence of foaming ability on surfactant concentration. When the concentration of surfactant increases, the foaming of solutions usually increases to a maximum value, then remains almost constant up to the solubility limit of this type of surfactant or decreases.

This dependence is characteristic of all substances. The increase in foaming capacity with increasing concentration is associated with micelle formation.

When the critical concentration of micelle formation is reached, the maximum foam volume is observed. Also, in the region of the critical concentration of micelle formation, the formation of an adsorption layer with maximum mechanical viscosity is completed. With a further increase in the concentration of surfactants in the solution, the rate of diffusion of molecules into the surface layer decreases, which explains some decrease in foaming ability.

Effect of temperature on foaming ability. In the region of positive temperatures, surfactant foaming usually increases with rising temperature, and then decreases.

Effect of pH on foaming ability. Fatty acids and their alkali salts practically do not form foam in an acidic environment.

The maximum foaming of fatty acids is usually possible at pH=8...9. Under these conditions, fatty acid molecules occupy the largest area per molecule in the monolayer and in the adsorption layers of the foam films.

With an increase in the length of the hydrophobic chain in sodium salts of saturated fatty acids, the maximum foaming ability is disturbed in the alkaline direction.

Protein solutions show the maximum foaming ability.

Solutions of lactalbumin and gelatin have the maximum foaming ability at pH=4.5.

The foaming capacity of gelatin solutions increases in an alkaline environment. In the case of adding electrolytes, the isoelectric point shifts, and at the same time, the foaming maximum also shifts.

Dependence of the foaming ability on the surface tension of the solution. As the surface tension of the solution decreases, its foaming ability increases.

Table 1.11. Technological factors affecting foaming

Technological factor	Effect on foaming
Sugar	Increases the stability of the foam, but slightly reduces its volume
Acid	In small concentrations, it improves foaming
Temperature	Low, < 6°C – optimal for whipping egg whites, sour cream, cream; High, 30-40°C – optimal for whipping melange
Method of whipping	The type of working body, the speed of rotation of the working body, the duration of whipping
Surfactant	Increase the foaming ability, properties and stability of the foam, speed up the whipping process

Foams are obtained in two ways:

- condensing;
- dispersive.

With the condensation method, gas or steam is released in the liquid as a result of rapid heating or a drop in pressure. To do this, the gas is first dissolved in a liquid under high pressure.

The dispersion method consists in the dispersion of air by intensive stirring or blowing gas through the liquid.

To obtain stable foams, it is necessary to use substances that stabilize them – **foaming agents**.

Typical foaming agents are surfactants and high molecular weight compounds (as well as emulsifiers):

- proteins (egg protein, gelatin, proteins of sunflower, soy, pea meal);
- polysaccharides (pectin, starch etc.);
- glycosides (saponins);
- alcohols;
- lipids (mono- and diglycerides, fatty acid esters, lecithin, choline phosphoglycerides, phospholipids).

According to Rebinder's classification, alcohols and fatty acids are type 1 foaming agents. With their help, less stable foams are obtained, which exist for several seconds.

The most stable foams can be obtained using high-molecular compounds, which are type 2 foaming agents.

Foaming agents reduce surface tension, improve the process of foam formation and give it stability.

Addition of stability occurs due to their adsorption at the boundary of phase separation and the formation of a highly viscous structured film that prevents the flow of liquid (Fig. 1.31).

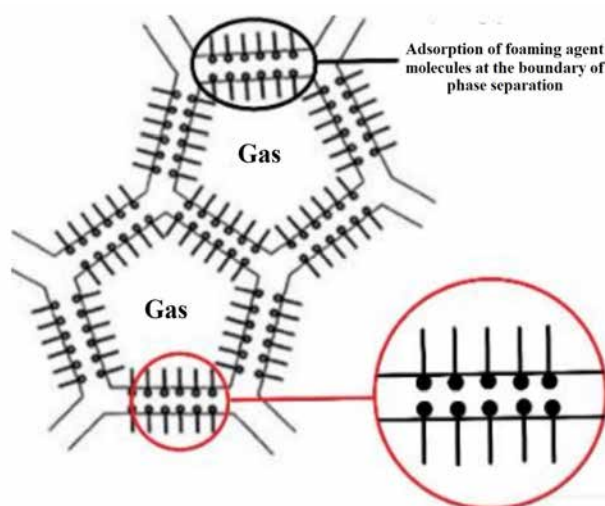


Fig. 1.31. Schematic representation of foam stabilization by foam-forming molecules

Temperature affects the stability of the foam, but the temperature effect has many simultaneous competing processes. At elevated temperatures, the pressure inside the bubbles increases, as well as the solubility of the surfactant, while the surface tension decreases, which improves the stability of the foam.

However, as the temperature increases, the thermal fluctuations of the adsorbed molecules increase. As a result, the mechanical strength of the surface layer created by surfactant molecules decreases, the viscosity of the solution decreases, which increases the speed of liquid moving from the foam, and the hydration conditions of the polar group of the surfactant change, which leads to a loss of foam stability.

However, in some foams obtained with the use of high-molecular substances (egg protein), heat treatment entails a transition from a liquid dispersion medium to a solid one. The resulting foam becomes stable. Examples of such foams are fruit candies, marshmallows, sponge cakes, etc.

Thus, the temperature effect on foam stability should be analyzed on a case-by-case basis.

The addition of liquid oils to foam protein systems leads to a decrease in the ability to foam and stability of the foam, which is associated with the destruction of the foam and consists in its ability to intensively replace the protein from the phase boundaries and entails the rupture of the interfacial adsorption layers.

On the contrary, the addition of solid fats increases the foaming ability and mechanical strength of foam systems.

The addition of liquid oils is effectively used in antifoam technologies. The reduction of the ability to foam and the stability of foams by liquid oils consists in the adhesion of oil drops to air bubbles (Fig. 1.32).

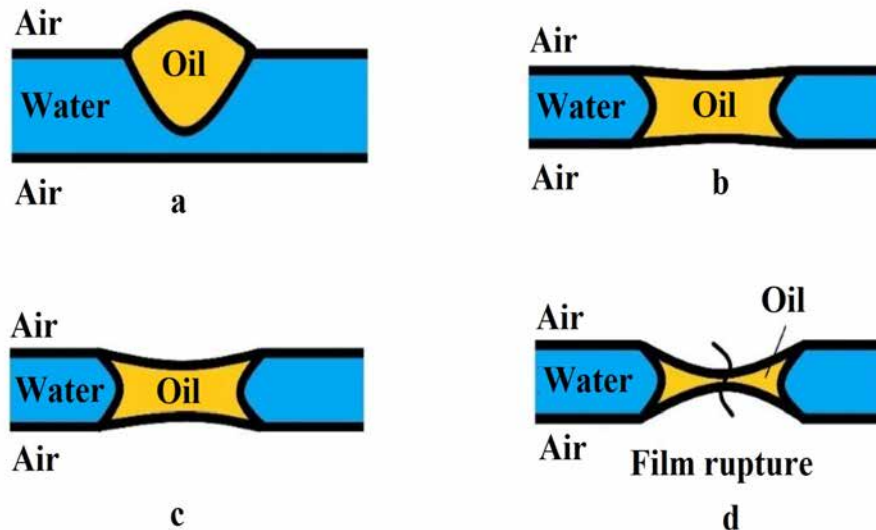


Fig. 1.32. Schematic representation of the foam film rupture mechanism: the connection of the film surfaces leads to an oil bridge with unbalanced capillary pressure at the oil-water and air-water boundaries (a, b); the bridge stretches over time until an unstable film of oil forms in the center of the bridge (c, d); the rupture of the oil film leads to the destruction of the entire foam structure

Questions for discussion and self-examination

1. Give the concept of dispersed systems and their classification.
2. Give a classification of the structures of food systems.
3. What are aerosols and what is their technological significance?
4. What properties do powders have?
5. What systems are called suspensions? Ways to stabilize the structure.
6. Emulsions. Classification, characteristics and stabilization conditions.
7. What are gelatinizers? The mechanism of the process of swelling and jelly formation.
8. Influence of technological factors on swelling and gelatinization
9. The use of emulsifiers in the technological process of creating food products in the conditions of restaurants.
10. Specify the types of foams and the conditions for obtaining them.
11. What does the first Plateau-Gibbs rule sound like?

Topic 1.3. Proteins: composition, characteristics

1.3.1. Classification and composition of proteins. Characteristics of amino acids

According to structural features, proteins are classified (Fig. 1.33).

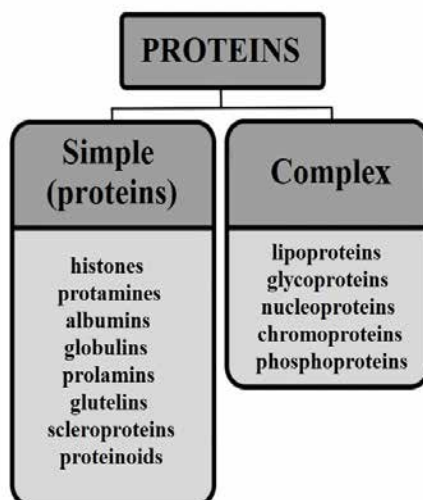


Fig. 1.33. Classification of proteins by structural features

Proteins are high-molecular nitrogen-containing organic substances, the molecules of which are built from amino acid residues. Proteins are an important part of animal and plant cells.

Protamines. Strongly alkaline proteins with a small molecular weight. They consist of 60-85 % arginine. Well soluble in water.

Histones. Proteins with basic properties. Consist of 20...30 % of lysine and arginine. Located mainly in the nucleus, they stabilize DNA.

Prolamins. Soluble in 60...80 % aqueous ethanol solution, all other simple proteins precipitate under such conditions. They contain 20...25 % glutamic acid and 10-15% proline.

Glutelins. Soluble in alkaline solutions. They consist in the vast majority of glutamine and lysine. Prolamins and glutelins are mainly proteins of plant origin, which make up the bulk of the gluten in cereal grains.

Albumins. Soluble in water and salt solutions. Molecular weight: albumins - 40,000...70,000. Albumins and globulins are globular proteins that are the main proteins of the blood plasma. Albumins make up 60 - 65% of the total blood plasma protein.

Globulins. They have a higher molecular weight and solubility in salt solutions of low concentration. The molecular weight is more than 150,000. Most of these proteins are in blood serum (plasma), milk, egg white, and muscles. Globulins are produced by the liver and the immune system.

Proteids are proteins consisting of a protein part and a non-protein prosthetic group (lipids, carbohydrates, nucleic acids, phosphoric acid or metal).

Classification of complex proteins – according to the nature of the prosthetic group:

Chromoproteins. Built from a simple protein and a colored prosthetic group (pigment). Hemoproteins (containing heme), magnesium porphyrins and flavoproteins (containing isoalloxazine derivatives) are distinguished. Chromoproteins have a number of unique biological functions: they participate in such fundamental life processes as photosynthesis, cellular respiration and transport of oxygen and carbon dioxide within the whole organism, redox reactions, perception of light and color, and others.

Metalloproteins. The prosthetic group includes iron, copper, cobalt, zinc and other elements. A large group of enzymes belongs to metalloproteins.

Nucleoproteins. These are complex proteins, the prosthetic group of which is nucleic acids. Depending on the nature of the nucleic acid, nucleoproteins are divided into ribonucleoproteins (RNPs), if they include ribonucleic acid – RNA, and if deoxyribonucleic acid – DNA.

Lipoproteins. The prosthetic group includes lipids and their derivatives. Most often, the prosthetic group is neutral fats – triglycerides. They are a part of biological membranes, blood, lymph, nervous tissues, etc. In a complex with proteins, lipids acquire new properties: they are able to dissolve in water and lose their ability to dissolve in organic solvents.

Phosphoproteins. They contain a residue of phosphoric acid. These proteins are part of egg proteins (albumin) and milk (casein).

Glycoproteins. Contains the remains of carbohydrates. They are part of blood, milk, eggs, enzymes, hormones. This group includes immunoglobulins, some hormones: gonadotropic, thyrotropin, corticotropin, thyroglobulin, an inhibitor of virus reproduction – interferon.

Amino acids are organic compounds containing (according to the name) amino group NH_2 and organic acid, i.e. carboxyl group COOH (Fig. 1.34).

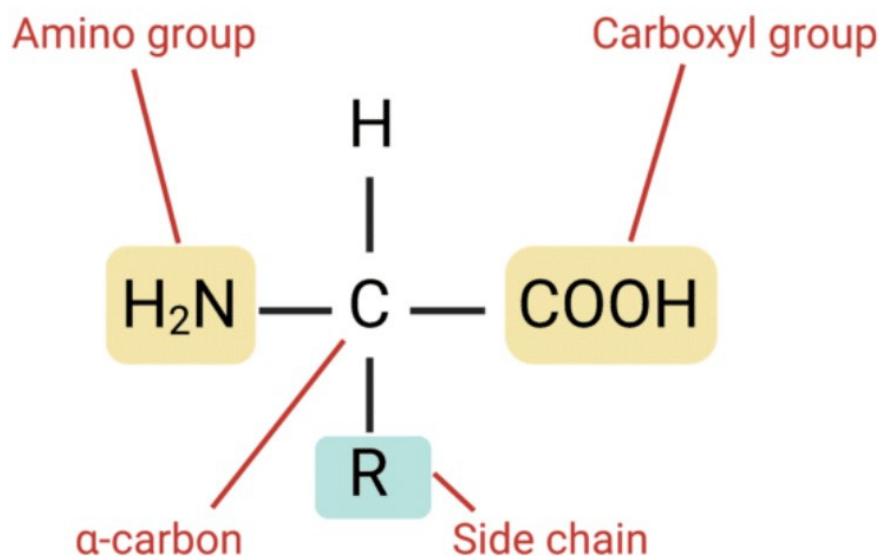


Fig. 1.34. The structure of an amino acid molecule

Of all the variety of existing amino acids (theoretically, the number of possible amino acids is unlimited), only those in which there is only one carbon atom between the amino group and the carboxyl group participate in the formation of proteins.

Proteins include 20 standard amino acids, that is, amino acids whose inclusion in protein molecules is coded at the genetic level.

All amino acids that make up proteins are α -amino acids, since their amino group is in the α -position, that is, next to the carboxyl group.

All amino acids, except glycine, have an asymmetric carbon atom (i.e., a carbon atom with four different substituents) and are therefore optically active compounds. Amino acids contained in proteins belong to the L-series. L-configuration - the amino group is located on the left, D-configuration - the amino group is located on the right.

There are several classifications of amino acids:

1) By nutritional value:

- Basic (proteinogenic) amino acids – 20 amino acids, the residues of which are part of proteins;

- Substitute amino acids – can be synthesized in the human body and animals from metabolic products: alanine, arginine, asparagine, aspartic acid, histidine, glycine, glutamine, glutamic acid, isoleucine, serine, tyrosine, cysteine;

- Partially replaceable amino acids – synthesized in the body in insufficient quantities (arginine, histidine).

- Conditionally replaceable amino acids – synthesized in the body from essential amino acids: cysteine (synthesized from the essential amino acid methionine), tyrosine (synthesized from the essential amino acid phenylalanine).

- Essential amino acids – amino acids that cannot be synthesized in the human and animal body (isoleucine, leucine, lysine, methionine, phenylalanine, valine, tryptophan, threonine).

Threonine participates in the production of collagen and elastin, stimulates the production of antibodies and immunoglobulins. It also optimizes lipid metabolism, provides complex restoration of damaged muscle fibers.

Methionine. An irreplaceable amino acid, a powerful antioxidant and oncoprotector. Methionine normalizes the work of the liver, stimulates the breakdown of fatty acids, participates in the production of nucleic acids and proteins. In particular, collagen. Medicines containing methionine are often prescribed in the treatment of osteoporosis, allergies, and dystrophy of muscle fibers. Methionine is also included in sports supplements for gaining weight.

Lysine. A bioactive agent that is part of almost all protein compounds. Lysine is necessary for the formation of bones, joints and ligaments. Especially - in children and teenagers. It participates in the production of antibodies, enzymes, hormones and digestive enzymes. Therefore, nutritionists recommend taking lysine for children and adults (during the recovery period after injuries, sprains and surgical interventions).

Tryptophan. An indispensable compound that regulates lipid metabolism. Tryptophan suppresses appetite, accelerates the process of breaking down fat deposits. It is used for the treatment and prevention of cardiovascular diseases,

relieves headaches. And in a complex with other amino acids, it helps to remove toxins and impurities.

Phenylalanine. An irreplaceable compound that is not produced by body cells. Phenylalanine is necessary for the production of collagen, insulin, and enzymes. It is used in the treatment of arthritis, diseases of the brain and cardiovascular system. Phenylalanine improves memory and mental concentration. Therefore, it is part of complex pre-workout supplements and products for weight gain.

Valin. An essential amino acid that acts as a stimulant. Valine is necessary for muscle metabolism, repair of damaged tissues and for maintaining normal nitrogen metabolism in the body. It is a branched-chain amino acid, which means it can be used by the muscles as an energy source.

Isoleucine. One of the essential amino acids necessary for the synthesis of hemoglobin. Isoleucine is also one of the three aforementioned amino acids. These amino acids are very necessary for athletes, because they increase endurance and contribute to the recovery of muscle tissue.

Leucine. Essential amino acid. It protects muscle tissues and is a source of energy, as well as promotes the restoration of bones, skin, and muscles, so their use is often recommended during the rehabilitation period after injuries and operations.

2) According to the structure of the lateral radical:

- acyclic amino acids;
 - aliphatic essential amino acids (monoamino-monocarboxylic) – glycine, alanine, valine, leucine, isoleucine;
 - aliphatic substituted amino acids;
 - hydroxyamino acids (serine, threonine);
 - sulfur-containing (methionine, cysteine);
 - carboxyamino acids (monoaminodicarboxylic acids) - aspartic acid, glutamic acid;
 - amides of dicarboxylic acids (asparagine, glutamine);
 - diamino acids (diaminomonocarboxylic acids) – lysine, arginine;
- Cyclic amino acids:
- aromatic amino acids (phenylalanine, tyrosine);
 - heterocyclic amino acids (tryptophan, histidine);
 - cyclic imino acid (proline).

3) By the polarity of radicals, that is, the ability of amino acids to interact with water at physiological pH values (about pH 7.0):

- non-polar (hydrophobic) (alanine, valine, leucine, isoleucine, proline, phenylalanine, tryptophan, methionine);
- polar uncharged (glycine, serine, threonine, tyrosine, cysteine, asparagine, glutamine);
- polar negatively charged (glutamic acid, aspartic acid);
- polar positively charged (lysine, arginine, histidine);

4) According to acid-base properties:

- acidic – with additional carboxyl groups in the side radical (monoaminodicarboxylic acids: aspartic and glutamic acids);
- the main ones – diaminomonocarbon (lysine, arginine) and histidine;

– neutral – the remaining amino acids, in which the lateral radical does not show either acidic or basic properties.

5) By chemical structure:

– aliphatic – glycine (Gly), alanine (Ala), valine (Val), leucine (Lei), isoleucine (Ile);

– oxyacids – serine (Ser), threonine (Tre);

– dicarboxylic – aspartic acid (Asp), glutamic acid (Glu);

– dibasic – lysine (Lys), histidine (His), arginine (Arg);

– aromatic – phenylalanine (Phen), tyrosine (Tyr), tryptophan (Try);

– sulfur-containing – cysteine (Cys), cystine (Cyt), methionine (Met).

6) By biochemical purpose:

– glucogenic – through a number of chemical transformations enter the pathway of glycolysis (glucose oxidation) - Gly, Ala, Tre, Val, Asp, Glu, Arg, His, Met;

– ketogenic – participate in the formation of intermediate products of lipid metabolism of ketone bodies – Lei, Ile, Tyr, Fen.

Amino acids can be divided into three groups. The first are synthesized in the body, they are called non-essential; the second - insufficiently synthesized in the body – semi-non-essential; the third - they come with food - are essential (8 such acids: Val, Leu, Ile, Phe, Trp, Thr, Lys, Met). There are 21 proteinogenic amino acids in living organisms.

Non-essential amino acids are able to replace each other in the diet, as they are converted into each other or synthesized from intermediate products of carbohydrate or lipid metabolism.

The absence of at least one essential amino acid in food causes a negative nitrogen balance, disruption of the central nervous system, growth arrest and severe clinical consequences such as vitamin deficiency.

An insufficient amount of one essential amino acid leads to incomplete assimilation of others.

This regularity obeys Liebig's law, according to which the development of living organisms is determined by that indispensable substance that is present in the smallest amount. The dependence of the functioning of the body on the number of essential amino acids is used in determining the biological value of proteins by chemical methods. The method of X. Mitchell and R. Block is most widely used, according to which the amino acid score (A.S.) is calculated.

The score is expressed as a percentage or a dimensionless value, which is the ratio of the content of an essential amino acid (A.A.) in the studied protein to its amount in the reference protein. When calculating the score as a percentage, the formula looks as follows:

$$\text{Amino acid score} = \frac{\text{mg of amino acid in 1.0 g of test prot}}{\text{mg of amino acid in 1.0 g of ref. prot}}$$

The amino acid composition of the reference protein is balanced and perfectly meets the needs of the human body in each essential acid, which is why it is also called "ideal".

The amino acid with the lowest value is called the first limiting amino acid. The value of the score of this amino acid determines the biological value and degree of assimilation of proteins. For example, A.S. chicken egg –1; cow's milk – 0.95; rice – 0.67; soybeans – 0.55; wheat – 0.53. Usually the score is calculated for the three most deficient amino acids: lysine, methionine, tryptophan 3:3:1.

The ratio of the sum of essential amino acids to the sum of replaceable ones should not be lower than 0.4.

Amino acids are amphoteric electrolytes, since the amino group has basic properties, and the carboxyl group has acidic properties. In aqueous solutions in the pH range of 4–9, amino acids exist mainly in the form of bipolar ions, which are called zwitterions.

The amino acid radical can be hydrophilic (polar) or hydrophobic (nonpolar), which ensures the spatial structure of proteins and their properties (Fig. 1.35).

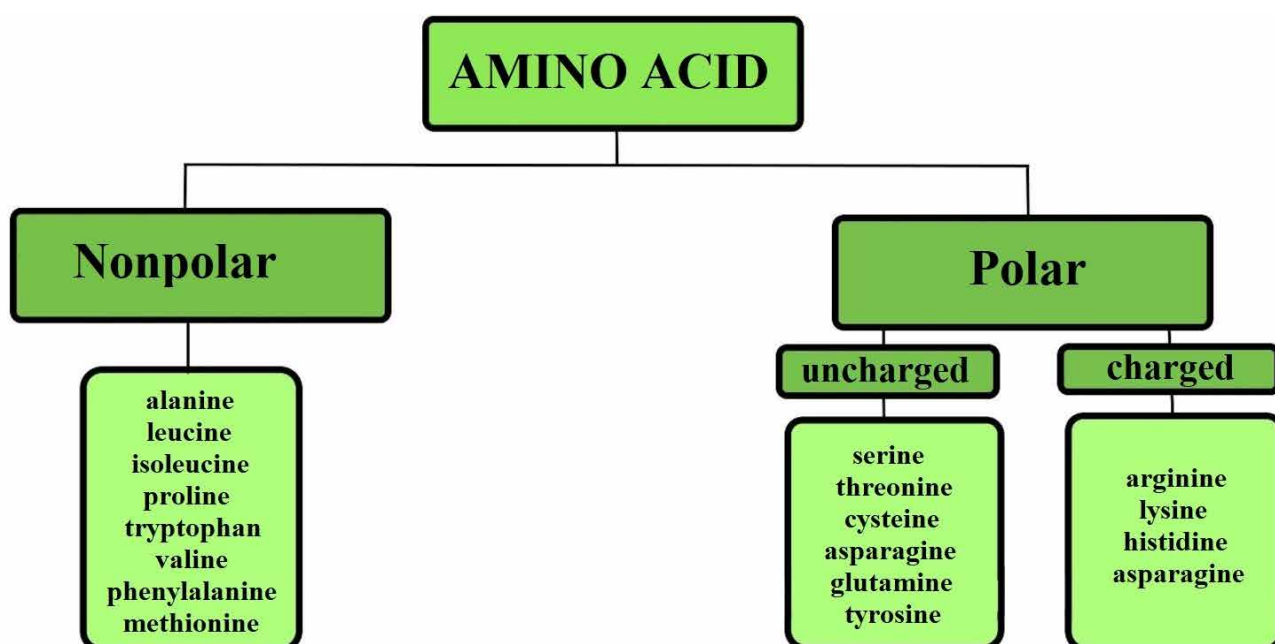


Fig. 1.35. Classification of amino acids

Proteins containing a large number of non-polar amino acids are insoluble in water, and proteins consisting of most polar amino acids are, accordingly, well soluble in water. This is due to the fact that in insoluble proteins, hydrophobic groups are located on the surface of fibrils, and in proteins that are well soluble in water, on the contrary, hydrophobic groups are located inside the molecules, and hydrophilic groups are located on the surface of molecules, which ensure high solubility.

Amino acids with non-polar or hydrophobic radicals:

- aliphatic amino acids – alanine, valine, leucine, isoleucine, methionine;
- aromatic – phenylalanine;
- heterocyclic – tryptophan. Imino acid is proline.

Amino acids with polar, uncharged radicals:

- glycine. hydroxyamino acids – serine, threonine, tyrosine. An amino acid with a sulfhydryl group is cysteine;

- with an amide group - asparagine, glutamine;
- Amino acids with negatively charged radicals:
 - aspartic acid;
 - glutamic acid.
- Amino acids with positively charged radicals:
 - lysine Arginine;
 - histidine.

1.3.2. Biological role of amino acids

The biological role of amino acids, first of all, consists in their participation in the metabolism of substances in the living organism. In addition, amino acids are involved in protein synthesis (they are part of protein molecules) and are a component of nucleic acids. The biological role of amino acids is also expressed in maintaining a constant pH level. It is not entirely correct to consider the biological properties of amino acids and their role separately from proteins, since these substances are closely related to each other.

Amino acids have a plastic property, that is, at the expense of proteins, they ensure the formation of all organs. Any tissue of the human body (connective, nervous, muscular or epithelial) consists of 80 % proteins. Another biological property of amino acids is that all substances that are responsible for the transmission of nerve impulses mostly consist of proteins.

Therefore, in case of their deficiency, the body is threatened with serious problems on the part of the nervous system.

Some amino acids are involved in the processes of glycogen biosynthesis in the liver. In their absence, certain chemical reactions will be disturbed, as a result of which malfunctions in the body may occur. Apart from the above-mentioned biological properties of amino acids, one more equally important property should be noted, which is to support the biosynthesis of many hormones. For their biosynthesis, nitrogenous compounds are required, in case of deficiency of which the body is threatened with serious consequences caused by the improper functioning of many organs.

Amino acids are part of sports nutrition and compound feed. Amino acids are used in the food industry as flavor additives, for example, the sodium salt of glutamic acid. The composition of natural proteins - biopolymers - includes approximately 20 different α -L-amino acids as monomer residues. All other amino acids in the composition of tissues of animals, plants and microorganisms (more than 200) exist in a free state and in the form of short peptides or complexes with other organic substances.

Knowledge of the structure and chemical properties of α -L-amino acids is necessary for understanding their reactivity, transformations, and biological activity in the human body in normal and pathological conditions, as well as their use in clinical practice for diagnosis and treatment. Disturbances in the metabolism of aromatic (phenylalanine, tyrosine) and branched (valine, leucine, isoleucine) α -L-amino acids in the human body are associated with genetic defects of their metabolic enzymes (hereditary disorders).

For example, the accumulation of phenylalanine in the blood is associated with a disease in which there is a delay in the child's mental and physical development (phenylketonuria), the accumulation of tyrosine (albinism) also affects the child's development.

1.3.3. Methods of separation and determination of amino acids

1) Separation of amino acids using ion-exchange chromatography Ion-exchange chromatography of amino acids is based on the different ability of the separated amino acids to ion exchange with one or another ionite. A mixture of amino acids obtained by acid hydrolysis of proteins is separated on a chromatographic column with a cation exchange resin. Such a synthetic resin contains tightly bound negatively charged groups (for example, sulfonic acid-SO₃⁻ residues) to which Na⁺ ions are attached. A mixture of amino acids is applied to the cation exchanger in an acidic environment (pH 3.0), where amino acids are mainly cations, that is, they carry a positive charge. Positively charged amino acids attach to negatively charged resin particles. The greater the total charge of the amino acid, the stronger its bond with the resin. Thus, amino acids lysine, arginine and histidine bind to cation exchangers the strongest, and aspartic and glutamic acids – the weakest. The release of amino acids from the column is carried out by washing (elution) them with a buffer solution with increasing ionic strength (that is, with increasing NaCl concentration) and pH. When the pH of the medium increases, amino acids lose a proton, as a result, their positive charge decreases, and therefore, the strength of binding with negatively charged resin particles. Each amino acid leaves the column at a certain pH value and ionic strength. By collecting the solution (eluate) in the form of small portions from the lower end of the column, fractions containing individual amino acids can be obtained.

2) The method of thin-layer chromatography: The chromatographic method belongs to the physico-chemical methods of separation and analysis of a mixture, in which its components are distributed between two phases - mobile and stationary. Depending on the atomic-molecular interaction of the components of 18 mixtures with a stationary phase, adsorption, ion exchange, distribution and gel chromatography are distinguished. Gaseous and liquid substances of any nature and in any quantity can be separated by chromatographic methods. The most common is chromatographic separation in tubes filled with sorbent (column chromatography), as well as in a thin layer of sorbent applied to a plate (thin-layer chromatography).

Qualitative reactions to amino acids

Ninhydrin reaction. Free α -amino acids form a blue-violet complex with ninhydrin (triketohydrin dehydrate). The reaction consists in the fact that when α -amino acids are heated with a solution of ninhydrin, α -amino acids are oxidized by the oxygen of ninhydrin and undergo oxidative deamination with the formation of ammonia and decarboxylation with the formation of aldehyde and CO₂. At the same time, ninhydrin is restored (Fig. 1.36).

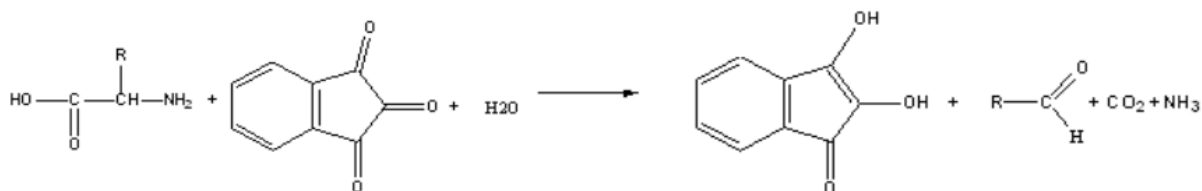


Fig. 1.36. Ninhydrin reduction reaction

The reduced ninhydrin condenses with ammonia and the oxidized ninhydrin molecule, forming a condensation product colored violet-blue (Fig. 1.37). This reaction is widely used for the quantification of amino acids and peptides.

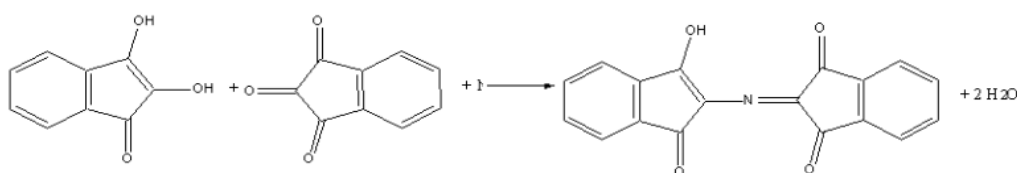


Fig. 1.37. Ninhydrin reaction

Fluorescamine reaction. This reaction is more sensitive than ninhydrin. Fluorescamine forms fluorescent complexes with α -amino acids. Fluorescamine itself and its hydrolysis products do not fluoresce, so they do not interfere with the quantitative determination of reaction products.

Xanthoprotein reaction. The xanthoprotein reaction is characteristic of cyclic amino acids tyrosine and tryptophan. This reaction is also given by simple aromatic compounds, for example, phenol, benzene. The xanthoprotein reaction consists in the fact that tyrosine and tryptophan form yellow nitroderivatives when heated with concentrated nitric acid. The cyclic amino acid phenylalanine is nitrated only in a mixture of concentrated sulfuric and nitric acids. Nitro derivatives of amino acids in an alkaline environment form salts of quinoid nature, colored in orange (Fig. 1.38). The name xanthoprotein comes from the Greek "xanthos" – yellow. This reaction is characterized by high sensitivity.

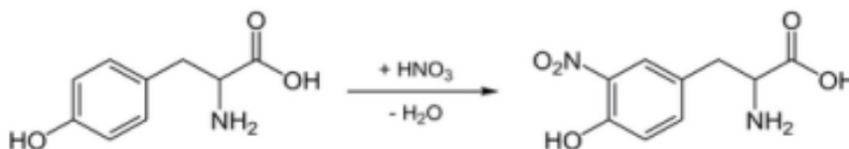


Fig. 1.38. Xanthoprotein reaction

Milon's reaction. This is a specific reaction to tyrosine (an amino acid containing a phenolic hydroxyl). Under the conditions of heating phenols and their derivatives with Milon's reagent (mercury nitrate (I and II) in 4M HNO₃ containing HNO₂ impurities) a red-colored mercury ortho-nitrotyrosine salt is formed.

Sakaguchi's reaction. The reaction is used to identify the guanidine group of the amino acid arginine. When guanidine reacts with sodium hypobromite (NaBrO) and α -naphthol in an alkaline medium, compounds with a red color are formed.

Ehrlich's reaction. The reaction is used to detect the indole ring of tryptophan, which upon interaction with p-dimethylaminobenzaldehyde in an acidic environment gives compounds with a purple color.

Foley's reaction. The reaction is used to determine cysteine and cystine – amino acids containing weakly bound sulfur. The principle of determination is that when the specified amino acids are boiled with an alkali solution, sulphide sulfur is split off. The latter is easily detected by the reaction of the formation of a black-brown precipitate of lead (II) sulfide. Methionine does not participate in the Foley reaction, since in this amino acid sulfur is tightly bound and does not split under the action of alkali (Fig. 1.39).

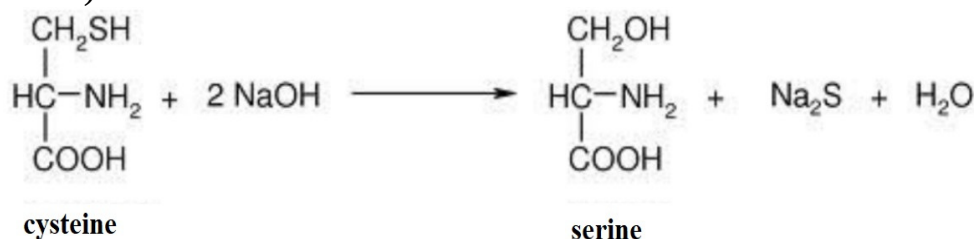


Fig. 1.39. Foley's reaction

1.3.4. Bonds in a protein molecule

The types of bonds in a protein molecule are presented in Fig. 1.40.

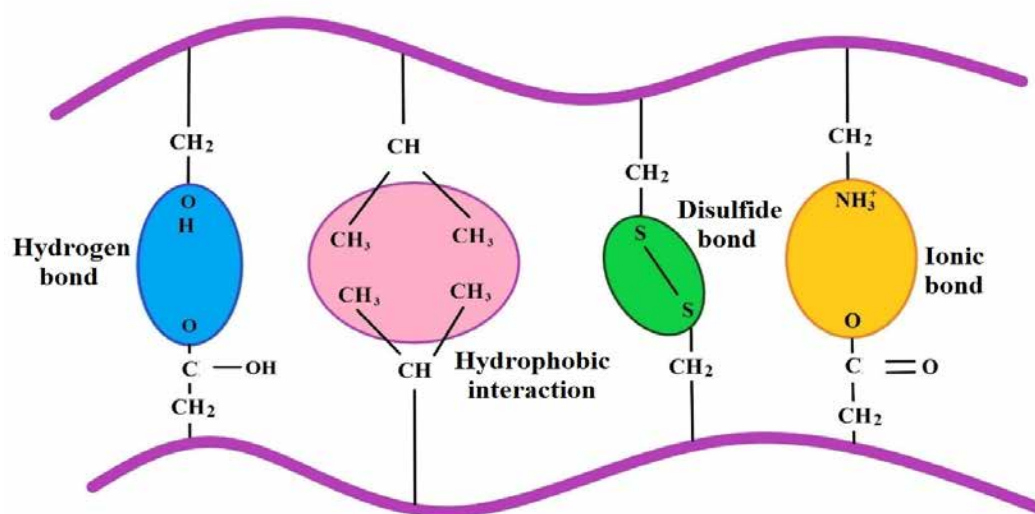


Fig. 1.40. Types of bonds in a protein molecule

A protein molecule is formed thanks to chemical bonds of different strengths. Characteristics of covalent and non-covalent bonds in proteins shown in Fig. 1.40 below.

Covalent.

1. A peptide bond is formed between the α -carboxyl group of one amino acid and the α -amino group of another amino acid, due to which the amino acids are connected to each other in a polypeptide chain and the primary structure of the protein is formed.

2. Disulfide bonds are formed between residues of the amino acid cysteine due to the oxidation of thiol groups in disulfide bonds. Disulfide bonds can occur between

the sulfhydryl groups of cysteine residues of different polypeptide chains or between two cysteine molecules of the same chain as a result of the detachment of hydrogen atoms from sulfhydryl groups.

Non-covalent.

1. Hydrogen bonds are formed between positively charged hydrogen and negatively charged (electronegative) elements (atoms of oxygen, nitrogen, phosphorus).

2. Ionic bond (electrostatic interaction) occurs in those cases when the side chains contain charged groups – NH_4^+ cations and SOO^- anions.

3. Hydrophobic bond (hydrophobic interactions) arise as a result of the interaction of nonpolar alkyl groups of side chains of amino acids alanine, valine, leucine, isoleucine due to van der Waals forces.

1.3.5. Spatial structures of proteins

According to the method of folding and association of polypeptide chains, four levels of the spatial structure of the protein are distinguished (Fig. 1.41):

- primary;
- secondary;
- tertiary;
- quaternary.

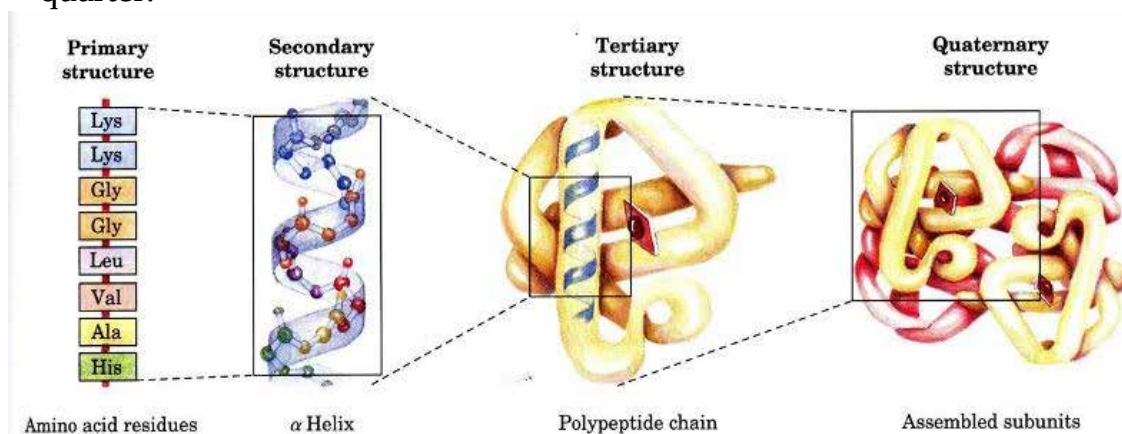


Fig. 1.41. Levels of the spatial structure of the protein

Amino acids are repeated in different combinations in a protein molecule. The sequence of alternating amino acids in the polypeptide chain affects the property of the protein molecule and is called the primary structure.

The primary structure of proteins is formed by peptide bonds, that is, covalent bonds. Polypeptide chains of amino acids by spatial arrangement form a helix, which forms the secondary structure of the protein.

The secondary structure of a protein is the spatial arrangement of individual sections of polypeptide chains, these sections can be ordered (α -helix, β -helix) or disordered.

The α -helix is right-handed and is stabilized by disulfide and hydrogen bonds formed between the amino acids of the polypeptide chain. In the α -helix, there are 37

amino acid residues for every 10 turns. The pitch of the spiral, that is, the distance between turns, is 0.54 nm, and the pitch of the turn is 26°. The period of identity, that is, the length of the segment of the helix is completely repeated along the length of the polypeptide chain and is equal to 2.7 nm (18 amino acid residues).

However, there are factors that prevent the formation of α -helices:

- the location of identically charged amino acids next to each other and mutual repulsion occurs;
- arrangement of amino acids with large radicals next to each other - spatial inconsistency (Fig. 1.42).

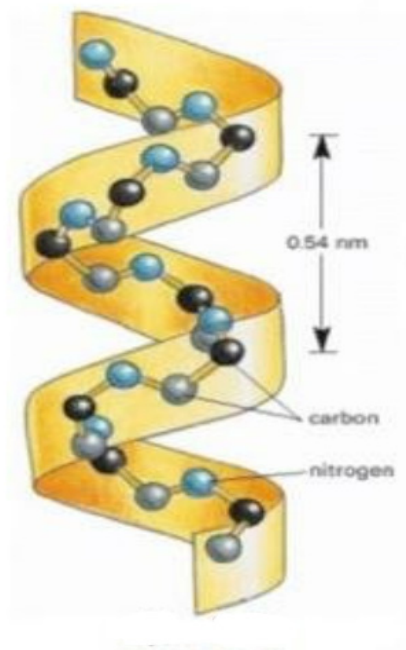


Fig. 1.42. Scheme of the α -helix of the secondary structure of the protein

The amino acid proline can disrupt the structure of the α -helix and change the direction of the polypeptide chain.

The β -folded secondary structure of the protein is represented by a folded layer where the polypeptide chains are interconnected by hydrogen bonds (Fig. 1.43).

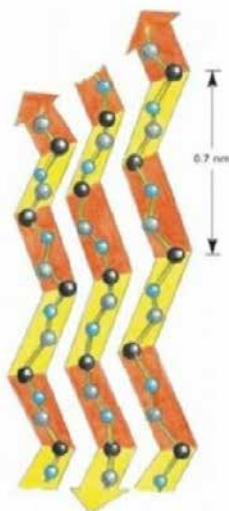


Fig. 1.43. β -folded secondary structure of the protein

This structure is characteristic of fibrillar proteins (collagen).

In the β -helix, there is a 51st amino acid for every 10 turns. According to this arrangement, the turns are closer to each other, compared to the α -helix. α - and β -structures are capable of mutual transitions.

Disordered structures are a disordered arrangement of the protein chain in space.

Tertiary structure is a spatial conformation of a polypeptide, which is formed by the elements of the secondary structure and is determined by the interaction between amino acid radicals. The tertiary structure is formed by covalent bonds (peptide and disulfide) and non-covalent bonds (hydrogen, electrostatic interactions, van der Waals forces, hydrophobic interactions of the side chains of amino acid radicals).

The quaternary structure of a protein is the arrangement of several polypeptide chains in a single protein complex. The quaternary structure is formed by hydrogen, hydrophobic, and, in some cases, disulfide bonds.

1.3.6. Characteristics of food proteins

Proteins of grain crops. The average protein content in cereals ranges from 7 to 17 %. The most protein-rich among cereals is wheat, the least amount of protein is found in rice and corn (7...9 %).

Proteins are unevenly distributed between the morphological parts of the grain.

The main amount of them falls on the endosperm (65...75 %); on the embryo up to 22%, on the aleurone layer up to 15.5 %.

Albumins dissolve in water. Globulins dissolve in aqueous solutions of various salts, they are insoluble in pure water.

Prolamins are the most characteristic proteins for the grain of most cereal crops. They dissolve in 60...80% ethanol solution. Prolamins include gliadin from wheat and rye (a component of gluten), hordein from barley, zein from corn, and avenin from oats. Glutelins dissolve in alkali solutions (0.1...0.2 %).

Gluten proteins are also contained in the grains of some varieties of barley, wheatgrass, etc.

The content of gluten in wheat grain and flour is an important indicator of quality. Raw gluten contains 2/3 (66 %) water and 1/3 dry matter, which mainly consists of proteins.

Gluten is a complex protein complex consisting of 2 fractions - gliadin and glutenin in a ratio of 1:1 (proteins make up 80...85 %, carbohydrates 10...15 %, lipids 2...8 %).

Gluten of different quality has the same amino acid composition and consists of the same protein components.

Disulfide (-S-S-) and hydrogen bonds play an important role in the formation of the gluten structure and its properties. It was established that gliadin has internal -S-S- bonds, that is, it consists of several polypeptide chains connected by disulfide bonds (Fig. 1.44).



Fig. 1.44. Disulfide bonds stabilizing the gluten protein molecule

The strength and at the same time mobility of the structure of the gluten molecule create specific rheological properties - elasticity, extensibility, etc. This is explained by the presence of a large number of non-covalent bonds, which are easily broken and re-emerge under various actions on the protein. The quality of gluten is closely related to the number of disulfide bonds, which is estimated by the ratio of the number of -S-S-bonds to the number of SH-groups.

Proteins of oil crops. The average content of protein substances in the seeds of certain oil crops varies from 16 to 28 %.

Proteins of oilseeds are a mixture of proteins similar in their properties. The proteins of oilseeds contain 10...30 % albumins and up to 90% globulins.

Proteins of aleurone grains (aleirins) are represented mainly by globulins (80...97 %) and a small amount of albumins and glutelins (1...2 %). Prolamins are practically absent.

Proteins of vegetables and fruits. The relatively low content of nitrogenous substances in potatoes (approximately 2 %), vegetables (1.0...2.0 %) and fruits (0.4...1.0 %) indicates that these types of food plant raw materials are not of great importance in the provision of proteins in food products

Potatoes, despite their low protein content, are more important as a source of nitrogenous substances due to their significant consumption, which is an average of 330 g per day, thus 6...8 % of a person's total daily need for protein is satisfied with this type of product.

The amount of protein nitrogen in potato tuberine is 1.5...2.5 times more than non-protein nitrogen, while in vegetables and fruits, on the contrary, it is less than 50%.

Tuberin protein contains all amino acids, including essential ones.

In terms of the content of essential amino acids, excluding tryptophan, tuberin surpasses wheat protein, approaching soy protein and egg protein in composition.

Meat proteins. The protein content in meat varies between 11...22 %. Proteins of muscle tissue are well balanced in terms of amino acid composition.

The main muscle proteins are myosin and actin.

Myosin has ATP-hydrolyzing activity and the ability to bind to insoluble F-actin. Actin - this protein accounts for 15 % of all muscle tissue proteins; exists in 2 forms - in the form of globular actin, which accounts for 25% of the total mass of muscle protein and fibrillar actin.

Myoglobin is a water-soluble protein, a chromoprotein, the prosthetic group of which is heme, its structure is represented by one polypeptide chain consisting of 153 amino acid residues; the content of myoglobin in muscle tissue is approximately 1 % of the sum of all tissue proteins.

Myogen consists of a complex of myogens A, B, C and makes up approximately 20% of all protein fibers. It is soluble in water, forming homogeneous solutions with low viscosity. The temperature of denaturation of salt-free myogen is 55...60 °C. Over time, myogen goes into an insoluble state.

Connective tissue proteins include collagen and elastin - the main fibrillar proteins of connective tissue.

Elastin is a specific protein of elastic connective tissue. Like collagen, elastin is rich in glycine and alanine, at the same time it contains a large number of lysine residues and little proline. It exists in the form of a network of cross-linked polypeptide chains, due to which it has great elasticity.

Milk proteins. The total protein content in milk ranges from 2.9 to 3.5 %.

Among them, two main groups are distinguished: caseins and whey proteins.

The main milk proteins are casein and whey proteins: α -lactoalbumin, β -lactoglobulin, immunoglobulins. The content of α -lactoalbumin is 0.1%.

α -Lactalbumin is necessary for the synthesis of lactose in milk from galactose and glucose. Another main milk protein is β -lactoglobulin, which has high thermal stability (can withstand heat treatment up to 100 °C), stable in an acidic environment.

Immunoglobulins perform a protective function, lactoferrin and lysozyme (enzyme) are carriers of antibacterial properties.

Casein – the main milk protein (2.7 %) is a phosphoprotein; it contains a large number of phosphoserine residues, which are formed as a result of enzymatic phosphorylation of hydroxyl groups of serine.

Casein is present in milk in the form of its precursor caseinogen (80% of cow's milk proteins). Contains methionine, lysine, tryptophan.

Egg proteins. The main component of egg protein is egg albumin – ovoalbumin is a glycoprophosphoprotein (2 % mannose and 1.2 % glucose).

Ovalbumin contains four thiol and one disulfide group. During the storage of eggs, the more thermostable S-ovoalbumin (coagulation temperature 92.5 °C) is formed from the native protein (coagulation temperature 84.5 °C).

The content of S-ovoalbumin increases from 5 % in fresh eggs to 81 % in eggs that have been stored for six months in the cold. In solutions, ovalbumin is unstable to mechanical influences. As a result, shaking quickly denatures and coagulates, this is interphase coagulation, which occurs due to the unfolding and aggregation of protein molecules.

Ovumucoid is an egg protein, chemically a glycoprotein, sensitive to heat. It contains galactose – 1...1.5 %; mannose – 4.3...4.7 %; glucose – 12.5...15.4 %. In an acidic environment, ovumucoid shows high resistance to thermal effects, and in an alkaline environment (pH = 9.0) it quickly denatures at 80 °C.

Ovomucin is an egg protein, chemically a glycoprotein with a carbohydrate content of approximately 20%. In solution, it is very resistant to heat. The complex of lysozyme and ovomucin helps to dilute the protein at pH = 9.0 during egg storage.

Avidin is a glycoprotein that contains approximately 10% carbohydrates. Its amino acid sequence matches the sequence of lysozyme by 12%. Avidin is able to form a biologically inactive complex with biotin (vitamin H).

The amount of protein in the yolk is 18 %. The temperature of denaturation of yolk proteins is 65 °C. Protein substances in the yolk are represented mainly by lipoproteins, which contain from 17 % to 38 % of bound lipids. Approximately 70 % of the total amount of protein is accounted for by lipovitellins; 24 % - for levetin; 9 % – on phosvitin.

Livetin is a protein fraction of well-soluble proteins in water. They are complete and contain much less phosphorus compared to lipovitelin.

According to the most important indicators, the biomass of microorganisms is characterized by a very high nutritional value. To a considerable extent, this value is determined by proteins: in most species, they make up a significant proportion of the dry mass of cells.

Questions for discussion and self-examination

- 1. Describe the structure and composition of a protein molecule.*
- 2. What are the types of bonds in a protein molecule and their influence on the functional properties of proteins?*
- 3. Give the classification of proteins.*
- 4. Features of the structure of amino acids.*
- 5. Describe the proteins of food products.*

Topic 1.4. Proteins: physico-chemical and functional properties

1.4.1. Physicochemical properties of proteins

The main physicochemical properties of proteins that ensure the course of the technological process, the quality and yield of finished products:

- molecular weight;
- amphoteric;
- isoelectric point;
- hydrophilicity and hydrophobicity;
- hydration, dehydration, solubility;
- denaturation;
- destruction.

The molecular weight of proteins, depending on the length of the polypeptide chain, can range from 6 thousand to more than 1 million.

Amphotericity of proteins. Amino acids, which make up protein, belong to amphoteric substances, as they show the properties of acids and alkalines at the same time.

This property is explained by the fact that all amino and carboxyl groups of amino acids are involved in the construction of peptide bonds. Amino groups remain free in molecules of diamino acids, and carboxyl groups remain free in molecules of monoaminodicarboxylic acids. For example, when a protein is dissolved in water, protons are split off from the carboxyl groups, and the protein acquires the properties of a weak acid.

Protons that appeared in the soluble form are attached to NH_2 -groups, as a result of which they change to the ionized form – NH_3^+ .

In a strongly acidic environment, a bipolar ion of an amino acid turns into a cation, capable of moving toward the cathode in an electric field, and in an alkaline environment, a bipolar ion of an amino acid turns into an anion. Thus, a protein molecule has both a positive and a negative charge.

It should be noted that the amphoteric nature of proteins is determined not only by the presence of free amino or carboxyl groups in the protein, but also by the presence of other functional groups. The SH group of cysteine and the OH group of tyrosine have slightly acidic properties.

The isoelectric point is the pH value that corresponds to the equality of the total number of positive charges and the total number of negative ones, that is, the total or effective charge of the globule is equal to zero.

The isoelectric point is the main electrochemical constant of proteins. Proteins at this point are electrically neutral, their swelling and solubility are the lowest.

The pH value of the protein solution at the isoelectric point corresponds to the termination of the transfer of protein macroions in the electric field. If the pH of the solution deviates from the isoelectric point, the effective charge will increase. In the pH region above the isoelectric point, the charge will be negative, and at pH below the isoelectric point, the protein will have a total positive charge

The stability of protein foams is observed at the isoelectric point. The change in the emulsifying capacity of the protein correlates well with the change in protein solubility when the pH deviates from the isoelectric point and with the change in the ionic strength of the protein solution. This feature is used in the isolation of proteins from raw materials (animal and vegetable) and in the processing of proteins in the process of food production.

Thus, by changing the pH of the medium in one direction or another from the isoelectric point, it is possible to increase the degree of protein hydration due to adsorption-bound water.

Proteins have a large number of carboxyl and amine groups in their composition. Depending on the ratio of acidic and alkaline groups, each protein has its own isoelectric point. Accordingly, for acidic proteins, the isoelectric point is within $\text{pH} < 7$, that is, in an acidic environment, and for alkaline proteins in an environment at $\text{pH} > 7$.

In the Table 1.12 values of the isoelectric point of individual proteins are given.

Table 1.12. The value of the isoelectric point of individual proteins

Protein	Isoelectric point, pH
Egg albumin	4.7
Serum albumin	4.59
Gelatin	5.05
Casein	4.7
Lactoglobulin	5.1
Phosphorylase	5.8
Hemoglobin	6.87
Chymotrypsin	8.6
Lysozyme	10.5
Myosin	4.6...5.2
Pepsin	1.0
Cytochrome	10.65

Depending on the amino acid composition of proteins, their solubility may vary. That is, the solubility of proteins is directly affected by the polarity of the side chains of amino acids that are part of them, namely: hydrophilicity and hydrophobicity.

As mentioned above, hydrophilicity and hydrophobicity depend on the ratio of polar and nonpolar groups located on the surface of the protein molecule. The more hydrophilic residues are included in the composition of proteins, the more their solubility will increase, and, conversely, if proteins mainly contain hydrophobic residues, their solubility decreases or they are insoluble.

The nature of the influence of water on the processes taking place during the production of food products is determined, first of all, by the total amount of water, and secondly, by the forms of its connection with components, mainly with proteins.

There are four forms of moisture connection with materials, in particular with components of food products:

- chemical;
- adsorption;
- osmotic;
- capillary-bound.

At the same time, chemically bound water is divided into hydrate water in the composition of hydroxyl groups (ionic bond) and water of molecular compounds in the form of crystal hydrates (molecular bond). Compared to all forms of bonding, chemically bonded water has the most energy.

Adsorption-bound water is formed as a result of the attraction of water dipoles by polar molecules located on the surface of the substrate and is characterized by an average bond strength. When such a connection is formed, water molecules can retain their properties, while physical adsorption occurs. If a water molecule splits into ions, chemical adsorption or chemisorption occurs. Simultaneously with the adsorption of water vapor or water on the surface of product molecules, diffusion of moisture into the mass of the sorbent is possible. At the same time, the absorption process is observed.

Wetting of capillary-porous bodies occurs as a result of moisture adsorption, the formation of a solution and its subsequent penetration into the cells of the food product due to the difference in the concentration of dissolved substances takes place. At the same time, osmotically bound water is formed.

Hydration of food proteins is caused by adsorption and chemically bound water.

Protein hydration is the ability of proteins to bind water, while they exhibit hydrophilic properties: they swell, increase in mass and volume.

The hydrophilicity of various proteins primarily depends on their structure. Hydrophilic amide (CO-NH^- peptide bond), amine (NH_2^-) and carboxyl (COOH^-) groups located on the surface of the protein macromolecule attract water molecules to themselves, orienting them on the surface of the molecule. Hydrated water, which surrounds the protein globules, prevents aggregation and precipitation, and, accordingly, ensures the stability of the protein solution.

During limited swelling, concentrated protein solutions form complex systems called jellies. Gels are non-flowing colloidal solutions characterized by plasticity and mechanical stability, which can retain their shape. Globular proteins can completely transition to a hydrated state and dissolve in water (milk proteins) and form a solution of low concentration.

In food technology, the ability of meat and fish proteins to provide additional hydration is used in marinating before frying. At the same time, meat and fish are treated with food acid (acetic, citric, lactic, etc.) or natural fruit juices containing a mixture of food acids. At the same time, the pH of meat and fish decreases to 3.0...3.5, that is, below the isoelectric point of the main meat proteins.

During heat treatment, the meat prepared in this way is less dehydrated, which makes it possible to obtain finished products with higher organoleptic quality indicators (juiciness, taste, consistency). Up to 8 % water is also added to minced

meat to obtain juicier chopped meat products (beefsteaks, schnitzels, cutlets, meatballs, zrazy, rolls, meatballs, meatballs, lyula-kebab).

In solutions of low concentration, protein molecules are fully hydrated due to the presence of an excessive amount of water. Such protein solutions are contained in milk, liquid dough, in some mixtures based on egg melange, etc.

In concentrated protein solutions and dehydrated protein gels, additional hydration of proteins occurs when water is added. This is observed, for example, when water or milk is added to the egg mass intended for making omelets. During further heat treatment, as a result of protein denaturation and structure formation, jelly is obtained.

The effectiveness of additional hydration in this case consists in improving the rheological parameters of the jelly - reducing its mechanical strength and elasticity.

At high concentrations of highly soluble salts, there are incomparably more salt ions than charged protein groups in the solution. At the same time, protein hydration with water can decrease, as the salt solution becomes a poor solvent for protein.

An increase in the concentration of salts in the solution also corresponds to an increase in the hydrophilicity of the solvent and an increase in the hydrophobic interaction between protein molecules.

As a result of hydration, proteins dissolve and swell. Protein dissolution is always preceded by a swelling process. It is characteristic of all high-molecular compounds and is never observed in low-molecular substances.

The dissolution process can be conditionally divided into four stages.

At the first stage, before dissolution, the system consists of pure components: low molecular weight liquid and protein.

The second stage of the process is swelling, which consists in the fact that liquid molecules penetrate the protein immersed in it, move the polypeptide chains and loosen it. The distance between molecules in a protein, as well as its mass and volume, increase.

The third stage of dissolution is that as the protein swells, the distance between the macromolecules increases so much that the macromolecules begin to detach from each other and pass into a layer of low-molecular-weight liquid. In the fourth stage of dissolution, polymer molecules are evenly distributed throughout the entire volume of the system, forming a true homogeneous solution.

Swelling, like dissolution, is selective. Proteins (polar polymers) swell well in polar liquids. For example, gelatin swells well in water.

The rate of swelling depends on the temperature. However, there are certain temperature ranges in which the protein denatures under the influence of heat, and therefore loses its ability to hydrate and swell.

The rate of swelling increases with an increase in the degree of polymer grinding, as this causes an increase in the contact surface of the swelling substance with the solvent.

The degree and speed of swelling is affected by the age of the protein: the younger it is, the greater the degree and speed of swelling.

The speed and degree of swelling of some proteins depend on the pH of the medium. For example, flour proteins swell better at pH <7, that is, in an acidic

environment. This dependence of swelling on the pH value is used in the preparation of some food products, for example, in the production of puff pastry.

Additional hydration of proteins is of great practical importance in the production of minced meat semi-finished products, when water and table salt are added to minced meat. When these components are mixed, the protein hydration process consists of two superimposed processes:

- dissolution of some proteins;
- swelling of others with the formation of jellies.

At the same time, the stickiness of the minced meat increases, as a result of which it is well formed in the form of semi-finished products intended for heat treatment.

Dry proteins of flour, groats, and legumes contained in products in the form of particles of dried protoplasm and aleurone grains swell when in contact with water, forming a solid, more or less dehydrated jelly.

A classic example of this type of hydration is the preparation of dough, in the process of which flour proteins swell when in contact with water, forming gluten. The rheological properties of dough prepared on the basis of flour and water largely depend on the ratio of these components. By changing this ratio, the degree of hydration of flour proteins is regulated and such properties of the dough as elasticity, viscosity, etc., are related to this process.

Such an indicator of the quality of finished products as juiciness and other organoleptic quality indicators related to it largely depend on the degree of protein hydration.

Dehydration is the loss of protein-bound water during drying, freezing, thawing of raw materials and heat treatment. Such important indicators as the moisture content of finished products and product yield depend on the degree of dehydration.

The loss of protein-bound water occurs under the influence of external influences. There is a distinction between irreversible dehydration of proteins, which occurs during freezing, frozen storage and thawing of meat, meat products, fish, during heat treatment of products, and reversible dehydration, which is a component of a purposeful technological process – sublimation drying of products.

During rapid defrosting of meat, dehydration of proteins is the result of incomplete restoration of protein systems disrupted during the freezing period. Dehydration of fish proteins is associated with their denaturation during freezing and subsequent storage. When defrosting these products, part of the water is released into the environment in a droplet-liquid state. Together with water, soluble substances are removed from the product - extractives, minerals, vitamins, proteins, etc.

Irreversible dehydration of proteins with the release of water into the environment occurs, for example, when cooking meat. About half of the water and soluble substances contained in the food enters the environment.

Reverse dehydration of protein substances can be demonstrated on the example of freeze drying of food products.

The sublimation drying method is based on the ability of ice to evaporate under certain conditions, bypassing the liquid phase.

During normal thermal drying, moisture evaporates from the outer surface of the material, and it continuously moves from the inner layers to the outer layers, causing

redistribution of water-soluble substances, salts, vitamins, etc. Such redistribution does not occur during freeze-drying.

Sublimation of ice starts from the surface of the material, then the sublimation zone deepens. Ice evaporates inside the product in the evaporation zone, and water vapor, overcoming the resistance of the dry layer, breaks through capillaries and cracks into the rarefied space of the drying chamber (sublimator), and then condenses and hardens in desublimators. The movement of steam inside the material is caused by the pressure difference in the drying chamber (sublimator) and condenser (desublimators).

In the process of sublimation drying, capillary-bound and osmotically bound water is removed from the product. Water, adsorbed by proteins, is removed from the product in its entirety, as its monomolecular layer, which is located on the surface of protein molecules, is very strongly connected to the protein.

X-ray structural studies have established that each polar group of the protein firmly holds a certain number of water molecules. This water, which was called "hydrate", can be removed only when the product is heated to 100 °C and above, which leads to protein denaturation. The amount of hydrated water can reach 5 % of the mass of dry protein.

The solubility of proteins depends on the pH of the medium and the presence of salts. At the pH corresponding to the isoelectric point, proteins have the lowest solubility, since the total charge of their molecules is zero and the particles are unable to repel each other due to electrostatic interactions with solvent molecules. In an acidic or alkaline environment, oppositely charged solvent ions (H^+ or OH^-) interact with the surface of protein particles, which are positively charged in an acidic environment and negatively charged in an alkaline environment, due to which the protein goes into solution. In an acidic environment, the protein has a positive charge in amino groups due to inhibition of dissociation of carboxyl groups ($-COOH$), and in an alkaline environment, a negative charge in carboxyl groups due to inhibition of dissociation of amino groups ($-NH_2$).

The solubility of proteins depends on the concentration of salts in a non-linear manner. When a small amount of salts is introduced, the solubility of proteins increases, because the ions interfere with the electrostatic interaction of the side groups of the protein with each other. High concentrations of salts, which reduce the hydration of polypeptide chains, on the contrary, strengthen hydrophobic interactions and lead to protein precipitation (salting out).

By solubility, proteins are divided into:

- albumins;
- globulins;
- prolamins;
- glutamines;
- protamines and histones;
- protenoids

Albumins are water-soluble proteins that precipitate when solutions are saturated with neutral salts. Albumins are widely distributed in nature (egg protein, milk).

The chemical composition is characterized by the content of leucine (15 %), a significant amount of sulfur-containing amino acids, lysine, aspartic and glutamic acids, as well as a small content of glycine.

Globulins, like albumins, are very common in animal and plant tissues. Unlike albumins, globulins do not dissolve in concentrated solutions of neutral salts. They are isolated by extraction with a 10 % salt solution.

They are coarsely dispersed and less hydrophilic than albumins. In terms of chemical composition, globulins are slightly different from albumins and contain more glycine (5 %) and a smaller amount of sulfur-containing amino acids.

Histones are alkaline proteins that contain 20–30 % alkaline amino acids. They dissolve in weak acids, precipitate with alcohol, do not contain tryptophan and, in most cases, cysteine and cystine.

Protamines dissolve in weak acids, do not precipitate during boiling. The content of diaminomono-carboxylic acids in their molecule is about 80 %, especially arginine.

Cysteine, tryptophan, and asparagine are not found in protamines, tyrosine, phenylalanine are often absent, so they do not give many color reactions to protein. Due to the high content of basic amino acids, protamines are a polyvalent organic cation that easily reacts with molecules that have an excess of negatively charged groups, for example, with nucleic acids.

Prolamins. This group of proteins is widespread in plants, dissolves well in 60...80% ethyl alcohol, and contains a lot of proline and glutamic acid. Lysine, arginine, and glycine are included in these proteins in very small amounts.

Glutelins, like prolamins, are proteins of plant origin, well soluble in alkaline solutions (0.2–2 % NaOH). They contain a large amount of glutamic acid and lysine.

Proteinoids are sparingly soluble proteins that do not dissolve in water, salt solutions, and acid and alkali solutions. Their composition is characterized by a high proportion of sulfur-containing amino acids. Proteinoids include fibrillar proteins: keratins, collagens, etc. They are characterized by high stability and elasticity.

Denaturation of proteins is a violation of the native spatial structure of the protein molecule under the influence of various external influences, which is also accompanied by a change in the biological and physicochemical properties of the product. In the process of denaturation, the quaternary, tertiary and secondary structures of the protein are destroyed without changing the primary structure (Fig.1.45).

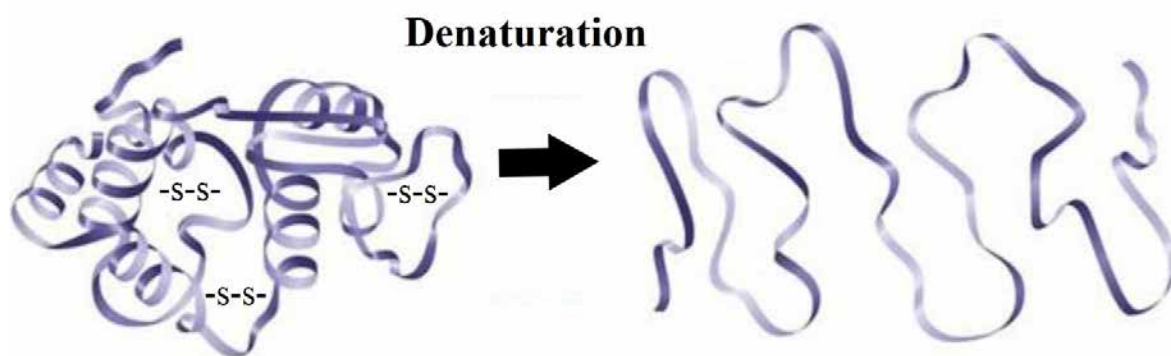


Fig. 1.45. Schematic representation of protein denaturation

In the process of denaturation, the colloidal state of the protein can change, its coagulation occurs.

From the outside, the loss of native properties by proteins is expressed in their folding and sedimentation. An example can be the coagulation of milk albumin during boiling.

At the same time, mainly hydrogen bonds are broken, the spatial structure of the protein changes, but the breaking of covalent bonds in the protein molecule does not occur.

Denaturation leads to the unfolding of the protein molecule (it no longer has spirals, layers, or any other types of sequential chain structure). In the denatured state, the amide groups of the peptide chain form hydrogen bonds with the water molecules surrounding them.

For example, when egg whites and cream are whipped, a foam is obtained, consisting of air bubbles surrounded by thin protein films, the formation of which is accompanied by the unfolding of polypeptide chains as a result of the breaking of bonds under mechanical influence. Thus, during the formation of films, partial or complete denaturation of the protein occurs. This type of denaturation is called **surface denaturation of the protein**.

Heat denaturation of proteins is of particular importance for technological processes. The mechanism of heat denaturation of proteins can be considered using the example of globular proteins.

The main molecule of a globular protein consists of one or more polypeptide chains. Such a structure is stabilized by weak bonds, among which hydrogen bonds, which form cross bridges between parallel peptide chains, play a major role.

During heat denaturation of proteins, water plays an active role, which participates in the formation of a new conformational structure of the denatured protein. Completely dehydrated proteins do not denature even with prolonged heating. The denaturing effect of external influences is stronger, the higher the hydration of proteins and the lower their concentration in the solution.

The temperature of protein denaturation increases in the presence of other heat-stable proteins and some substances of a non-protein nature, such as sucrose. This property of proteins is used when during heat treatment it is necessary to increase the temperature of the mixture (for example, when pasteurizing ice cream mixtures, making egg-butter creams), preventing delamination or structure formation in the protein colloidal system.

The appearance of previously hidden radicals or functional groups on the surface of a protein molecule after denaturation changes the physicochemical and biological properties of proteins. As a result of denaturation, the properties of proteins change irreversibly.

For example, it is not possible to prepare dough from heated flour, and cutlets from cooked meat, since denatured proteins do not have the ability to hydrate and form viscous elastic-plastic masses suitable for the formation of semi-finished products.

In more concentrated protein solutions, upon protein denaturation, a solid gel is formed that holds all the water contained in the colloidal system. As a result of the

aggregation of denatured protein molecules, a structured protein system is formed. Denaturation of proteins in concentrated solutions with the formation of a continuous gel occurs during heat treatment of meat, fish (sarcoplasmic proteins), chicken eggs and various mixtures based on them.

For example, to prepare omelets, add 38...75 % milk to the egg melange. The lower limits refer to fried omelettes, the upper ones to steamed omelettes. To prepare omelets from egg whites used in dietary nutrition, milk is added in the amount of 40 %, regardless of the method of heat treatment, since the concentration of proteins in the egg white is much lower than in the yolk.

Protein coagulation is a process of changing the colloidal state of proteins under the influence of various factors (temperature, pH of the medium, etc.). Depending on the properties and concentration of the protein, coagulation can proceed with the formation of final products with different aggregate states.

The coagulation temperature (temperature gel point) is the lowest temperature at which the protein changes its colloidal state.

Reaching the temperature gel point, systems with a low concentration of protein separate into two phases, one of which, protein, aggregates in the form of local flocculates, films, and the second is presented in the form of water.

Regardless of the type of protein, systems with a low concentration of protein due to the physical lack of protein in the system are not capable of gelation throughout the system, so delamination and syneresis are typical and objective stages of protein denaturation and coagulation. For example, milk during boiling (formation of lactalbumin films, scales), eggs dissolved more than 1.6 times with liquid (water, milk), chopped meat and fish masses that are excessively hydrated, liquid batter for pancakes .

If the system is highly concentrated in terms of the mass fraction of protein, then denaturation and the type of coagulation mostly depend on the type of protein. Such protein systems are capable of shaping, which is implemented in many technological processes: production of egg products, chopped fish, meat products, production of sausage products, etc.

Gel formation has a different character depending on the type of protein. Typically, when a protein forms a colloidal solution with water, it does not lose moisture as a result of coagulation, retaining it due to immobilization. Lyogels are formed under these conditions. In nature, the number of such proteins is small - proteins of eggs, blood plasma, animals, proteins of the biological fluid of krill. In terms of technology, they are quite scarce.

If the proteins are sufficiently hydrated, but concentrated, and form a dispersion with water, then, as a rule, coagulating during denaturation, they form gels that retain their shape, but are characterized by intense syneresis, that is, coagules. Coagules are obtained from a dispersion of meat and fish. Flour proteins behave similarly, but their objective loss of moisture is hidden by pasteurization of starch. The formation of gels of the second kind during coagulation and the accompanying processes is a key technological task, since most food products are formed thanks to this process. Realizing the ability of the protein to gel, as well as regulating this process, it is possible to control the quality of the final products.

Thus, by mixing proteins capable of forming lyogels with proteins capable of forming coagels, it is possible to reduce synergistic processes.

By introducing sucrose and other simple sugars or soluble dextrans, it is possible to increase the coagulation temperature of proteins, i.e. thermally stabilize them, which is widely used in the technology of sweet dishes and sauces using eggs. On the contrary, the use of high concentrations of salt, alcohol and other dehydrators lowers this temperature.

Sometimes coagulation processes are used to isolate proteins. An example can be the process of obtaining sour milk cheese, rennet cheese, hard cheese, casein.

Co-precipitation of proteins during coagulation is coprecipitation, with the production of products – coprecipitates. Coprecipitation occupies the most important place in the technology of extracting whey proteins from milk. Dry, soluble, egg-milk co-precipitates, etc. are produced.

One of the stages of changing proteins in the process of technological processing is the destruction of proteins.

Protein degradation – the destruction of the primary protein structure. The depth of destructive processes depends on many technological factors:

- temperature;
- pressure;
- the presence of enzymes;
- the presence of some components in an active form, etc.

Under the influence of chemical factors – chemical modification, for example, with acid anhydrides, oxidation, reduction, plasticine reaction, enzymatic modification, a violation is also possible at the level of the primary structure, which is a manifestation of destruction.

A typical example of temperature-dependent destruction of protein substances is the destruction of the protein component in the reaction of melanoid formation.

As you know, when high temperatures are used, especially in the process of frying and baking, protein substances are able to react with sugary substances with the formation of sucroamine complexes, after the breakdown of which the amine component, or more precisely, the amino acid residue in the process of oxidative deamination and decarboxylation, decomposes into an aldehyde with the number of atoms one less carbon than in the original amino acid, carbon dioxide, as well as ammonia. That is, the amino acid as a constituent part of the protein is destroyed, which leads to a change in the nutritional and biological value of the protein.

One of the examples of destruction is a change in the structure of collagen during heat treatment, which is important for the formation of the quality of meat products.

During heating in a humid environment at a temperature of 58...62 °C, collagen is welded, its denaturation and partial hydrolytic disintegration occur at the site of peptide bonds with the formation of high- and low-molecular products. During denaturation, the triple helices of native collagen are rearranged into single-chain, disorderly coiled molecules.

The destruction of the triple spirals of collagen occurs in three stages:

- breaking bonds within polypeptide chains;

- breaking of side bonds between chains;
- breaking hydrogen bonds between peptide chains and water molecules.

During the gradual and careful heating of collagen to 100 °C, it breaks down into gluten and polypeptides with a higher molecular weight. Under conditions of rapid and intense heating, gelatines are formed, the molecular weight of which is smaller.

The following technological factors influence the transformation of collagen into gluten:

- **Ambient temperature.** For example, when frying meat, poultry, and fish, when the temperature inside the product does not exceed 80...85 °C, the transition of collagen into gluten proceeds slowly.

In this regard, technological processing by the method of frying is possible only for such parts of carcasses, which contain relatively little collagen and the morphological structure of the connective tissue is simple, the collagen fibers are thin, located parallel to the direction of the muscle fibers.

Fish collagen is destroyed much more easily than meat, because the connective tissue of fish has a relatively simple morphological structure, collagen contains less oxyproline, it is subject to denaturation and destruction at lower temperatures.

- **The reaction of the environment.** For example, acidification of the environment with food acids or products, supplements containing these acids accelerates the transition of collagen into gluten.

- **Grinding.** For example, grinding meat contributes to a decrease in the hydrothermal stability of collagen. This is explained by the fact that when grinding meat in a meat grinder, collagen fibers are crushed into smaller fragments, the surface of contact of protein with the environment increases many times.

The destruction of collagen to gluten is also accelerated in an alkaline environment. It is used in the meat industry to produce gelatin, which is dried gluten. Raw materials for obtaining gelatin are such by-products of meat cattle slaughter as tendons, tails, ears, lips, pork skin, etc.

When cooking meat, part of the gluten passes into the broth (0.5...1 % of the meat mass). When cooking jellied meats using by-products of the second category (legs, heads, tails), the composition of the meat is selected so that the gluten content in the broth does not exceed 3% by the end of cooking. When cooking bone broths, bone collagen (ossein) also denatures and turns into gluten. However, bone ossein is quite resistant to hydrothermal effects - to obtain broth with a 3% concentration of gluten, crushed bones must be boiled for about 5 hours. This process can be intensified by pre-roasting the bones at 280 °C for 30 minutes. However, the organoleptic quality indicators of such broths are low.

1.4.2. Functional properties of proteins

The functional properties of proteins are their physico-chemical and technological properties that determine their change in the process of processing raw materials and food production and provide a certain structure of finished products with notable consumer properties.

The main functional properties of proteins:

- solubility;

- viscous-elastic-elastic properties;
- water-binding (hydration) capacity;
- fat-binding capacity;
- emulsifying property;
- foaming property;
- ability to gel (drag formation);
- adhesive properties;
- texturing.

The high functional properties of proteins depend on their ability to dissolve in water, participate in the formed foams, stabilize emulsions, and create highly structured gels.

The ability of proteins to dissolve is the basis of the technological processes of isolating concentrates. The solubility of proteins is of great importance in the production technology of beverages, bakery, flour confectionery and pasta products. Thus, proteins with high solubility are used in the production of beverages.

In the production of flour products, the use of highly soluble proteins negatively affects the visco-elastic properties of the dough. Flour proteins have low solubility, but they are able to form highly structured colloidal systems - gels. Wheat flour proteins (gliadin and glutenin) have a high hydration capacity due to the presence of hydrophilic groups. Absorbing water, gliadin and glutenin bind it osmotically, the process of their swelling occurs and gluten is formed. The amount and quality of gluten has a significant impact on the structural and mechanical properties of the dough and, accordingly, the finished product.

Viscoelastic-elastic properties. Wheat gluten proteins have a pronounced complex of these properties, which determine the texture of finished products. The glutenin fraction of proteins is responsible for the elasticity and elasticity of proteins

Water-binding and fat-binding capacity. Proteins are able to bind and retain water and fat, which depends on the amino acid composition. For example, flour proteins are characterized by a high fat-emulsifying property and foaming ability. Due to the fat-binding ability of proteins, the finished product is characterized by a better uniform texture, the separation of fat is prevented, and the loss of raw materials during heat treatment of meat raw materials (cooking, frying, baking, etc.) is reduced. The fat-dissolving ability of proteins is widely used in the technology of production of sausage products.

The emulsifying property of proteins is widely used to stabilize fat emulsions. Emulsions based on proteins are obtained by dispersion. However, as is known, emulsions are unstable systems and in order to stabilize them, emulsifiers are used, in the role of which protein substances can be used. Substances that act as an emulsifier are stabilized at the interface of phases and contribute to the reduction of interfacial surface tension, which prevents the passage of coalescence (fusion) of the particles of the dispersed phase and keeps them in the dispersion medium, which ensures the aggregative stability of emulsions. Proteins as emulsifiers are widely used in the food industry. For example, dry milk, sodium caseinate, and egg powder are used as emulsifiers in the production technology of emulsion-type sauces.

The foaming property of proteins is their ability to form highly concentrated dispersed liquid-gas systems (foams). The ability to foam is due to the fact that proteins can reduce the surface tension at the liquid-gas interface. In the process of foam formation (mechanical dispersion), proteins are adsorbed at the liquid-gas interface and form a structured film that prevents the liquid from draining. The foaming capacity is characterized by such indicators as the volume of the foam, its multiplicity, dispersion, stability. The foaming ability depends on a number of technological factors – temperature, pH of the medium, presence of salts, carbohydrates, lipids. The foaming ability of egg albumin, caseinates, and protein hydrolyzates is widely used in food production technology.

As is known, the ability of egg albumin to form foams during mechanical whipping is used in the technology of production of flour confectionery products with a foamy structure - biscuits, production of creams, marshmallows, meringue, pastilles, soufflés, sambuks.

Also, one of the important functional properties of proteins is their **ability to gel**. Colloidal solutions of proteins can change from a freely dispersed state to a bound-dispersed state - a gel state.

As mentioned above, during the interaction of a protein molecule with water dipoles, water molecules penetrate into the space between the polypeptide chains, due to which protein swelling occurs, colloid solutions are formed (for example, proteins of animal origin, myosin, actin, collagen are characterized by limited swelling). Between some proteins in the colloidal solution, intermolecular interactions are formed and a three-dimensional spatial network of gel (swollen protein) is formed, in the middle of which water molecules are contained. Gels in their composition can contain up to 99.9% water and at the same time exhibit the properties of solid bodies and be characterized by elasticity, elasticity.

The structure of gel formation plays an important role in the formation of structural and rheological properties of food products.

The process of gel formation in food systems can occur in different ways:

- by heating or cooling the liquid system – thermotropic gels;
- by changing the ionic composition of the system – ionotropic gels;
- concentration of liquid and dispersed systems that contain a structure former (gel former) - lyotropic gels.

For example, thermotropic gels are formed during heat treatment of cooked sausage mince or cooling of gelatin solutions.

During heating, denaturation and destruction of collagen occurs, that is, its welding with the formation of water-soluble gelatose. During cooling, gelatin solutions form structured gels (wells).

The process of lyotropic gelation is used in the production of cured meat products. The process of gel formation is influenced by the composition and sequence of polypeptide chains in the composition of various proteins, technological factors (temperature, pH of the medium, presence of ions).

In order to ensure the stability of the technological process, improve the quality and expand the range of food products, the functional properties of proteins are regulated.

Regulation of protein properties is achieved by changing the conditions of isolation, drying, physical, physicochemical effects, enzymatic and chemical modification. Processing parameters change the amino acid and fractional composition of proteins, cause denaturation, aggregation or interaction with other components (lipids, carbohydrates, etc.).

Well-known methods of regulating properties are **physicochemical** and **enzymatic**.

Physico-chemical methods include: dissolving proteins before drying in a solution of acids, alkalis in order to change their charge or ionic composition, thermal denaturation, etc.

At the same time, protein solubility, gel-forming, fat-emulsifying ability, and texturing ability increase.

Proteases of plant, microbial or animal origin are used for enzymatic modification of functional properties. The advantages of obtaining such proteins are soft release modes, preservation of biological value and the possibility of adjusting the degree of hydrolysis, deamination, etc.

Questions for discussion and self-examination

- 1. What are the physical and chemical properties of proteins, their characteristics.*
- 2. Describe the solubility of proteins and their hydrophilic and hydrophobic properties.*
- 3. Hydration and dehydration of proteins, role in technological processes.*
- 4. Describe the processes of denaturation, coagulation and destruction of proteins.*
- 5. Describe the functional properties of proteins.*

Topic 1.5. Lipids: composition, characteristics

1.5.1. Characteristics of food lipids

Lipids are a group of organic compounds, the chemical composition of which are derivatives of fatty acids, alcohols, aldehydes, built with the help of ether, ester, phosphoroether and glycosidic bonds, the common properties of which are insolubility in water and the ability to dissolve in organic solvents.

In plants, lipids accumulate mainly in seeds and fruits. In animals and fish, lipids are concentrated in subcutaneous, brain and nervous tissues, as well as tissues surrounding important organs (heart, kidneys).

The content of lipids in individual food products is shown in the table. 1.13.

Table 1.13. Lipid content in certain food products

Foodstuff	Lipid content, %
Animal fats are rendered	99.7
Butter	72.5...82.5
Vegetable oils	99,9
Meat	1.7...49.3
Bird	5.0...39.0
Fish	0.3...30,9
Sausages are cooked	13.5...29.6
Anchovies	17.0...31.6
Sausages	19.1...30.8
Boiled and smoked sausages	27.5...39.0
Semi-smoked sausages	17.4...44.6
Raw-smoked sausages	41.5...47.8
Milk	0.05...6.0
Sour cream	10.0...40.0
Cheese is hard	0.6...18.0
Cheeses	9.0...32.2
Wheat flour	0,9...1.8
Rye flour	1.1...1.7
Soy	17.3
Pasta	0,9...1,3
Wheat bread	0,9...1,3
Vegetables	0.1...0.3
Mushrooms	0.4... 0.9
Cream	10.0...35.0

1.5.2. Classification of lipids.

There are different classifications of lipids (Fig. 1.46, 1.47).

Depending on the purpose and use, preference is given to either liquid or solid fats. Fats solid at room temperature are more valuable raw materials in food production.

Animal fats are divided into two groups: fats from terrestrial animals and fats from marine animals and fish.

The fats of terrestrial animals include triglycerides of saturated fatty acids (40-60% of the total content of fatty acids), unsaturated acids, and (most often) monounsaturated oleic acid.

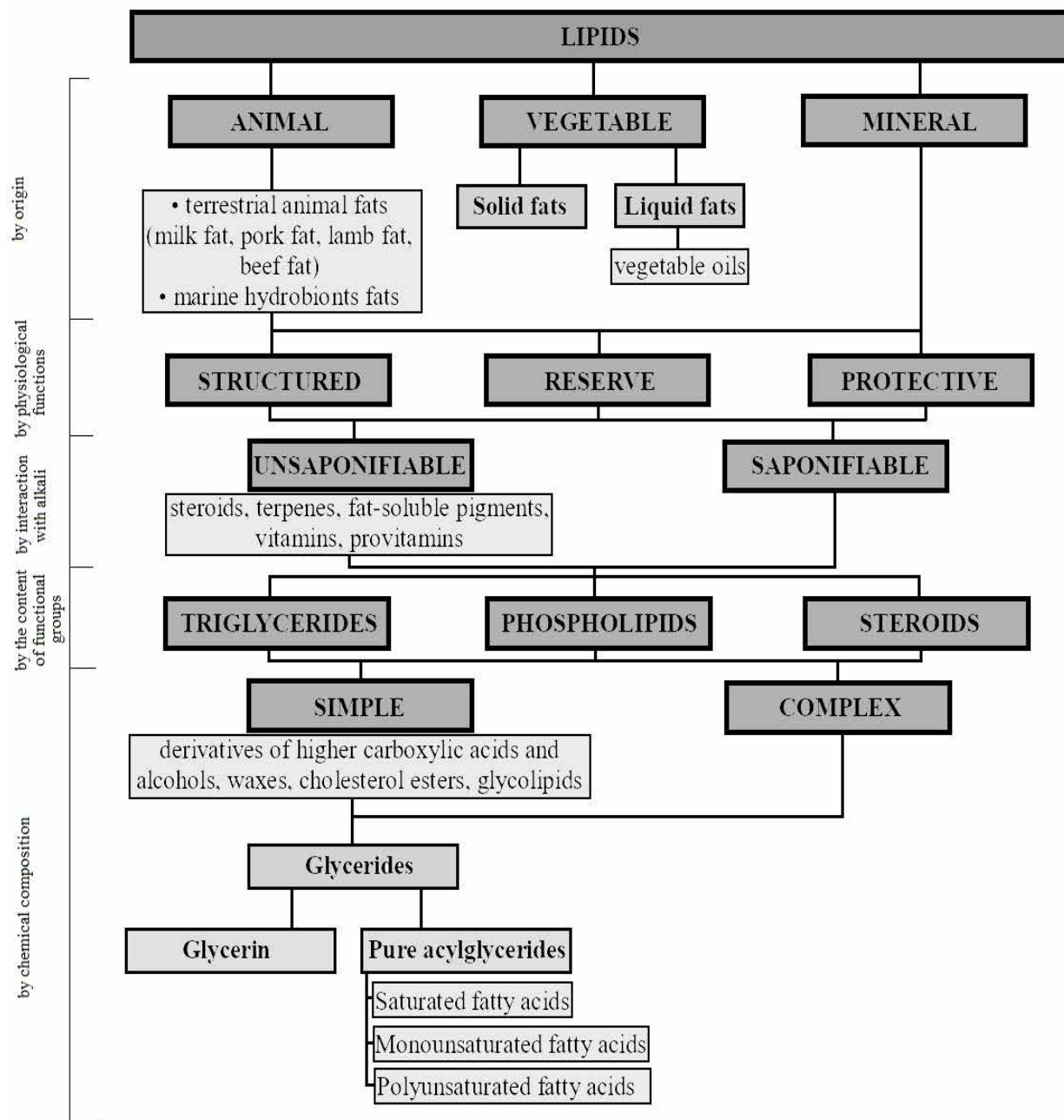


Fig. 1.46. Classification of lipids

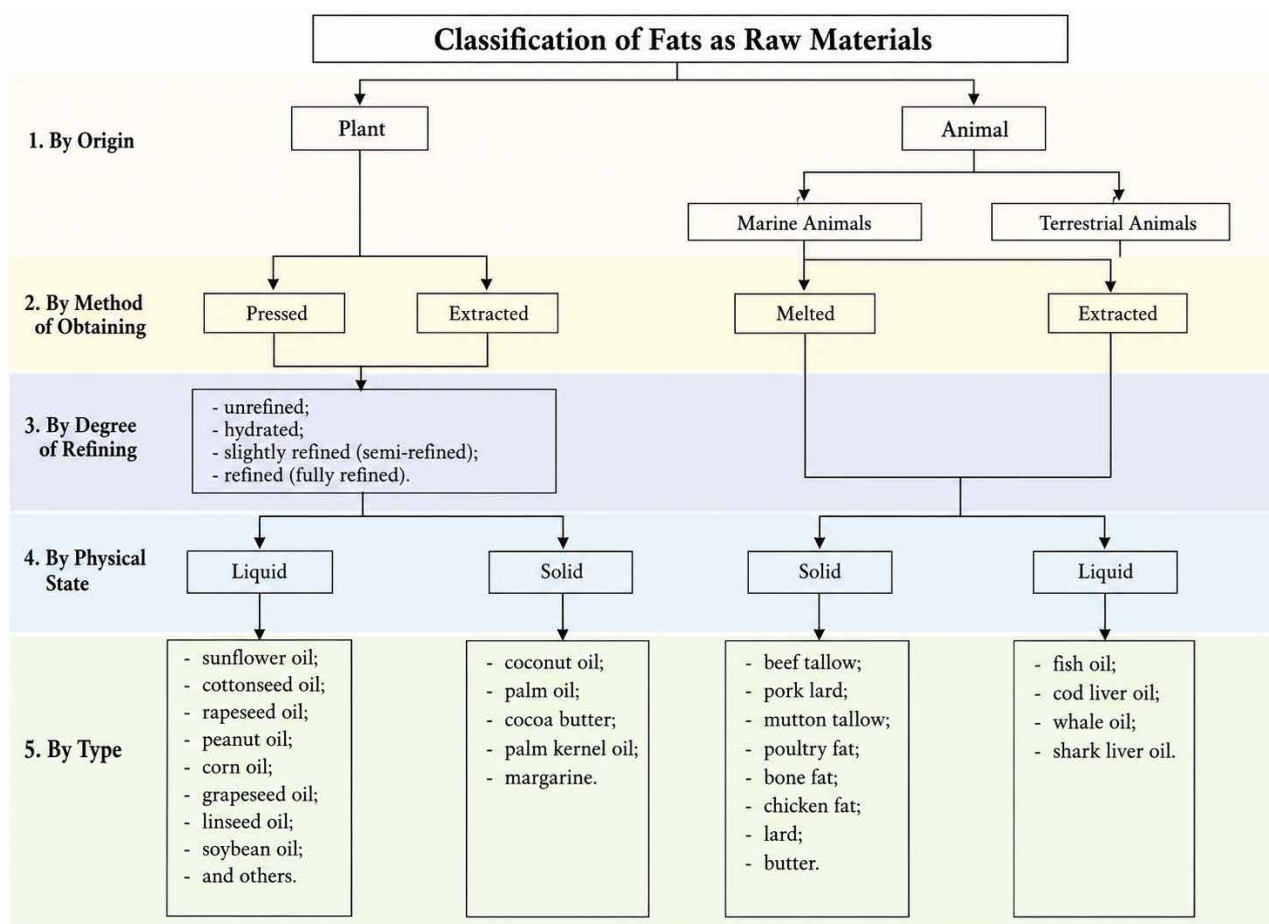


Fig. 1.47. Classification of lipids as raw materials (fat)

The fatty acid composition of the fats of marine animals and fish is different – it is completely dominated by polyunsaturated fatty acids (up to 70...80 %), which are important biologically active substances.

Rendered animal fats. The group "rendered animal fats" includes the fats of terrestrial animals. Beef, pork, and lamb fats are most widely used.

The raw material for the production of rendered animal fats is adipose tissue (crude fat) and bones of cattle, pigs, sheep, and poultry. The quality of raw fat depends on the fatness and age of the animal. The yield of raw fat ranges from 0.4 to 7% of the live weight of the animal.

Crude fat is divided into two groups:

The first group – adipose, peri-renal, peri-cardiac, trimmings of fresh lard, etc. (from this group, more fat is melted in the subcutaneous tissue);

Group II – stomach fat, intestinal fat, fatty trimmings, etc.

Melting is carried out on special equipment by wet and dry methods.

Wet method: raw materials are constantly in contact with water or steam, as a result of which rendered fat, broth, and slag are formed. During the dry heating method, raw materials come into contact with the heated surface of the device, as a result of which fat and slag are formed.

To obtain fat from bones, raw materials are sorted, washed, crushed and fat is melted from it under the influence of steam, pressure, high-frequency current, etc.

The obtained rendered animal fats are separated from lard, broth, free fatty acids, etc. impurities by settling, filtering, separation, neutralization. Sometimes, in order to preserve the nutritional value of fats and increase their shelf life, they are treated with antioxidants.

The quality of the finished fat is affected by the temperature at which it is melted. Thus, high-grade fats are obtained at a temperature of 65-70 °C. The second phase of heating at a temperature of 75-95 °C produces fat of the first grade. Residual fat from the bladder is melted in autoclaves at a temperature of almost 120 °C and a pressure of 0.20-0.22 MPa. This is how low-quality fats are obtained: collective or technical.

In terms of biological value, rendered animal fats are inferior to oils. This is due to the lower content of: polyunsaturated fatty acids; vitamin E; vitamin A; absence of phospholipids (lecithin); a lower degree of absorption (73-65 %, against 95-98 % absorption of oils).

Among animal rendered fats, pork fat has the highest biological value, as it contains more essential linoleic acid, vitamin E, has the lowest melting point and is absorbed by 96 %. Pork fat is the only one of all animal fats that is close to the "ideal fat formula", the balance of fatty acid composition in which is 70%: 30% unsaturated and saturated acids, respectively. Beef (84 %) and lamb (73 %) fats are the worst absorbed. The melting point of beef fat is 40-51 °C, mutton fat is 44-45 °C.

Margarine. Margarine is a specially prepared edible fat, similar to butter in taste, color, aroma, consistency, and structure. Margarine is a highly dispersed emulsion of fat in the water phase. The fat content in margarine reaches 82 %, moisture - no more than 17 %, carbohydrates – 1 %, protein – 0.3 %, digestibility 94-97 %.

Margarine is widely used in bakery and confectionery production, as well as directly in food as a substitute for butter. In margarine, the fatty acid composition and natural biologically active substances are modeled: margarine is balanced according to the fatty acid composition, enriched with biologically active substances, vitamins A, E, K, β -carotene, phospholipids.

The main component of margarine is palm oil, obtained as a result of hydrogenation of oil or transesterification of fats. In addition to tallow, the margarine recipe includes: liquid vegetable oils (sunflower, corn, soybean); transesterified fats; animal fats (beef, pork, butter); dairy products (including dry, fermented milk); salt, sugar, citric acid; dyes (most often β -carotene); emulsifiers, flavoring agents.

Depending on the use, margarine is divided into the following groups: sandwich bars; soft sandwiches of improved quality; dining rooms; for industrial processing and catering.

Margarines for industrial processing do not enter the retail trade network, they include: margarine for the bakery industry; margarine for the confectionery industry (confectionery cream); confectionery margarine for puff pastry; dairy-free margarine of the highest and 1st grades.

Among the physico-chemical indicators of the quality of margarines, which are standardized, are the mass fractions of fat (60-82 %), table salt (0.2-0.7 %), moisture and volatile substances (17-40 %), acidity (1.5-2.5), heating temperature (27-35 °C). They limit the amount of preservatives (benzoic acid - 0.1%; ascorbic acid – 0.06 %),

heavy metals and control microbiological indicators (BHCP coliforms, salmonella, yeast, molds, etc.).

Confectionery, bakery, cooking fats. Fats of this group are an anhydrous (without water-milk phase) mixture of tallow with refined oils, animal rendered, transesterified fats.

Depending on the purpose, these fats may contain such additives as phosphatide concentrate, dyes, flavorings, antioxidants, vitamins.

Fats of this group are obtained in the same way as margarine, but without thorough emulsification. These are mainly fatty mixtures.

Cooking fats, unlike margarine, contain less moisture (up to 0.3 %), more fats (99.7%), less biologically active substances (vitamins, unsaturated fatty acids). The melting point of these fats is 26-36 °C, digestibility is 96.5%. They are used for frying products in the main way and deep-frying.

Confectionery fats:

- solid confectionery fat – transesterified fat with a high melting point – up to 45°C, (used for making fat glaze);

- confectionery fat for waffle and cooling fillings – contains 20-40% of coconut or palm oil and straw mass of low hardness (has a plastic consistency);

- confectionery fat for candies and food concentrates with a melting point of 35-37°C (has a solid consistency).

Liquid fat for the baking industry is made from a mixture of oil and tallow (87 and 13%, respectively) or only from transesterified vegetable fat.

Physico-chemical indicators of confectionery fats that are normalized: mass fraction of fat (not less than 99.7 %), moisture and volatile substances (not more than 0.3 %), acid number (0.4-0.8 %), melting point (26-36 °C). The content of antioxidants (if they are added) and pesticides is also regulated.

Nutritional value of fats. Vegetable and animal fats are a mandatory component of food, a source of energy and plastic material for the human body, a supplier of vital substances (essential fatty acids, phospholipids, fat-soluble vitamins, sterols, etc.).

The recommended amount of fat in the human diet is 90-107 g per day, they provide 30-33 % of the energy value of the diet.

Insufficient intake of fat in the body can lead to a number of disorders of the functions of the central nervous system, weakening of immunobiological mechanisms, pathological changes in the skin, kidneys, and organs of vision. With a fat-free diet in animals, growth stops, body weight decreases, sexual function and water exchange are disturbed, steroid hormone secretion in the adrenal glands decreases, the body's resistance to the influence of adverse factors is weakened, and life expectancy is shortened.

With a sharp decrease in the intake of fats with food, the digestibility of vitamins and provitamins that are included in vegetable food deteriorates, the energy value of food decreases, and its organoleptic positive qualities decrease. In addition, low-fat food does not stay in the stomach for a long time, as a result of which the food center is reflexively excited - a feeling of hunger arises. However, excessive use

of fats is also undesirable, because it causes obesity, the occurrence of cardiovascular diseases, and premature aging.

In the composition of food products, a distinction is made between "visible fats" (vegetable, animal, butter, margarine, cooking fat) and "invisible" (fat in meat and meat products, fish, milk, cereals, bakery and confectionery products). The division is conditional, but widely used.

The most important sources of fats in food are vegetable oils (99.8 %), butter (61.5-82.5 %), dairy products (3.5-30 %), chocolate (35-40 %), cookies (10-11 %), cereals, cheeses, sausage products.

The nutritional value of fat is determined by the needs of the human body based on its ability to absorb it. Vegetable oils and fats have different absorption coefficients by the human body (Fig. 1.48).

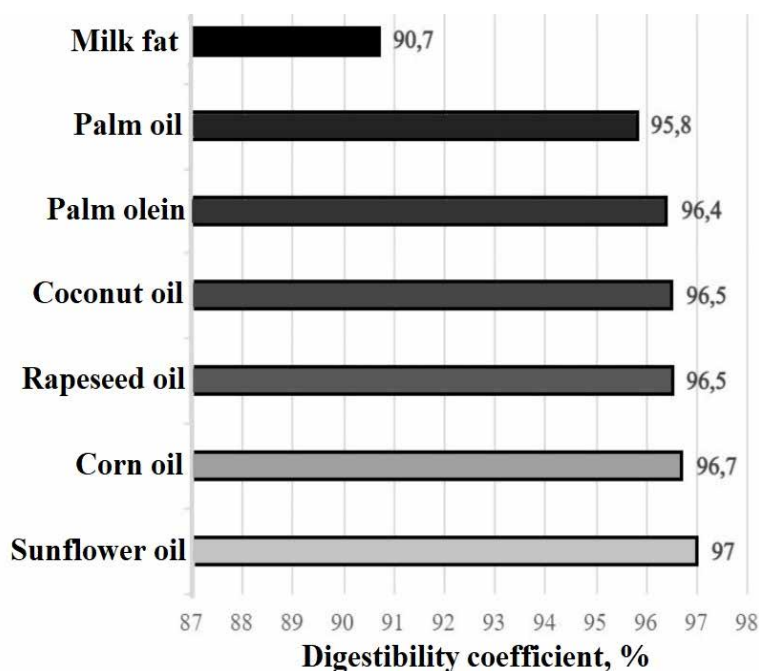


Fig. 1.48. Digestibility of certain types of oils and fats

Simple lipids are esters of fatty acids and alcohols.

Complex lipids are esters of fatty acids and alcohols that contain other substituents on the hydroxyl group.

Lipid derivatives are compounds obtained as a result of hydrolysis of the first two groups (simple and complex lipids).

Various lipids include aliphatic hydrocarbons, squalene and other terpenes, vitamins E, K and other compounds.

The most important and widespread group of simple lipids are acylglycerols. Acylglycerols (or glycerides) are esters of glycerol and higher carboxylic acids.

Glycerides make up the bulk of lipids (up to 95 %) and, in fact, they are called fats or oils, depending on their origin.

Fats mainly include triacylglycerols (Fig. 1.49, a), as well as diacylglycerols (Fig. 1.49, b) and monoacylglycerols (Fig. 1.49, c).

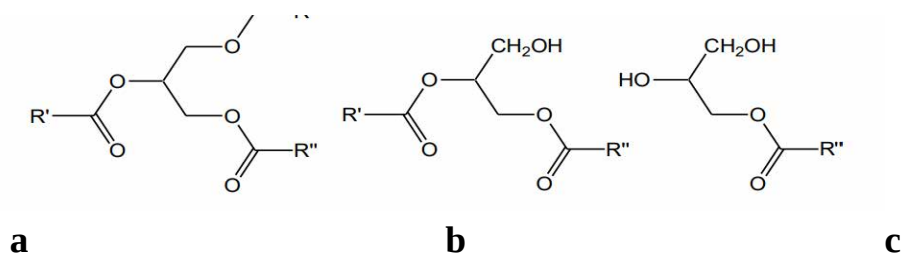


Fig. 1.49. Composition of fats:
triacylglycerols (a), diacylglycerols (b) monoacylglycerols (c)

Triacylglycerols whose molecules contain the same fatty acid residues are called simple, and different ones are called mixed.

Fats of natural origin contain mixed triacylglycerols.

Pure acylglycerols are colorless, tasteless and odorless substances. The color, smell and taste of natural fats are determined by the presence of specific impurities characteristic of each type of fat. The melting and solidification temperatures of acylglycerols do not coincide, which is due to the presence of several crystal modifications.

Another important group of simple lipids are waxes – esters of higher monobasic carboxylic acids and monoatomic (containing one OH group) high molecular weight (with 18-30 carbon atoms) alcohols.

The shells of sunflower seeds contain up to 0.2 % of wax from the mass of the shell, in soybean seeds – 0.01 %, rice – 0.05 %. Waxes are an important component of the wax coating of the grape berry (tabl. 1.14).

Table 1.14. Higher alcohols

Formula	A trivial name
Saturated	
$\text{CH}_3-(\text{CH}_2)_{10}-\text{CH}_2\text{OH}$	Lauryl alcohol
$\text{CH}_3-(\text{CH}_2)_{12}-\text{CH}_2\text{OH}$	Myristyl alcohol
$\text{CH}_3-(\text{CH}_2)_{14}-\text{CH}_2\text{OH}$	Cetyl alcohol
$\text{CH}_3-(\text{CH}_2)_{16}-\text{CH}_2\text{OH}$	Stearyl alcohol
$\text{CH}_3-(\text{CH}_2)_{22}-\text{CH}_2\text{OH}$	Carnauba alcohol
$\text{CH}_3-(\text{CH}_2)_{24}-\text{CH}_2\text{OH}$	Ceryl alcohol
$\text{CH}_3-(\text{CH}_2)_{26}-\text{CH}_2\text{OH}$	Montana alcohol
$\text{CH}_3-(\text{CH}_2)_{28}-\text{CH}_2\text{OH}$	Myricyl alcohol

Most waxes are hard, elastoplastic, sometimes even brittle substances at room temperature. Only some waxes have a liquid consistency at room temperature. Waxes are widely distributed in nature. In plants, they cover leaves, stems, and fruits with a thin layer and protect them from wetting with water, drying, and the action of microorganisms. Beeswax protects honey and bee larvae. Lanolin – animal wax –

protects the sheep's hair and skin from the action of water. In phytoplankton, waxes perform the function of cellular fuel.

By origin, waxes are divided into animal (bee, lanolin, spermaceti), vegetable (carnauba, flax) and fossil (montane).

Animal waxes include beeswax, which bees secrete with their glands; woolly, which accumulates in relatively large quantities in the wool of sheep; spermaceti oil and spermaceti, which, in turn, is contained in the cavities of the skull of the sperm whale.

Beeswax contains up to 72% of esters of mostly ceryl and myricyl alcohols of palmitic, cerotic, and melisinic acids, of which myricyl palmitate $C_{15}H_{31}COOC_{30}H_{61}$ makes up 33 %, free HCA – 13%, alkanes up to 12%. The heating temperature is 62-70 °C. Beeswax is used as a component of polishing agents and medicines.

Lanolin (from the Greek lana - wool, oleum - oil) is extracted from the fat sweat of sheep (the content of such wax in sheep's wool reaches 25 %). It is a light yellow substance with a weak specific smell, the melting point is 36-42 °C. According to its chemical composition, it is a mixture of esters of cetyl and ceryl alcohols, as well as, unlike other waxes, cholesterol and its hydroxy derivatives, with myristic, palmitic, and cerotic acids. Characteristic for lanolin is the content of cerotin-ceryl ester $C_{25}H_{51}COOC_{26}H_{53}$.

Lanolin is resistant to oxidation, unlike other waxes, it forms stable aqueous emulsions. Thanks to this, it is used as an ointment and cream base, into which water-soluble drugs are injected.

In the food industry, lanolin is used to cover the surface of apples, peaches, pears, and citrus fruits in order to extend their shelf life. In addition, lanolin is used to glaze dragees and candies.

Spermacet is contained in the cranial cavity (spermacet sac) of the sperm whale. It consists of 98% cetyl palmitate $C_{15}H_{31}COOC_{16}H_{33}$ (cetyl ester of palmitic acid). The heating temperature is 45-54 °C. The smell is specific, somewhat reminiscent of the smell of ragweed. It is used as a cream and ointment base in perfumery, for soap, as pharmaceutical preparations for the treatment of chronic ulcers.

Vegetable waxes. Carnauba wax covers the leaves of the Brazilian wax palm *Copernicia cerifera*. It contains up to 80% esters of myricyl alcohol with carnauba $C_{23}H_{47}COOH$ and cerotic acids; other esters of HCA C_{16} - C_{28} and VS C_{30} - C_{32} ; free (mainly Montan). Carnauba wax is a hard, brittle mass that can be ground into a powder. Its color is from grayish-yellow to greenish-yellow. The heating temperature is 83-91 °C. It is used in the confectionery industry to give gloss to chocolate and sugar dragees.

The linseed wax that covers the flax stalks contains about 35% ceryl alcohol esters with oleic, linolenic, palmitic and stearic acids.

Fossil waxes. In addition to animal and vegetable waxes, montana (lignite) wax is also known – a mineral fossil product that has nothing to do with the food industry.

The composition of simple lipids of vegetable oils and fats includes glycolipids – a structurally diverse group of neutral lipids, which include monoose residues.

They, usually in small quantities, are contained in plants (lipids of wheat, oats, corn, sunflower), animals.

Glycolipids perform structural functions, participate in the construction of membranes, and play an important role in the formation of wheat gluten proteins, which determine the baking qualities of flour.

Most often, D-galactose, D-glucose, and D-mannose are involved in the construction of glycolipid molecules.

Representatives of complex lipids are **phospholipids**.

Phospholipids (phosphatides) are lipids which, in addition to glycerol and higher fatty acids, give phosphate acid and amino alcohol during hydrolysis. Phospholipids are divided into two classes: lecithins and cephalins (cephalins), which differ in amino alcohol.

Lecithins (from the Greek lethitos - yolk) contain choline - $\text{HO-CH}_2\text{-CH}_2\text{-N}^+(\text{CH}_3)_3$.

Kephalins contain colamine (ethanolamine) $\text{HO-CH}_2\text{-CH}_2\text{-NH}_2$, as well as serine - $\text{HO-CH}_2\text{-CH(NH}_2\text{)-COOH}$ (Fig. 1.50).

Lecithins (phosphatidylcholines) were first isolated in 1845 from egg yolk. They are also found in the liver and heart muscle. There are especially many of them in vegetable products – seeds of oil crops, peas, cereals. According to their chemical structure, they are diacylglycerophosphates, in which the phosphate group is additionally esterified with choline.

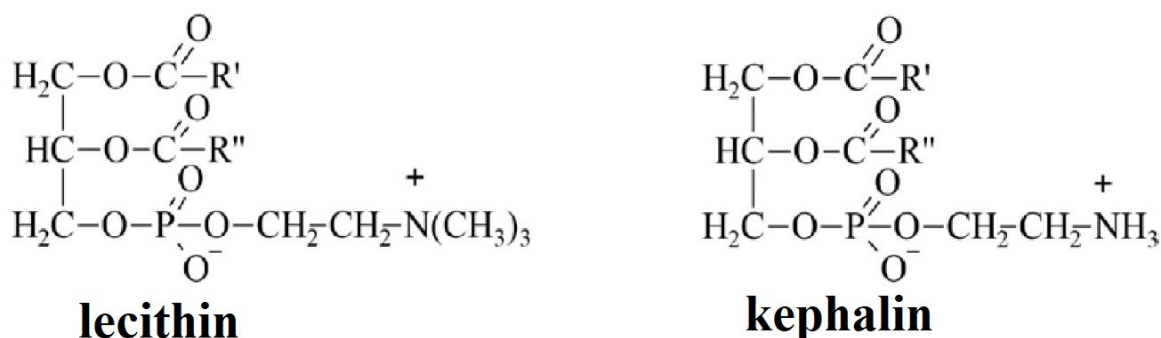


Fig. 1.50. Structural formulas of lecithin and kephalin

Both saturated and unsaturated higher fatty acids participate in the formation of phosphatidylcholine molecules. In most cases, lecithins contain one residue of saturated and one residue of unsaturated fatty acids (mostly $\text{C}_{16}\text{-C}_{22}$).

Lecithins are obtained from natural sources by successive extraction of lipids, isolation by fractional precipitation and chromatographic separation on silica gel.

Lecithins are soluble in alcohol and ether, kephalins - only in ether. Kephalins are a mixture of phosphatidylethanolamines with phosphatidylserines.

The composition mostly includes stearic and oleic acids. Using the example of phosphatidylethanolamine, it is possible to follow its hydrolysis, which occurs similarly for other complex lipids (Fig. 1.51):

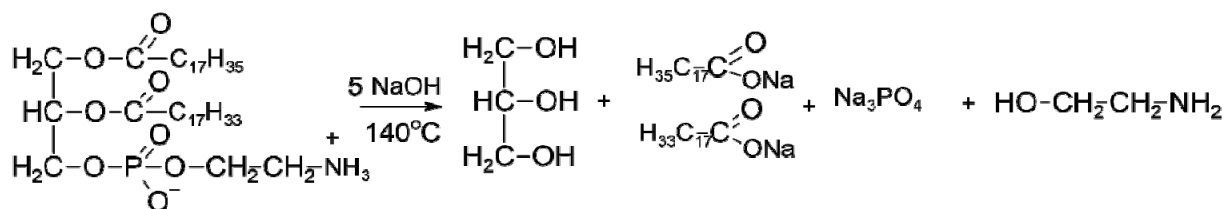


Figure 1.51. Kephalin hydrolysis

As a result of complete hydrolysis, a mixture of glycerin, stearate and sodium oleate, ethanolamine and sodium phosphate is formed.

Phosphatides are surfactants. The molecule contains a hydrophilic (polar) fragment called the "head" and a hydrophobic (non-polar) fragment - the "tail". The "head" includes the remains of the carboxyl group of carboxylic acids, the nitrogen-containing component, and phosphoric acid, and the "tail" includes the remains of the aliphatic part of HCA (Fig. 1.52). Therefore, phospholipids are amphiphiles (have an affinity for both polar and non-polar solvents).

Amphiphilicity is the ability of some compounds to exhibit both hydrophilic and hydrophobic (lipophilic) properties due to the presence of charged or polar and nonpolar parts in their molecules. A large organic cationic or anionic group mainly acts as a hydrophilic part, while a long hydrocarbon chain acts as a hydrophobic part. Amphiphilic substances show surface activity at the boundary between the aqueous and hydrophobic phases.

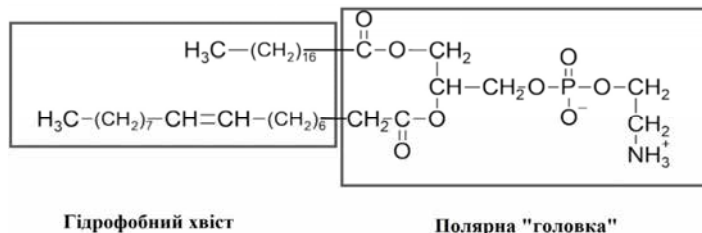


Figure 1.52. Amphiphilicity of phospholipids

In nonpolar solvents, phospholipid molecules form micelles, in which hydrophobic parts make up the outer layer, and hydrophilic parts make up the inner layer. In polar solvents, the opposite is true.

Due to their amphiphilic nature, phospholipids can form emulsions. They are used as emulsifiers in bakery and confectionery production, for the production of mayonnaise, margarine. Lecithin (E322) is used to make chocolate (reduces its viscosity).

Phospholipids are a group of lipids important in nutrition, which take part in the construction of cell membranes and transport of fat in the body. They contribute to better assimilation of fats and prevent fatty liver. The total human need for phospholipids is up to 5-10 g per day.

Sterols are alicyclic substances that belong to the group of steroids, usually they are crystalline monoatomic alcohols (sterols) or their esters (steroids).

They distinguish:

- zoosterols released from animal fats;
- phytosterols (from plants);
- mycosterols (from mushrooms).

The content of sterols in some seed cultures is given in the table. 1.15.

Table 1.15 – Sterol content

Name	Sterol content, %
Cotton	1.60
Soy	0.35
Turnip	0.30
Linen	0.40
Peanut	0.25

Sterols have a crystalline structure, and zoosterols and phytosterols differ in the form of crystals, which allows to identify the nature of the fat (establish its origin).

Among animal sterols, **cholesterol** is important (Fig. 1.53). It is a normal structural component of all cells and tissues, participates in the exchange of bile acids, synthesis of a number of hormones, vitamin D (part of which is formed under the influence of ultraviolet rays from the same cholesterol).

The normal content of cholesterol in the blood is 1.9-2.1 g/l. An increase in its level up to 2.6 g/l is very dangerous - atherosclerosis occurs and develops in a person, the complicated consequences of which are heart attacks and strokes.

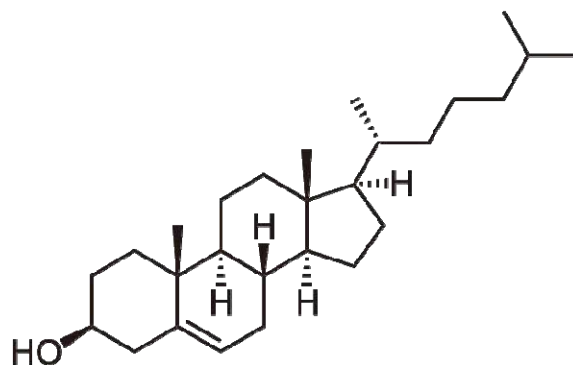


Fig. 1.53. Structure of cholesterol

Cholesterol content in food products is given in table 1.16.

A lack of cholesterol in the blood (less than 1.5 g/l) causes damage to the adrenal glands, enlargement of the thyroid gland. A clear lack of cholesterol is found in the case of cirrhosis, infectious hepatitis and other liver diseases. About 80% of cholesterol is formed in the body in the liver and other organs from saturated fatty acids. The remaining 20 % comes with food. But relevant studies have established a clear connection – the more cholesterol comes with food, the smaller its amount is synthesized by the liver and vice versa.

Table 1.16. Cholesterol content in certain food products

Food product	Content, mg/100 g
Brain	2300
Egg yolk	1480
Kidneys	375
Fish roe	> 300
Butter	240
Animal meat	70
Fish	55
Cheese	90

The composition of dietary fats included in the human diet can significantly affect the level of cholesterol in the body. If there is a lot of vegetable fats (oils) in the diet, the cholesterol content decreases, if a large amount of animal fats are consumed, the concentration of cholesterol in the blood increases.

Pure cholesterol – pearly plates, greasy to the touch. It is insoluble in water, sparingly soluble in organic solvents. The melting point of cholesterol is 149 °C.

In the process of cooking meat and fish, up to 20% of cholesterol is lost. The usual daily ration is 500 mg of cholesterol. In countries where the least amount of animal fat is consumed (most African countries, India, Japan), the cholesterol content in the blood of residents is much lower than in the USA, England, Finland. It is known that a 1 % reduction in cholesterol in the blood leads to a 2% reduction in the risk of cardiovascular disease.

Of the phytosterols, plant foods contained in fat, β -sitosterol is considered the most active. It is an antagonist of cholesterol, delays its absorption in the small intestine. β -Sitosterol is found in large quantities in vegetable oils, especially in soybean oil. β -Sitosterol is also found in the pulp of grapefruit fruits (both in unbound form and in the form of glucoside), in grapefruit seeds it is present only in free form. It serves as an obstacle to the absorption of cholesterol, thereby preventing an increase in the level of cholesterol in the blood. Eating foods containing phytosterol lowers the level of cholesterol in the blood.

1.5.3. Fatty acid composition of fats and oils

The properties of fats are mainly determined by their fatty acid composition. Fatty acids mainly have an even number of carbon atoms and an unbranched structure.

Table 1.17 lists the most common higher carboxylic acids included in fats.

Depending on the nature of the bonds between carbon atoms, fatty acids that are part of lipids are saturated and unsaturated (Fig. 1.54, Table 1.18).

Table 1.17 The most important acids that are isolated from natural fats

	A trivial name	Formula
Higher saturated carboxylic acids	Butyric acid (C ₄) Caproic acid (C ₆) Caprylic acid (C ₈) Capric acid (C ₁₀) Lauric acid (C ₁₂) Myristic acid (C ₁₄) Palmitic acid (C ₁₆) Stearic acid (C ₁₈) Arachinic acid (C ₂₀)	CH ₃ (CH ₂) ₂ COOH CH ₃ (CH ₂) ₄ COOH CH ₃ (CH ₂) ₆ COOH CH ₃ (CH ₂) ₈ COOH CH ₃ (CH ₂) ₁₀ COOH CH ₃ (CH ₂) ₁₂ COOH CH ₃ (CH ₂) ₁₄ COOH CH ₃ (CH ₂) ₁₆ COOH CH ₃ (CH ₂) ₁₈ COOH
Higher unsaturated carboxylic acids with one double bond	Dodecenoic acid (C ₁₂) Tetradecenoic acid (C ₁₄) Palmitoleic acid (C ₁₆) Oleic acid (C ₁₈) Eicosenoic (gadoleic) acid (C ₂₀) Erucic acid (C ₂₂)	CH ₃ CH ₂ CH=CH(CH ₂) ₇ COOH CH ₃ (CH ₂) ₃ CH=CH(CH ₂) ₇ COOH CH ₃ (CH ₂) ₅ CH=CH(CH ₂) ₇ COOH CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ COOH CH ₃ (CH ₂) ₉ CH=CH(CH ₂) ₇ COOH CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₁₁ COOH
With two double bonds	Linoleic acid (C ₁₈)	CH ₃ (CH ₂) ₄ CH=CHCH ₂ CH=CH(CH ₂) ₇ COOH
With three double bonds	Linolenic acid (C ₁₈) Eleostearic acid (C ₁₈) Digomo-γ-linolenic acid (C ₂₀)	CH ₃ -(CH ₂ CH=CH) ₃ -(CH ₂) ₇ COOH CH ₃ -(CH ₂) ₃ -(CH=CH) ₃ -(CH ₂) ₇ COOH CH ₃ (CH ₂) ₃ -(CH ₂ CH=CH) ₃ -(CH ₂) ₆ COOH
With four double bonds	Arachidonic acid (C ₂₀)	CH ₃ (CH ₂) ₄ -(CH=CHCH ₂) ₄ -(CH ₂) ₂ COOH
With six double bonds	Docosahexaenoic acid (C ₂₂)	CH ₃ (CH ₂ CH=CH) ₆ -(CH ₂) ₂ COOH
With a triple bond	Taric acid (C ₁₈)	CH ₃ (CH ₂) ₁₀ -CH≡CH-(CH ₂) ₄ COOH
With cycles in the carbon chain	Steric acid (C ₂₀)	CH ₂ CH ₃ (CH ₂) ₇ C≡C(CH ₂) ₈ COOH
With cycles in the carbon chain	Haulmugric acid (C ₁₈) Hydnocarpic acid (C ₁₆)	(CH ₂) ₁₂ COOH (CH ₂) ₁₀ COOH
Hydroxy and keto acids	Lycanic acid (C ₁₈) Ricinoleic acid (C ₁₈)	CH ₃ (CH ₂) ₃ (CH=CH) ₃ (CH ₂) ₄ CO(CH ₂) ₂ COOH CH ₃ (CH ₂) ₅ CH(OH)CH ₂ CH=CH(CH ₂) ₇ COOH

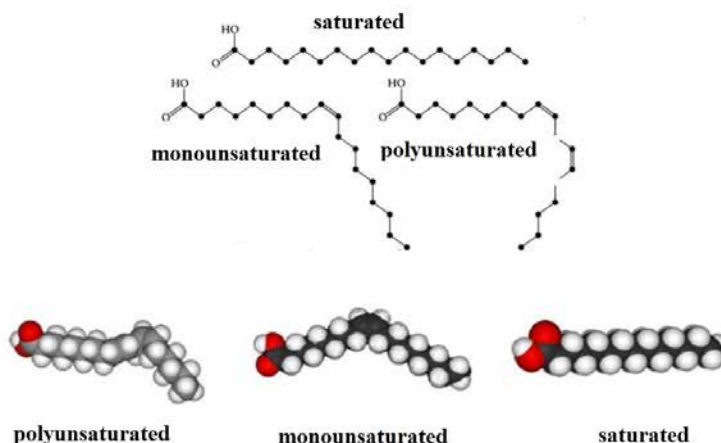


Fig. 1.54. Schematic representation of fatty acids

Table 1.18. Main carboxylic acids included in oils and fats

Acid	Formula	Notation (symbol)
Saturated acids		
Lauric acid	$\text{CH}_3-(\text{CH}_2)_{10}-\text{COOH}$	C^0_{12}
Myristic acid	$\text{CH}_3-(\text{CH}_2)_{12}-\text{COOH}$	C^0_{14}
Palmitic acid	$\text{CH}_3-(\text{CH}_2)_{14}-\text{COOH}$	C^0_{16}
Stearic acid	$\text{CH}_3-(\text{CH}_2)_{16}-\text{COOH}$	C^0_{18}
Arachinic acid	$\text{CH}_3-(\text{CH}_2)_{18}-\text{COOH}$	C^0_{20}
Unsaturated acids		
Oleic acid	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	C^{18}_{18} -9-cis
Erucic acid	$\text{CH}_3-(\text{CH}_2)_7-\text{CH}=\text{CH}-(\text{CH}_2)_{11}-\text{COOH}$	C^{22}_{22} -13-cis
Linoleic acid	$\text{CH}_3-(\text{CH}_2)_4-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	C^{218}_{18} -9-cis, 12-cis
Linolenic acid	$\text{CH}_3-(\text{CH}_2)_3-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	C^{318}_{18} -9-cis, 12-cis, 15-cis
Arachidonic acid	$\text{CH}_3-(\text{CH}_2)_3-\text{CH}=\text{CH}-(\text{CH}_2)_4-\text{CH}=\text{CH}-(\text{CH}_2)_3-\text{COOH}$	C^{420}_{20} -5-cis, 8-cis, 11-cis, 14-cis
Oxyacids		
Ricinolenic acid	$\text{CH}_3-(\text{CH}_2)_5-\text{CHOH}-\text{CH}_2-\text{CH}=\text{CH}-(\text{CH}_2)_7-\text{COOH}$	C^{18}_{18} -9-cis, 12-ol

To date, unsaturated fatty acids are divided into omega (ω) classes, which are designated depending on the location of the double bond closest to the methyl or ω -carbon. Accordingly, monounsaturated fatty acids – oleic and oleopalmitic – are defined as ω -9 and ω -7, polyunsaturated – linoleic, arachidonic and linolenic – ω -6, polyunsaturated – α -linolenic, docosahexaenoic and eicosapentaenoic – ω -3.

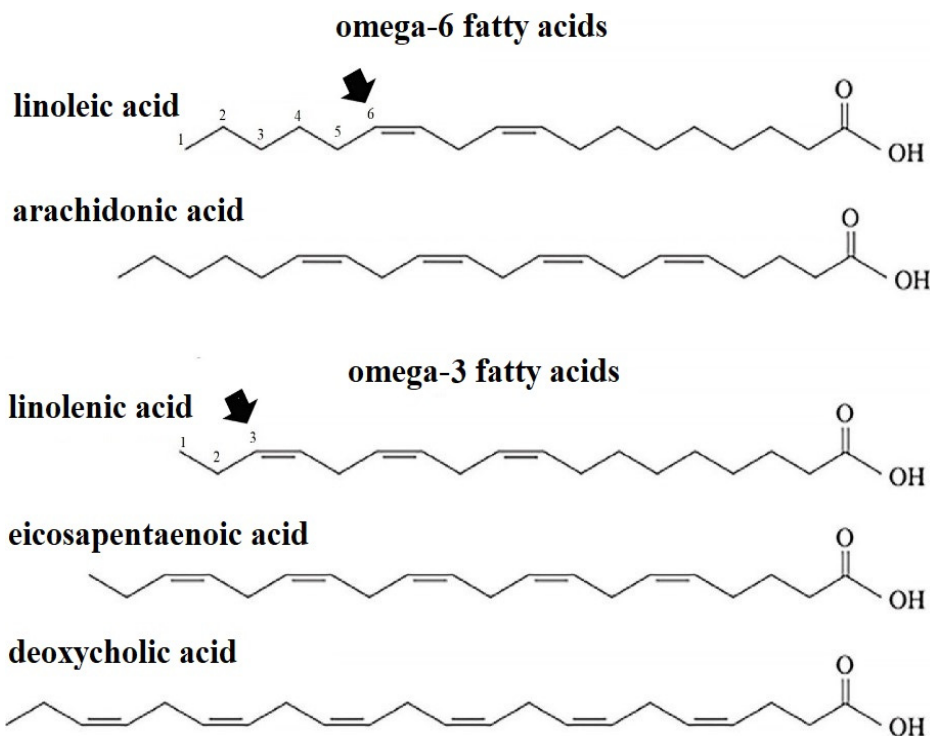


Fig. 1.55. Omega-6 and omega-3 fatty acids

It should be noted that linoleic and linolenic acids are not synthesized in the body of animals and humans and are ingested only with food. They are necessary for

the synthesis of prostaglandins and thromboxanes. Therefore, these acids were called essential carboxylic acids. The main sources of these acids are hemp, linseed, sunflower, corn oils, rapeseed oil. Insufficiency of linoleic acid in the body can lead to growth retardation, changes in skin cells, endocrine glands and genitals. Insufficiency of linolenic acid leads to a decrease in learning ability.

Saturated fatty acids do not participate in addition reactions. They are divided into low- and high-molecular depending on the content of the number of carbon groups and the length of the carbon chain.

Unsaturated fatty acids can exist in the form of both cis and trans isomers. For example, oleic acid, an 18-carbon monounsaturated fatty acid found in olives, has one double bond starting at carbon 9. In fig. 1.56 depicts cis- and trans-structures using structural-linear formulas. The cis structure is the most common isomer found in naturally occurring unsaturated fatty acids. In the cis isomer, the carbon chain has a "bend" at the site of the double bond. The trans-isomer – elaidic acid, is a straight chain without a bend at the place of the double bond. Most of the fatty acids found in the human body are cis fatty acids, with the exception of retinoic acid, which is present in the eye. As a rule, natural saturated fatty acids are solid, and unsaturated fatty acids are liquid.

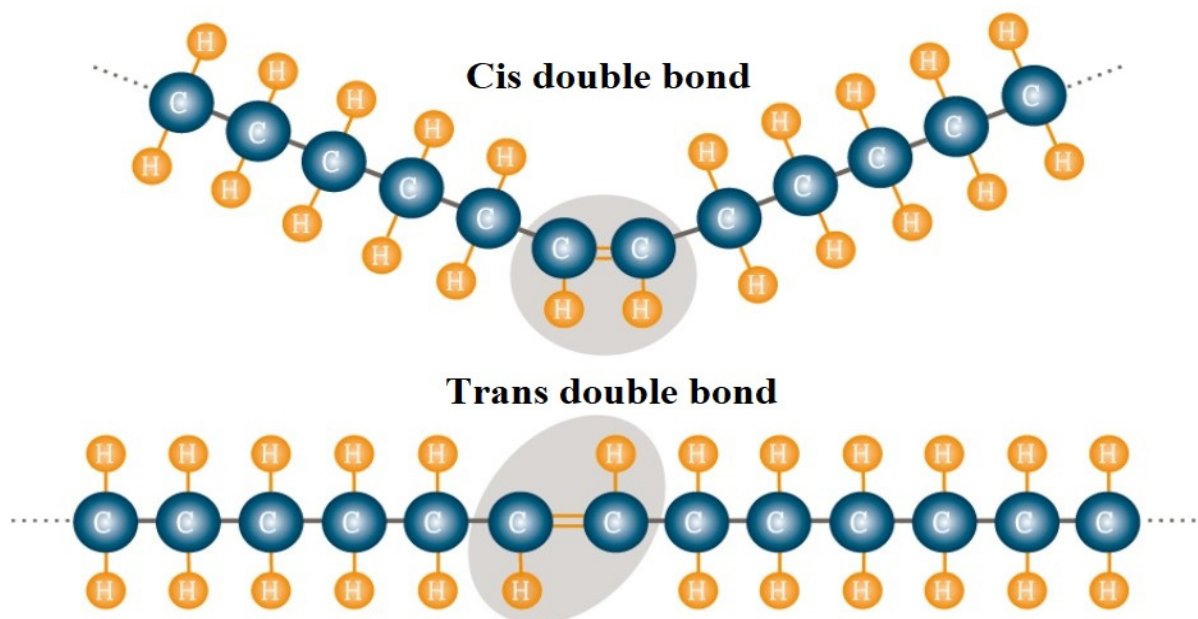


Fig. 1.56. Cis and trans isomers of fatty acids

Unsaturated fatty acids are divided by the number of double bonds:

- monoenes – contain one double bond;
- diene – contain two double bonds;
- triene – contain three double bonds;
- tetraene – contain four double bonds;
- pentane – contain five double bonds;
- hexane – contain six double bonds.

The melting point of unsaturated fatty acids, due to the content of more double bonds, is lower than the melting point of saturated ones. As the molecular weight of saturated fatty acids increases, so does their melting point. Saturated fatty acids are found in fats of animal origin (Figure 1.57).

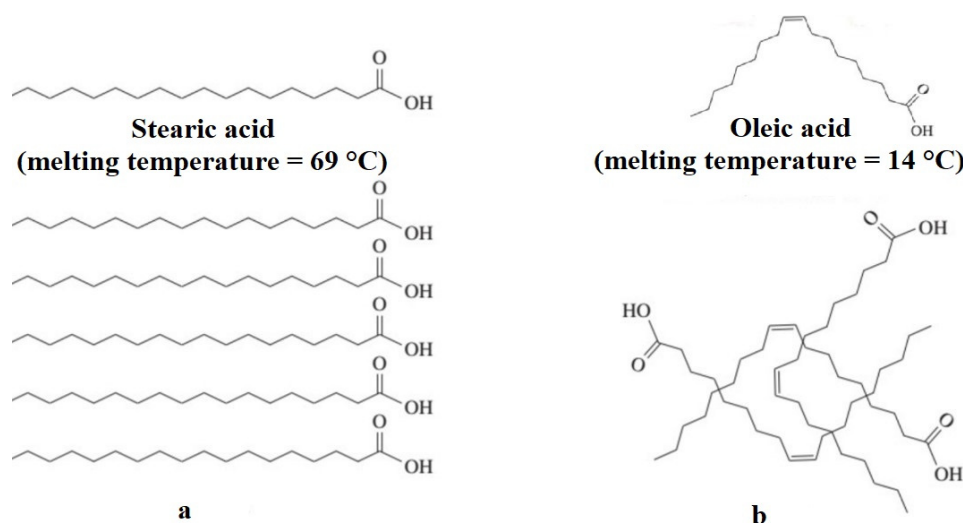


Figure 1.57. Melting points of saturated (a) and unsaturated (b) fatty acids – influence of structure

According to the length of the chain, fatty acids are divided into:

- Short-chain – $1 \leq C \leq 6$
- Medium chain – $8 \leq C \leq 12$ Long chain – $14 \leq C < 18$

Among the long-chain ones, there are also:

- Acids with a very long chain $20 \leq C < 26$
- Acids with an ultra-long chain $28 \leq C < 38$

The most common acids contain from 12 to 18 carbon atoms and have unbranched carbon chains with an even number of carbon atoms. Exceptions are cyclic acids (haulmugro, sterculic, dignocarpic). Of all the acids contained in natural fats, oleic acid is the most common. Saturated fatty acids with an odd number of carbon atoms ($C_{13}...C_{25}$) are relatively rare and occur only as traces in triacylglycerides, for example, in the milk of mammals.

Fatty acids with $C > 20$ are considered anti-alimentary. The longer the acid chain, the worse the acid is metabolized in the human body, acids with $C > 20$ are not metabolized in mitochondria, but only in peroxisomes, which are membrane vesicles containing enzymes necessary for the oxidation of these acids. The accumulation of these acids in peroxisomes is associated with the deterioration of the transmission of impulses by nerve cells.

Stearic and palmitic acids predominate in animal fats from saturated fatty acids, and oleic acids from unsaturated ones.

The content of linoleic acid does not exceed 10%, linolenic acid and arachidonic acid are present in small quantities only in pork.

Table 1.19. Fatty acid composition of the main animal fats

Fatty acids	Beef fat	Lamb fat	Pork fat	Bone fat	Butterfat	Fish Oil
Stearic acid	27...29	25...31	12...16	max 20	10...11	4...5
Palmitic acid	2.0...2.5	25...27	25...30	max 20	24...26	13...15
Myristic acid	–	2.0.4.0	–	–	9.0...10.1	1.0
Oleic acid	2...5	36...43	41...51	50...55	31...34	23...25
Linoleic acid	–	3...4	3...8	5...10	3...4	25...27
Linolenic and arachidonic acid	–	–	max 2	–	–	0.3...2

It should be noted that fish oil (Fig. 1.58) as a fat of animal origin is in a liquid state, as compared to others, it contains a larger amount of unsaturated fatty acids, in particular linoleic.

**Fig. 1.58. Appearance of fish oil**

Unsaturated fatty acids are contained in vegetable oils (Table 1.20), which determines their mostly liquid consistency.

Table 1.20. Fatty acid composition of some vegetable oils

Type of oils and fats	Fatty acid composition, %			
	MSFA	SFA	PSFA	
			ω -6	ω -3
Coconut oil	5-8	85-90	1.5-2.5	–
Sunflower oil	44-47	10-12	45-68	–
Corn oil	26-30	10-14	42-45	1.2-2.0
Rapeseed oil	64-69	6-8	15.0-30.0	3.0-13.0
Palm oil	35-39	46-50	8-10	–
Palm olein	50-54	32-36	10-12	–
Olive oil	69-74	10-15	4.0-12.0	–
Linseed oil	17-20	8-11	8.5-30	35-65

The most common unsaturated acids in oils are linoleic, linolenic, arachidonic, eicosapentaenoic, docosahexaenoic, myristoleic, palmitoleic, oleic acids.

Irreplaceable (essential) fatty acids – linoleic, linolenic and arachidonic, which are not synthesized in the human body and have a very important physiological value, and must enter the body with food.

Oleic acid, which is present in a significant mass fraction in olive oil, as well as in sunflower and rapeseed oils, has no physical activity, but enhances the activity of linoleic acid.

Fats of plant origin with a solid aggregate state, the composition of which is dominated by saturated fatty acids (76.0...83.0 %), include coconut and cocoa beans (Fig. 1.59).



a



b

Fig. 1.59. Appearance of coconut fat (a) and cocoa beans (b)

Questions for discussion and self-examination

1. What are lipids? Describe their structure.
2. Comparison of the fatty acid composition of oils and animal fats.
3. Melting point of saturated and unsaturated fatty acids. Differences.
4. Describe the types of fat as raw materials.
5. Determination of amphiphilicity.

Topic 1.6. Lipids: changes during the technological process and storage

1.6.1. The main changes in lipids during technological processing

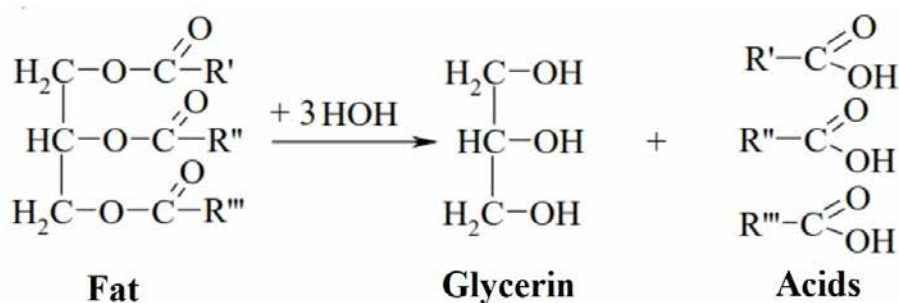
During technological processing, the fats included in the composition of raw materials change their properties.

Changes in lipids during technological processing are as follows:

- hydrolysis;
- hydrogenation;
- transesterification;
- auto-oxidation;
- thermal oxidation and terpolymerization;
- pyrolysis

Hydrolysis, or saponification, occurs under the influence of acids, alkalis, and enzymes (Fig. 1.60).

a) saponification with alkalis:



b) saponification with water:

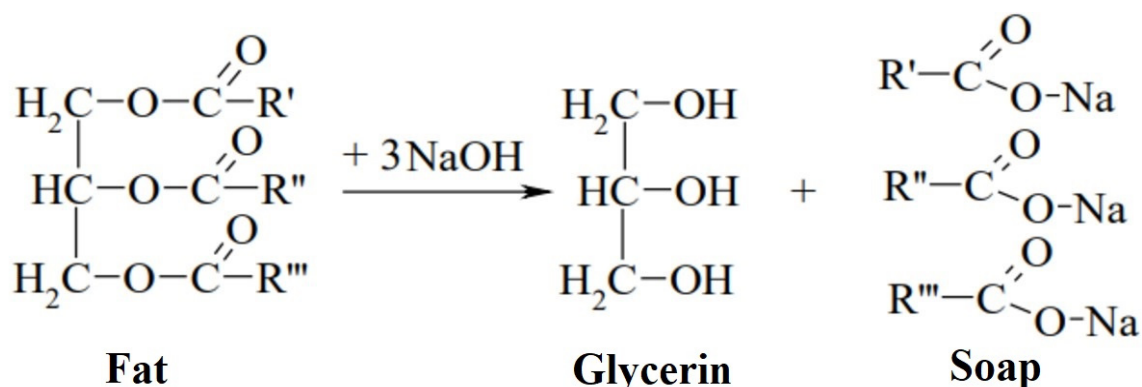


Fig. 1.60. Flow chart of the saponification process:

a) saponification with alkalis; b) saponification with water

The products of saponification with water are free fatty acids and glycerin.

Hydrolysis of lipids can occur under the influence of biological catalysts – enzymes. Enzymes that break down lipids are lipoxigenases.

Enzymatic oxidation is characteristic of the lipid complex of oilseeds, stored grain, and their processing products (flour, groats). The process of enzymatic rancidity takes place with the participation of lipase and lipoxigenase enzymes.

Lipase catalyzes the hydrolysis of triacylglycerols, and lipoxigenase catalyzes the formation of hydroperoxides of unsaturated fatty acids, mainly linoleic and linolenic (Fig. 1.61). Free fatty acids are oxidized faster than their residues included in fat molecules.

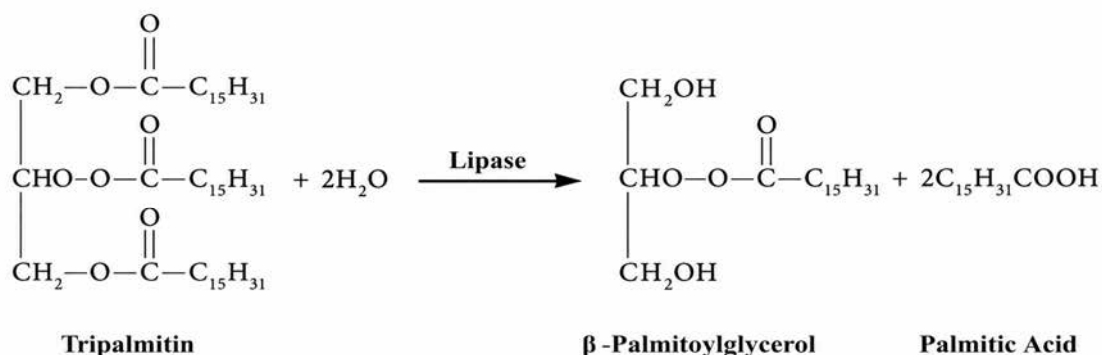


Fig. 1.61. Scheme of the enzymatic action of lipase

Hydrogenation of fats is a process of saturation with hydrogen atoms, in the presence of a catalyst, of unsaturated fatty acids. Upon saturation of double bonds with hydrogen atoms, liquid fat turns into a solid state.

Hydrogenation changes the fatty acid composition of fats and oils and makes it possible to obtain a product with a higher melting point, plasticity, and more resistant to oxidation. Fats interact with hydrogen during heating to 180...240 °C in the presence of catalysts (crushed nickel) (Fig. 1.62). By changing the reaction conditions accordingly, it is possible to carry out selective hydrogenation, that is, to hydrogenate first the residues of linolenic acid, then linoleic and, if necessary, oleic acid.

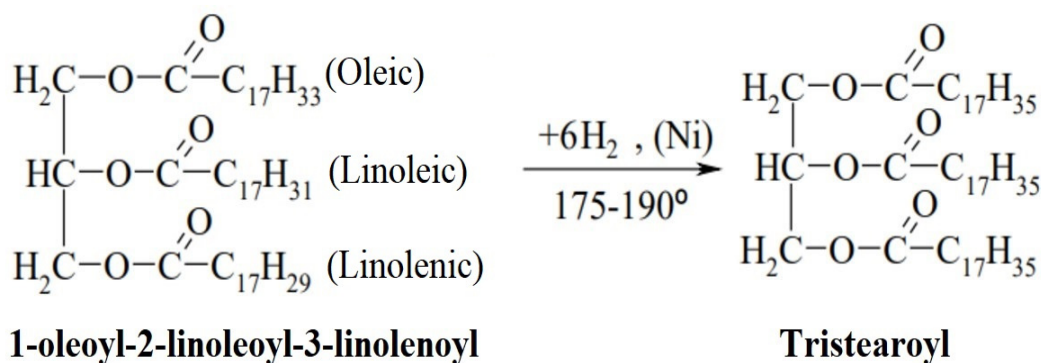


Fig. 1.62. Scheme of hydrogenation of liquid fat

The product of the reaction is called hydrogenated fat ("artificial lard") and serves as the basis for the production of margarine, other edible fats, and is used in the production of soap. To make margarine, hydrogenated fat is emulsified in milk pre-treated with *Bacillus aidii* *levolactiti* bacteria, which produce lactic acid. Further, food additives are added to the formed emulsion. In the case of incomplete hydrogenation, the hydrogenated fat obtained is used for the production of soft varieties of margarine. It should be noted that there is an opinion about certain harmfulness of hydrogenated vegetable oils for humans. Systematic use of such fats and products based on them (biscuits – up to 30...50% trans isomers, french fries – about 40 %, chips – 30 %, etc.) increase the risk of ischemic heart and brain diseases; contribute to the development of atherosclerosis. This is associated with the appearance of trans-carboxylic acids in such oils (fats).

The latter occur under harsh conditions of the hydrogenation process as a result of isomerization of cis-configuration acids, which is mostly characteristic of natural unsaturated acids.

Transesterification of fats. It consists in the exchange of two different triglycerides with fatty acid residues (Fig. 1.63). For example, oil and solid fat (animal fat, hydrofat, palm oil) are mixed and the mixture is heated to 25...90 °C in the presence of a catalyst. At the same time, acid residues pass from one triglyceride to another. A mixture of various triglycerides with a melting point of 31...34 °C is formed. Culinary fats, margarine, confectionery and bakery fats are produced on the basis of food hydrogenated fat through transesterification.

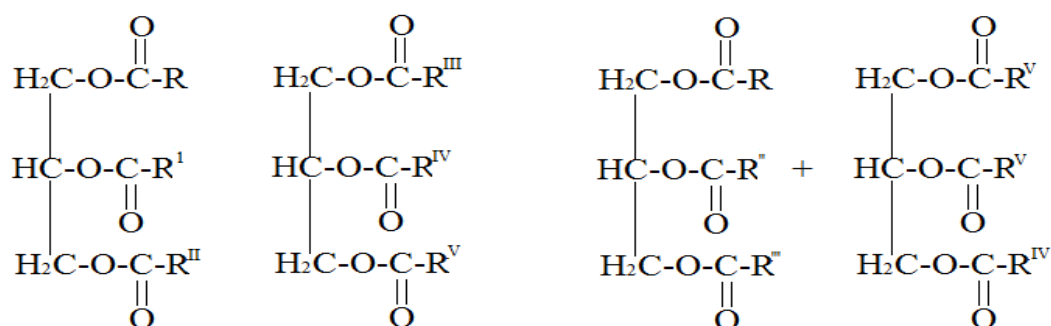
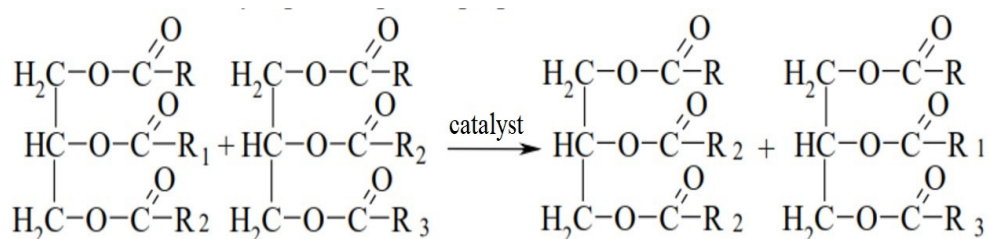
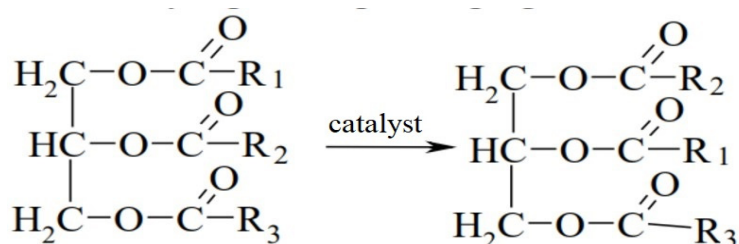


Fig. 1.63. Scheme of transesterification of fats

Reaction of intermolecular transesterification:

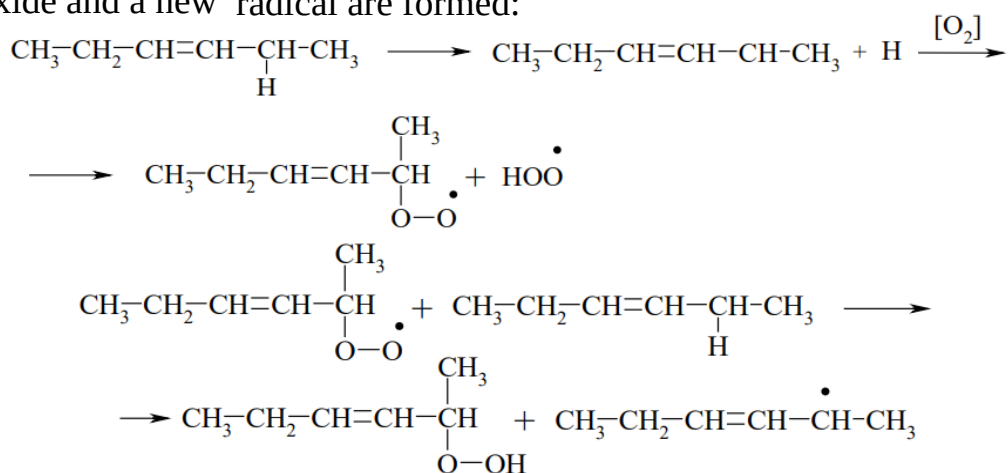


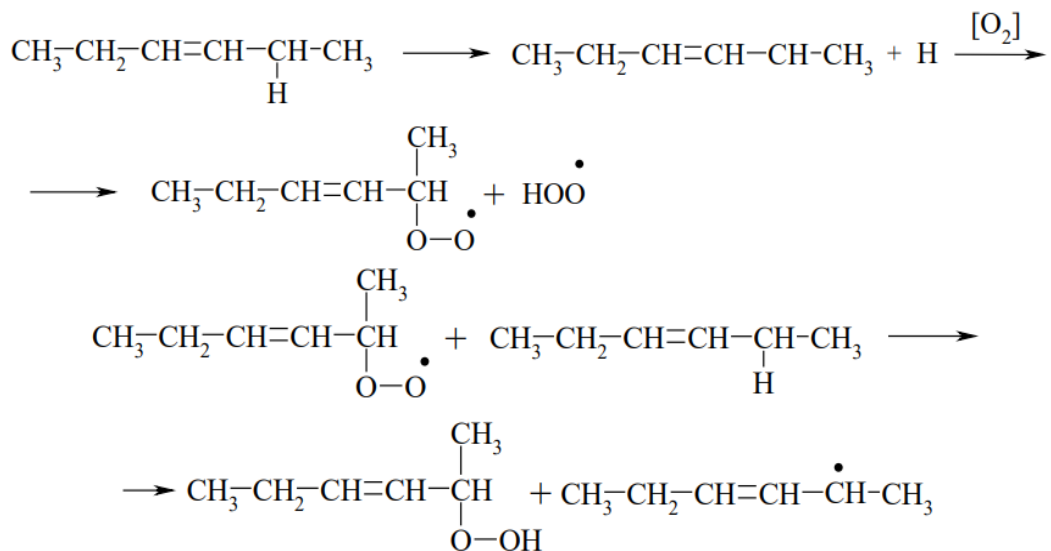
Intramolecular transesterification reaction:



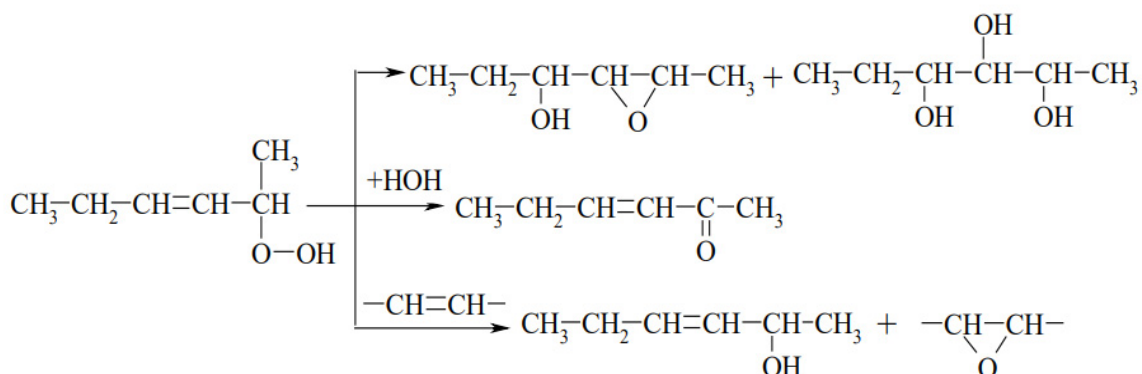
Fats and oils that contain radicals of unsaturated fatty acids are **oxidized** by air oxygen. Primary oxidation products are hydroperoxides. Hydroperoxides are unstable substances and as a result of their transformation, secondary oxidation products are formed - oxy- and epoxy compounds, alcohols, aldehydes, ketones, acids and their derivatives.

The mechanism of fat oxidation, discovered by M. Semenov, is based on the peroxide theory of Bach and Engler. At the first stage, the $-\text{CH}_2-$ group, which is located in the α -position relative to the double bond, is oxidized mainly. As a result of the homolytic breaking of the bond between Hydrogen and Carbon in the α position, a radical is formed, which upon interaction with air oxygen forms a peroxide radical. After the interaction of this radical with a new fat molecule, hydroperoxide and a new radical are formed:

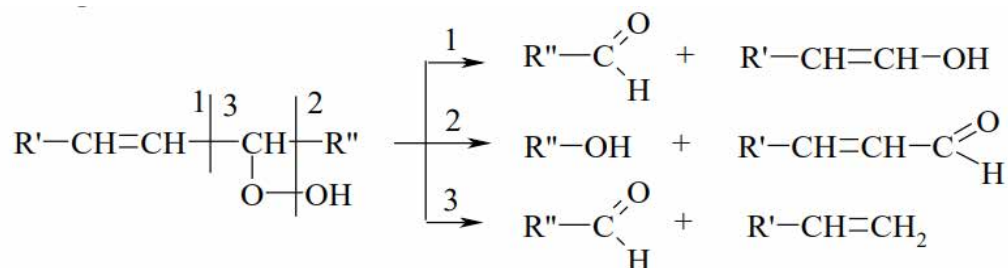




The primary products of fat oxidation are hydroperoxides. These are unstable compounds, they turn into secondary products of fat oxidation - epoxy compounds, ketones, aldehydes, alcohols and their derivatives:

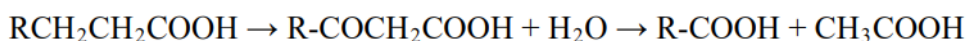


During the formation of secondary oxidation products, the carbon chain can be broken:



As a result of polymerization and polycondensation of oxidation products, the so-called "crosslinking" of molecules and chain breakage occurs, which leads to the formation of low molecular weight compounds. The speed of the oxidation reaction intensifies with an increase in: the degree of unsaturation of HCA, which are part of fat; humidity level; temperature and oxygen content; the presence of metal ions (iron, manganese, copper). The presence of antioxidants – substances that form stable compounds with free radicals – has an extremely large influence on the rate of

oxidation. Natural antioxidants include tocopherols, phenolic compounds, in particular quercetin. The activity of antioxidants increases in the presence of their synergists, in particular, citric and ascorbic acids, lecithin. In the animal body, fatty acids are oxidized to carbon dioxide and water. Today, all intermediate stages of this complex process are known. Oxidation begins with the $-\text{CH}_2-$ group, which is in the β -position relative to the carboxyl group ($-\text{COOH}$). β -keto acid, which is formed in this case, decomposes as a result of hydrolysis with the formation of a new carboxylic acid and acetic acid.



The newly formed acid is subject to similar oxidation until acetoacetic acid $\text{CH}_3\text{COCH}_2\text{COOH}$ is formed. The latter is oxidized in tissues (mainly in muscles) to CO_2 and H_2O .

Auto-oxidation. Occurs when fats come into contact with air O_2 (autooxidation). The resulting auto-oxidation products are capable of polymerization and polycondensation. The auto-oxidation process primarily depends on the lipid composition: the oxidation process is accelerated by increasing the degree of unsaturation of fatty acids that are part of acylglycerols.

The process of auto-oxidation is accelerated by increasing humidity, access to light, and the presence of catalysts. Slows down at low temperatures (storage in refrigerating chambers), in the environment of inert gases and CO_2 .

Thermal oxidation of fats occurs during heating of fats and fatty raw materials with free access of oxygen. Thermal oxidation of lipids occurs at temperatures of $140\ldots 200\text{ }^\circ\text{C}$.

The initial stages of oxidation follow the same mechanism. However, the speed of these reactions during heating increases sharply, especially at the stage of formation of secondary oxidation products. At a certain stage of oxidation, double bonds react (with the formation of epoxides). In the later stages of thermal oxidation, dicarbonyl compounds with diketone groups and dioxyacids are formed in the fat.

Thermal oxidation is also accompanied by the splitting of fatty acids, which are oxidized, with the formation of a large number of low molecular weight volatile compounds (aldehydes and carboxylic acids). Further stages of thermal oxidation are accompanied by **thermopolymerization**.

Polymer non-volatile products are formed at the thermopolymerization stage. The initiator of polymerization are free radicals, which are formed during oxidation. Unsaturated fats with compatible systems of double bonds are easier to polymerize (as in oxidation). Thermopolymerization occurs due to "crosslinking" of fatty acid chains. Dimers and trimers are formed. Cyclic structures of fatty acid chains and radicals can also be formed. For example, thermopolymerization is noticeable in highly saturated linseed oils. It quickly oxidizes in the air, and as a result of polymerization, it forms a flexible hard film. Such oils are called "drying" and are used for the production of oleum and linoleum. At a high temperature, the thermopolymerization process is accelerated. The processes of thermal oxidation and thermopolymerization are closely related.

1.6.2. Changes in lipids during cooking

The fat contained in the food melts during the cooking process and part of it passes into the broth.

The amount of fat entering the cooking medium depends on its composition and the nature of the content in the product, the duration of cooking, the size of the pieces and other factors. Up to 95 % of the fat coming from the product is localized on the surface of the broth and only a small part (3.5...10 %) is distributed throughout the volume of the broth in the form of small fat balls (emulsified fat).

Emulsified fat worsens the organoleptic quality indicators of the broth, it loses its transparency, and a greasy aftertaste appears. Boiling of liquid and, as a result, emulsification of fat enhances its hydrolysis due to a significant increase in the contact surface between fat and water.

The presence of sodium chloride and food acids in the liquid also enhances fat hydrolysis. The free fatty acids formed as a result of hydrolysis, which give the broth an unpleasant taste, have increased reactivity, can form potassium and sodium salts (soap), are oxidized by oxygen in the air and dissolved in water with the formation of peroxides, hydro-peroxides, oxyacids instead of double bonds ties Therefore, in order to reduce undesirable physical and chemical changes in lipids when cooking food products, slow boiling of liquid and periodic removal of fat from its surface is used.

1.6.3. Changes occurring in lipids during frying

Frying products with the addition of fat is carried out in one of two ways: with a small amount of fat (about 8 % by weight of the product) and deep-frying, when the product is completely immersed in fat; the optimal ratio of fat and product in this case is 4:1. Usually, prepared culinary semi-finished products intended for frying are placed in fat heated to 160...180 °C.

The duration of frying varies widely – from 5...8 minutes to several hours (meat in large pieces, poultry carcasses). The depth of physical and chemical changes corresponds to this. When frying products, the first method involves the melting of fat, its absorption by the product, hydrolysis, oxidation of lipids with the formation of peroxides, hydroperoxides, oxyacids, pyrolysis (smoke formation) to volatile low molecular weight products, including acrolein – an aldehyde released as a result of the pyrogenetic decomposition of glycerol. Acrolein is a powerful substance. Getting into the atmosphere of production workshops, it has an irritating effect on the mucous membranes of the eyes and respiratory organs. Different fats under the same conditions have different smoke formation temperatures (°C): rendered pork fat – 221, cottonseed oil – 223, food lard – 230.

In addition to the type of fat, the smoking temperature is influenced by the content of free fatty acids in it, the ratio of the heated surface of the fat to its volume, the material and size of the vessel in which the heating is carried out. Thus, an increase in the content of free fatty acids in pork fat from 0.02 to 0.81 % reduces its smoke formation temperature to 150 °C. When heating the same amount of fat of the same type in two frying pans with a diameter of 15 and 20 cm, the smoke formation

temperature was 185 and 169 °C, respectively. Some heavy metals (iron, copper, etc.) catalyze the pyrolysis of fat, lowering its smoke formation temperature.

1.6.4. Changes in frying fats

The duration of deep-frying products is short. For example, at a frying temperature of 180 °C, portioned pieces of fish and potatoes are fried in cubes for about 5 minutes, pies, donuts, chebureks – 6 minutes.

The readiness of the deep-fried product is assessed by the color of the specific painted crust on its surface. After deep-frying, some products are fried in the oven for 5...7 minutes to reach a temperature of 80...85 °C in the geometric center of the product (stuffed cutlets, portions of fish, etc.). Thus, the depth of physico-chemical changes in fat is affected not so much by the process of frying products, but by the duration of using deep-frying (2...3 changes or more). Also, the temperature of frying fat affects the course of physical and chemical processes in lipids. Thus, at a temperature of 200 °C, fat hydrolysis occurs 2.5 times faster than at 180 °C. At the same time, the processes of polymerization of glycerides and fatty acids are noticeably accelerated.

During continuous frying, fat is evenly removed from the bath with the finished product and replenished by automatic addition of fresh fat. The amount of fat that is carried with the finished product depends on the type of product and the degree of its grinding. Thus, crispy potatoes absorb up to 40 % of fat as a result of frying, donuts – up to 27 %.

An important factor in preserving the quality of deep-fried fats during frying is the degree of contact of the fat with oxygen in the air, without access to which even long-term heating at 180...200 °C does not cause noticeable oxidative changes in the fat. Heating the fat in a thin layer, frying products with a porous structure, intensive foam formation and stirring of the fat contribute to increasing the contact with air. The rate of fat oxidation can be significantly slowed down by introducing a small amount of antioxidants (oxidation inhibitors), whose mechanism of action is different. Some natural (carotene, tocopherol isomers) and artificial (butyloxylanisole, butyloxytoluene, phenol derivatives) antioxidants bind free radicals, turning them into an inactive state.

However, at high frying temperatures, most natural and artificial antioxidants are destroyed or evaporated. The chemical composition of fried products has a noticeable effect on the rate of thermal oxidation of fat, which is explained, in particular, by the content of a significant amount of antioxidants in some of them. So, the proteins included in the products are capable of providing an antioxidant effect; some substances formed as a result of melanoid formation reactions have a reducing effect and can interrupt the chain of oxidative transformations. In addition, the resistance of lipids to oxidation depends on the degree of their unsaturation. Other things being equal, unsaturated fatty acids are oxidized faster than saturated fatty acids.

However, technological factors such as temperature, air access, duration of heating, cookware material, frequency of frying play a more significant role in thermal oxidation processes. At the first stage of deep-frying products, the same

physico-chemical changes in lipids occur as during normal frying: acid and peroxide values increase, iodine value decreases.

Further deep-frying of products is accompanied by the decomposition of peroxides, hydroperoxides and oxyacids and the coloring of thermostable oxidation products: carbonyl and dicarbonyl compounds, fatty acids with conjugated double bonds, and polymerization products (Fig. 1.64).

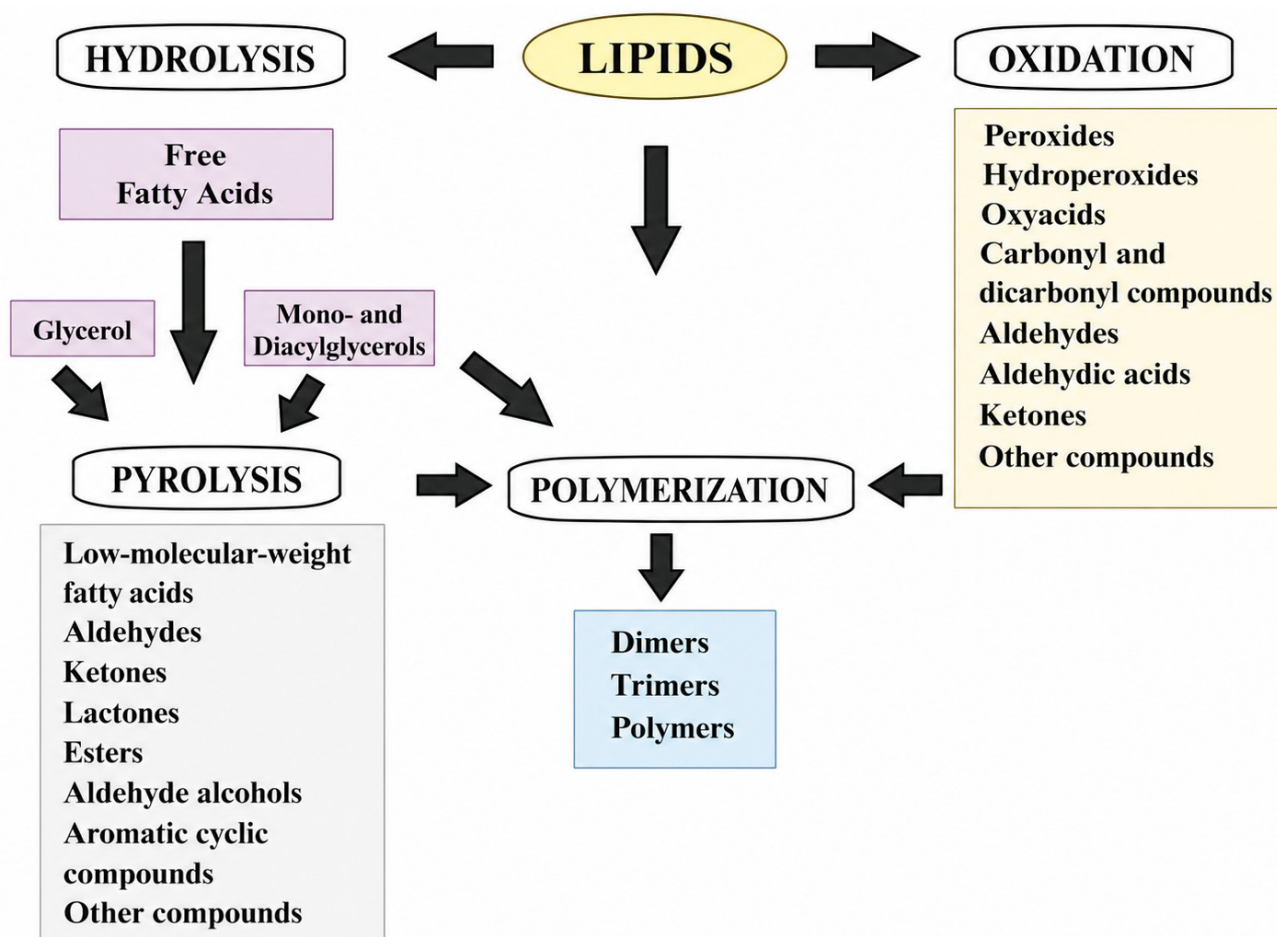


Fig. 1.64. Principle scheme of physicochemical changes in deep-fried lipids during frying of products

1.6.5. Changes in organoleptic indicators of lipid quality during technological processing

In the process of deep-frying food products, pigments contained in fat (carotenoids, chlorophyll, gossypol, etc.) are easily destroyed by heating, as a result of which the fat becomes lighter at the beginning of heating, and darkens to the color of strong coffee as it is further heated.

There are several reasons for darkening of fat. One of them is the contamination of fat with substances of pyrogenetic decomposition, which are formed during the charring of small particles of fried products. Another reason is the reactions of melanoid formation and caramelization. The next reason for the appearance of a dark color is the accumulation of oxidation products of the fat itself. For example, two adjacent carbonyl groups (-CO-CO) determine the appearance of the color of the compounds of which they are a part. Such compounds easily enter into condensation reactions, which leads to further strengthening of the color.

Another reason for the darkening of fats is the presence of chromogens (lightly colored or colorless substances) in some of them. During oxidation and the action of other factors, chromogens are intensively colored. Pure non-oxidized triglycerides are tasteless and odorless. However, in the deep-frying process, volatile substances (substances with a short chain) are formed, of which more than 220 species have been found in heated deep-frying fats. Some of them give a certain smell to fried products and the fat itself.

For example, carbonyl derivatives containing 4, 6, 10, or 12 carbon atoms give fried foods a pleasant odor, while carbonyl components containing 3, 5, or 7 carbon atoms adversely affect the odor of fried foods. An additional amount of odorous components is formed by the interaction of amino acids (especially methionine) and product proteins.

With long-term use for deep-frying, the fat acquires a dark color and at the same time a burning-bitter taste. In addition, he has a pungent burning smell.

1.6.6. Types of spoilage of fats

The main types of fat oxidation are distinguished

- 1) germination;
- 2) decay;
- 3) ossification.

Germination is associated only with the hydrolysis of fats and is the initial stage of ripening of the liver with the accumulation of free fatty acids. Fats acquire an unpleasant sour taste during fermentation.

Decay is caused primarily by the elimination of unsaturated fatty acids, which are found in free walls and those that are formed as a result of acidification. As a result of rancidity, low-molecular products accumulate in fats: aldehydes, ketones, low-molecular fatty acids. In this case, the fat acquires a bitter taste and a sharp, unpleasant smell. Rancidity of fats can occur as a result of chemical and biochemical processes.

Ossification is the deepest process of ripening grapes, as a result of which not only the taste changes, but also the consistency, the temperature of heating increases, the pulp is not affected, which is associated with the destruction of carotenoids as a result what fat acquires the whole flavor.

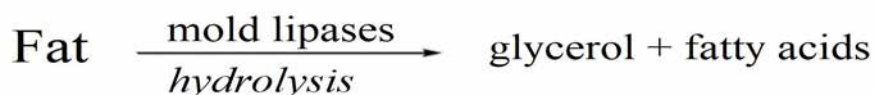
During ossification, a significant amount of oxycompounds is formed as a result of the decomposition in the light of primary organic peroxides and the appearance of free radicals due to photochemical action on fat. The resulting radicals interact with fatty acid molecules to form oxyacids.

The oxyacids formed are involved in the polymerization process, as a result of which high-molecular compounds are formed and the fat acquires a characteristic fatty smear consistency.

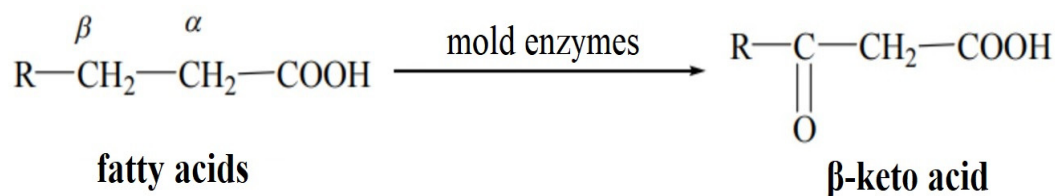
Decay of tendons and tendon products is the result of complex chemical and biological processes. Two main ways of bending are accelerated: 6-oximic and xymic.

Biochemical decay of tendons is caused by specific lungs, the activity of which slows down with a decrease in temperature, slows down and stops completely at high temperatures. A soft palate is characterized by the accumulation of methyl alkyl ketones

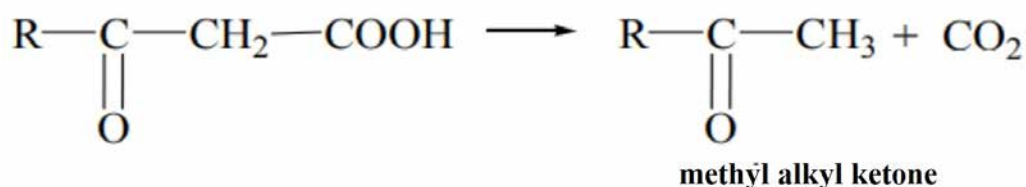
It is believed that lipases of the lungs cause initial hydrolysis of the fats:



The acids that are formed undergo β -elimination with:



β -ketocycles are easily decarboxylated:



Methyl alkyl ketones have an unpleasant taste and smell.

In the process of **chemical germination**, which occurs in fats under the influence of air oxygen, free fatty acids accumulate, sometimes low molecular weight, not characteristic of this fat, the peroxide number increases, aldehydes and ketones are formed, which give the rancid smell of fat.

1.6.7. Factors affecting changes in the lipid component during storage

A number of factors affect the speed of processes occurring in fats during storage:

1) the chemical composition of fat, which in turn depends on the type, grade and quality of the initial fat-containing raw materials, etc. It should be noted that, other things being equal, fat with more unsaturated acids oxidizes faster;

2) the content of natural antioxidants in fat significantly affects its stability during storage. For example, vegetable oils are more unsaturated than animal fats, but rich in fat-soluble vitamins with antioxidant properties;

3) the content of oxidation catalysts in fats, in particular metals with variable valence, significantly reduces their resistance to oxidation during storage; the possibility of transition of metals from containers, dishes or packaging material also affects;

4) storage temperature: an increase in temperature, as a rule, increases the rate of chemical reactions, so the amount of peroxides formed during the oxidation of fats also increases with an increase in temperature. On the other hand, an increase in temperature, especially up to 40...45 °C and above, sharply increases the rate of decomposition of hydroperoxides with the formation of secondary oxidation products;

5) air access: the rate of initiation of the process depends on the partial pressure of oxygen (on the amount of oxygen entering the reaction zone);

6) access to light: light is the starter of the initiation of a chain of oxidative transformations in fats.

1.6.8. Stabilization of fat-containing food products

Fats of animal and vegetable origin include natural antioxidants.

The most active of them are tocopherols (vitamin E). Pyrocatechin derivatives and tannins also have an antioxidant effect.

During technological processes: the production and purification of fats, these antioxidants can be partially removed, which leads to a sharp decrease in the resistance of fats to oxidation and necessitates the introduction of certain food additives - antioxidants.

Animal fats, as a rule, contain less tocopherols compared to vegetable fats. Therefore, the additional introduction of tocopherols to them dramatically increases the resistance of animal fats to rancidity.

Antioxidants are used to prevent oxidative deterioration of fats and products containing fats and increase their shelf life.

Natural antioxidants include tocopherols, gallic acid esters, some flavonoids, phenolic diterpenes, etc.

Ascorbic acid and its derivatives are used to prevent oxidative deterioration of fats, in particular margarine, ghee, and other products.

Sodium ascorbate (ascorbate) is used instead of ascorbic acid.

Ascorbyl palmitate and ascorbyl stearate – esters of ascorbic acid with palmitic, stearic, myristic and other high-molecular fatty acids also have antioxidant properties. Effective when used together with phospholipids and tocopherols.

Tocopherols in the form of a mixture of isomers are found in significant quantities in vegetable oils.

Synthetic antioxidants - butylhydroxyanisole, butylhydroxytoluene, salts of gallic acid and tert-butylhydroquinone, which have a similar mechanism of action, have become the most widespread.

Butylhydroxyanisole is used to slow down the oxidation of rendered animal fats and salted lard. This antioxidant is resistant to high temperatures, so it can be added to products subject to cooking, drying, frying, etc.

Butylhydroxytoluene, or ionol (E 321), is also used in the food industry to slow down the oxidation of animal rendered fats and salted lard.

Extracts of some plants have high antioxidant activity.

Antioxidant properties are also shown by some spices: anise, cardamom, coriander, dill, fennel, ginger, red pepper.

A number of substances with antioxidant effect have been synthesized. Such substances include phenol derivatives - butoxyanisole and butoxytoluene, and esters of gallic acid - ethyl gallate and propyl gallate.

Phenolic antioxidants are used to preserve fats and oils, confectionery, fish and meat products. 3-tert-butyl-4-oxyanisole, 3,5-di-tert-butyl-4-oxytoluene and nordihydroguaiaretic acid became the most widespread.

Questions for discussion and self-examination

1. *What changes occur with lipids during technological processes?*
2. *Describe the auto- and thermal oxidation of lipids.*
3. *What changes occur in the structure of lipids during oxidation?*
4. *Describe the process of transesterification of fats?*
5. *How does the taste, smell, and color of deep-fried fats change during culinary use?*
6. *What are antioxidants? For what purpose are they used?*

Topic 1.7. Carbohydrates: characteristics and properties

Carbohydrates are organic compounds, an elementary storehouse of all kinds of atoms, such as carbon, water, and sour. The formula for carbohydrates is $C_n(H_2O)_m$.

1.7.1. Physiological functions and food value of carbohydrates

Carbohydrates in the form of various derivatives are part of the cells of any living organism and play the role of structural material, energy supplier, substrates and regulators of specific biochemical processes.

Combining with nucleic acids, proteins and lipids, carbohydrates form high molecular complexes that are the basis of subcellular structures and represent the

basis of living matter. The main source of carbohydrates in food is vegetable products.

Among the important physiological functions of carbohydrates, the following should be noted:

1) Energy function. Carbohydrates are the main source of energy for the human body. Energy is necessary for the vital activity of cells, tissues and organs. As a result of biological oxidation of carbohydrates, energy is released, which is accumulated in the form of energy-rich compounds, for example, ATP, which takes part in providing significant energy needs of the body.

2) Plastic function. Carbohydrates are used for the synthesis of nucleic acids, amino acids, proteins and are part of various tissues and fluids, acting as a plastic material.

3) Protective function. Carbohydrates play an important role in the body's defense reactions, especially those that occur in the liver. Carbohydrates are also the main components of plant tissue membranes and take part in the formation of cell membranes.

4) Support function. Fiber and other polysaccharides form a strong framework of plants, make up their mechanical and supporting tissues. Together with proteins, carbohydrates are part of cartilage, which performs a supporting function in humans and animals.

5) Regulatory function. Carbohydrates take part in metabolism. If the metabolism of carbohydrates is disturbed, they accumulate in the body, which leads to the development of acidosis (increased amount of acetone in the blood). Ballast substances stimulate intestinal peristalsis, contribute to the removal of cholesterol from the body, prevent the absorption of poisonous substances from the large intestine and improve digestion. Monosaccharides also play a significant role in the regulation of osmotic processes.

6) Specialized function. Some carbohydrates and their derivatives have biological activity, performing specialized functions in the body. Thus, heparin prevents blood clotting in blood vessels, and hyaluronic acid prevents the penetration of bacteria through the cell membrane.

Certain carbohydrates perform special functions in the body, for example, they participate in the conduction of nerve impulses, the formation of antibodies, ensure the specificity of blood groups, and the normal activity of the central nervous system. Carbohydrate reserves in the human body are limited. Their number does not exceed 1% of body weight, and during intensive work, this reserve quickly decreases. Carbohydrates must enter the body with food every day.

A person's daily need for carbohydrates is 400-500g. Carbohydrates make up about 1% of the total weight of the human body. Carbohydrates are divided into those that are digested in the body and ballast substances according to their nutritional value.

The first type of carbohydrates includes monosaccharides, oligosaccharides and polysaccharides - glycogen, dextrans, starch. Ballast substances or dietary fibers include such polysaccharides as fiber, hemicelluloses, pectin substances, inulin, gums, mucus; Carbohydrates of the first type, with the exception of monosaccharides,

are split in the digestive tract, absorbed and then directly utilized in the form of glucose or converted into fat or deposited in the form of glycogen.

The main processes occurring during carbohydrate metabolism include the following:

- 1) splitting in the gastrointestinal tract of polysaccharides and disaccharides that come with food. Monosaccharides are absorbed from the intestines into the blood;
- 2) synthesis and breakdown of glycogen in tissues;
- 3) glucose is anaerobically split with the formation of pyruvate (anion or salt of pyruvic acid $\text{CH}_3\text{COCOO}^-$);
- 4) aerobic metabolism of pyruvate (respiration);
- 5) secondary pathways of glucose catabolism;
- 6) interconversion of hexoses;
- 7) the formation of carbohydrates from non-carbohydrate products (pyruvic, lactic acid, glycerol, amino acids, etc.).

Carbohydrates in the form of glucose circulate in the blood and provide the body's needs. The normal content of glucose in the blood is 80...120 mg in 100 ml, or 3.3...5.5 units.

An excess of carbohydrates is converted into glycogen, which is used as a source of glucose when there is an insufficient amount of carbohydrates in food. When the function of the pancreas is disturbed, which begins to produce an insufficient amount of the hormone insulin, the processes of glucose utilization slow down, the level of glucose in the blood increases significantly, and sugar is detected in the urine. Such a disease is called diabetes. Carbohydrates that are not digested in the body make up dietary fiber. They are not disposed of by the body, but they play an important role in digestion.

Among the important functions of dietary fibers, the following should be noted:

- 1) stimulation of the motor function of the intestines;
- 2) obstruction of cholesterol absorption;
- 3) normalization of the composition of intestinal microflora, slowing down of putrefactive processes;
- 4) impact on lipid metabolism, the violation of which leads to obesity;
- 5) adsorption of bile acids;
- 6) promoting the reduction of the content of toxic substances in the vital activity of microorganisms and the removal of toxic substances from the body.

A person's daily need for dietary fiber is 20...25 g. A lack of dietary fiber in the diet leads to impaired metabolism, deterioration of digestion and general weakening of the body. At the same time, the predominance of coarse vegetables in food, which contain a lot of dietary fiber, is also undesirable, because it leads to incomplete digestion of food, impaired absorption of minerals and vitamins.

1.7.2. Classification of carbohydrates

All carbohydrates are divided into two large groups: monosaccharides (simple carbohydrates or monosaccharides), polysaccharides (compound carbohydrates or polyoses), which are made up of several excess monosaccharide molecules linked to each other (Fig. 1.65).

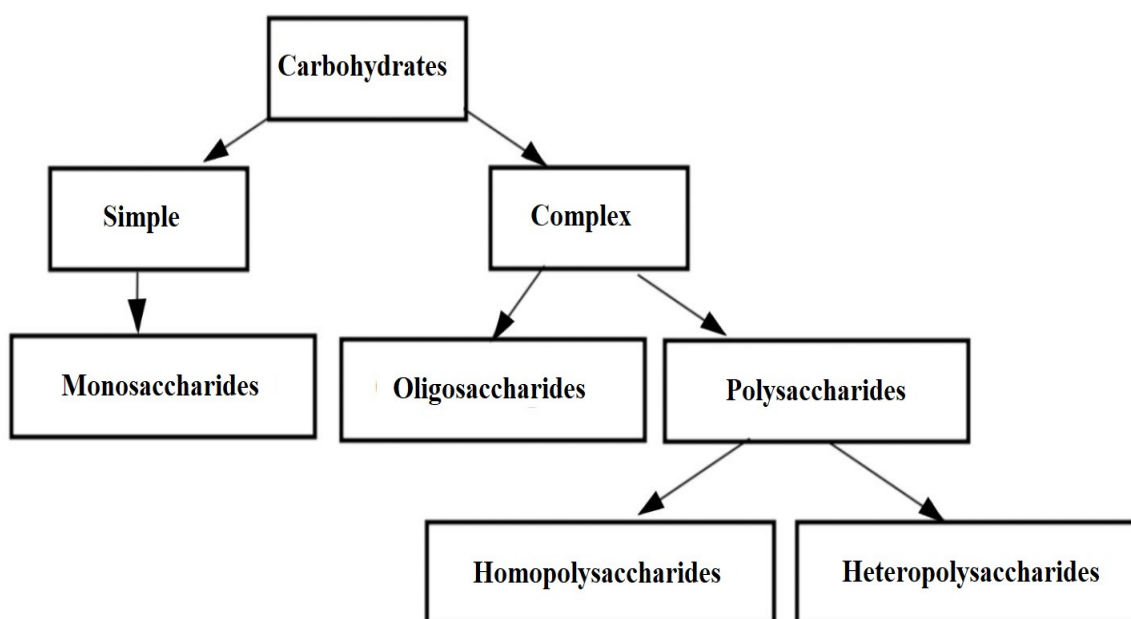


Fig. 1.65. Classification of carbohydrates

Polysaccharides (golosides) are folded carbohydrates, the molecules of which break down into monosaccharides during hydrolysis. Homo-, hetero- behind the warehouse of monosaccharide surpluses.

Monosaccharides – crystalline, barless substances, good for water, licorice for relish. To be governed by strong reinforcing (reducing) authorities. Renewal of honey in honey oxide, sribla in srib oxide (srib mirror reaction), Fehling's solution - clear reactions to monosaccharides. The stench itself oxidizes to acid.

Monosaccharides are rich in atomic aldehydes and ketone alcohols.

Depending on the nature of their functional groups, they are divided into: aldoses and ketoses; depending on the number of carbon atoms in a molecule – triose, tetrose, pentose, hexose, etc.

Natural monosaccharides containing more than 9 carbon atoms have not been identified.

The carbon atoms in monosaccharide molecules are numbered in such a way that the C atom of the carbonyl group has the lowest number.

Monosaccharides are present in the D- or L- series following the configuration of the remaining chiral (asymmetric) carbon atom of monosodium (Fisher's method).

Glyceraldehyde is present in the acid of the solution. The D form is more frequent.

In nature, monosaccharides appear in cyclic forms: the hydrogen of the hydroxyl group (at the 5th carbon atom), which often has a positive charge, passes to the acid of the aldehyde group with an often negative charge. As a result, the first carbon atom and the acid atom at 5 carbon atoms share the same valence, for the sake of which these atoms are bonded to each other by an acid-liquid mixture (Fig. 1.66).

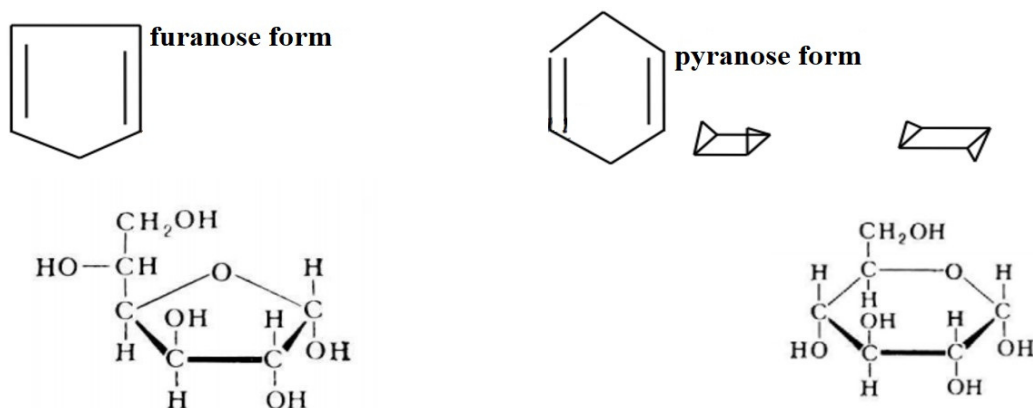


Fig. 1.66. Cyclic forms of monosaccharides

Cyclic form. D-glucofuranose Cyclic form. D-glucopyranose. The thermodynamically most stable form is the pyramidal (six-membered) form.

The most important monosaccharides include glucose and fructose. D – glucose, or grape zuccor, is extremely widely represented in food and plants.

It is found in plants, roots, flowers, leaves and fruits of most plants, both in appearance and rich in oligosaccharides (maltose, sucrose, lactose, raffinose) and a number of glycosides.

Glucose produces the main polysaccharides of the plant cellulose – cellulose, starch, glycogen. Grapes, sweet apples, berries, etc. are especially rich in glucose.

Glucose is characterized by the right wrapping of a plane-polarized light ($\alpha_D^{20} = +52.3^\circ$), in which case in foreign literature it is often referred to as dextrose.

Glucose dissolves very well in water and easily mixes with syrups. In alcohol, glucose breaks down much more severely.

With alcohol and water, when slightly heated, it crystallizes into the form of anhydrous crystals, and with water at a temperature of 20°C , it appears as a crystal hydrate with one molecule of water. Glucose crystals have a white color and a pleasant sweet taste.

There is less licorice, less sucrose, and it does not mask the aroma and taste of other flavors in the grub components. In a clean diet, glucose is absorbed by the body faster than all other carbohydrates.

D- fructose, or fruit sucrose, is the most important representative of ketosis, which is also widely found in rosemary.

The left form of D-fructose ($\alpha_D^{20} = -93^\circ$) is called levulose. Along with glucose, fructose is present in many licorice fruits, kavuns, and copper. The high sweetness of honey (with a relatively low content of peels – 7 %) is explained by the fact that they contain mainly fructose, which is 1.4 times sweeter than sucrose.

Fructose is very important to crystallize in the crystals of the contents.

1.7.3. The power of monosaccharides

Let's look at the chemical influence of monosaccharides, which may be of greater importance for the production of food products:

1. Renewal of the aldehyde or ketone group of monoses with the creation of rich atomic alcohols – alditives. Carefully replenish D-glucose and remove D-glucite (sorbitol); D-xylose – pentite (D - xylitol), which is widely used in food preparations. When D-fructose is renewed, the mixture of two hexitols is created – D-glucite and D-manitou (Fig. 1.67).

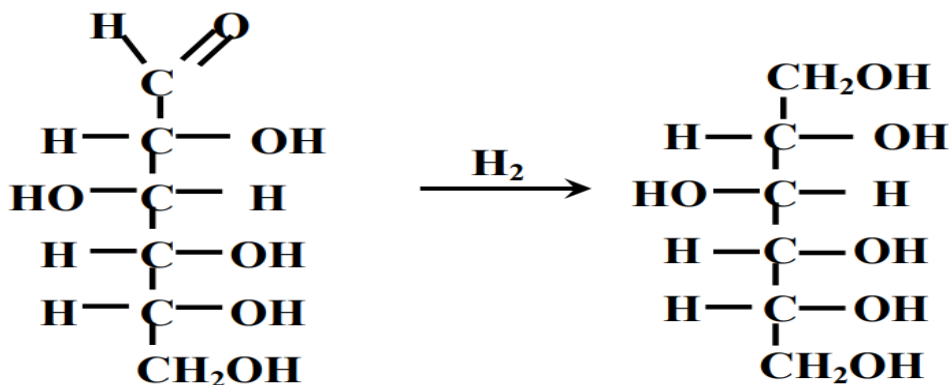


Fig. 1.67. Renewal of the aldehyde or ketone group of monoses

The conversion of glucose into sorbitol is one of the stages in the synthesis of vitamin C (on an industrial scale), when glucose is catalytically hydrolyzed with water.

2. Dehydration by acids. Aldoses are more resistant to acids, lower than acids. Protein is due to its natural monosaccharide and can be hydrolyzed in an acidic medium.

Thus, when evaporated D-glucose (and other aldoses) in the presence of diluted mineral acids, the following reactions are possible:

- intermolecular condensation (“reversion”), which leads to the formation of di-, tri-, tetra- and other oligosaccharides or
- intramolecular condensation – with solutions of 1,6 - anhydro – β -pyranose.

In more acidic environments, in the presence of acids, deep dehydration occurs, leading to the dissolution of hydroxymethylfurfural, and then (at boiling water) until further decomposition into levulinic and formic acid.

3. Interaction with alkalis. When developing technological schemes involving carbohydrates, it is necessary to ensure the increased sensitivity of monoses to the environment.

When diluted in the cold, D-glucose undergoes epimerization, often transforming into stereoisomeric aldose (D-manose), as well as isomerization into D-fructose. In more fervent conditions, in the presence of alkalis, there is a regrouping with the formation of saccharic acids, as well as a complex reaction of the breakdown of monosaccharides with the formation of three carbon fragments - pyruvic acid, lactic acid, etc.

4. There are 5 types of isomerism of monosaccharides:

1. Isomerism of aldoses and ketoses with an open chain and with the same number of carbon atoms in the molecule. For example: glucose, manose, galactose, fructose have the same molecular formula, so they are isomers.

2. Optical isomerism (stereoisomerism) of the closed forms of monosaccharides is due to the presence of asymmetric carbon atoms in the molecule. Natural glucose is a D-isomer, wraps the polarization plane to the right, which is designated D (+) - glucose. Natural fructose is left-handed, which is designated D (-) - fructose. 3. Monosaccharides D- or L-series (according to the configuration of the remaining chiral carbon atom):

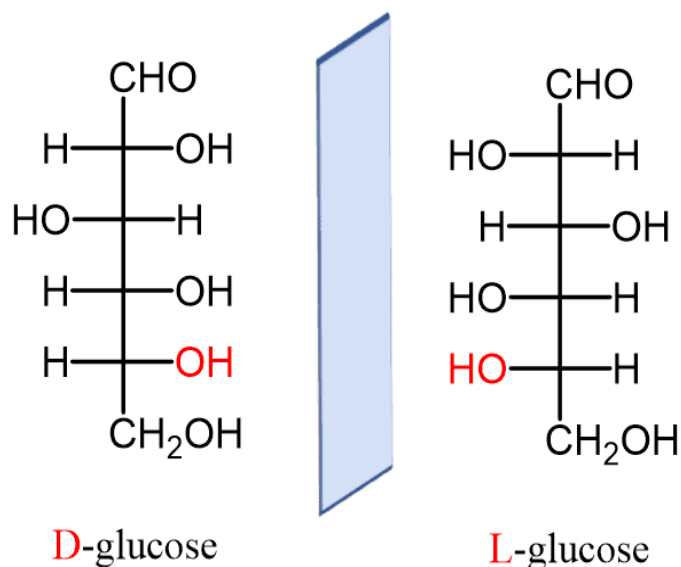


Fig. 1. 68. Optical isomerism

4. **Stereoisomers of cyclic forms** are divided into α - and β -forms depending on the location of hydrogen and hemiacetal hydroxyl at the first carbon atom relative to the plane of the ring. In perspective formulas (according to Haworth), hemiacetal hydroxyl in the α -form is directed downward from the plane of the ring, and in the β -form – upward (Fig. 1. 69).

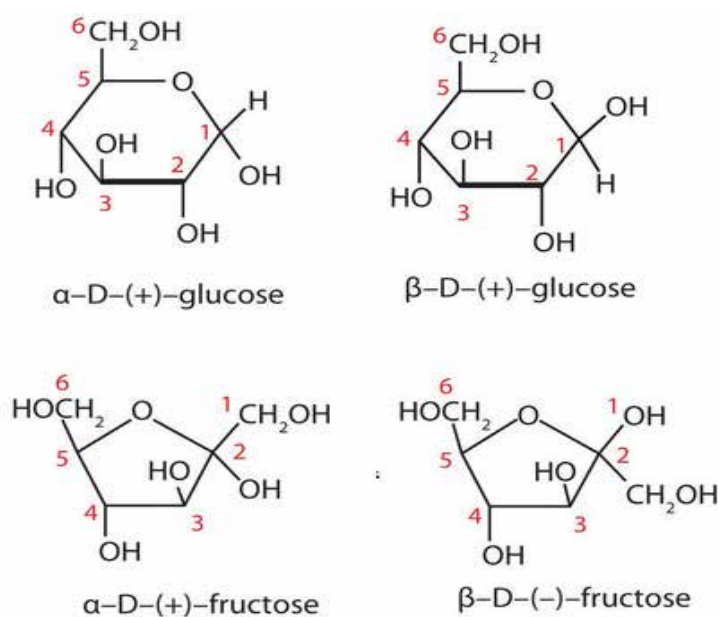


Fig. 1. 69. Stereoisomers of cyclic forms

5. Cyclochain tautometry is caused by the transition of open forms of monosaccharides into cyclic ones and vice versa. Open and cyclic forms of monosaccharides are tautomeric forms and are tautomeric isomers.

Tautomers are such isomers that can spontaneously transform into each other, forming an equilibrium system.

Tautomer transformations are possible if a substance capable of tautometry is in a liquid state. Under the action of alkalis and oxides of some metals, monosaccharides are easily converted into saccharides - derivatives of the alcoholate type.

The different solubility of glucosate and calcium fructose is used to separate glucose and fructose.

1.7.4. Characteristics and properties of oligosaccharides

Oligosaccharides belong to the class of holosides.

All holosides can be considered as dehydration products of two or more monosaccharide molecules.

Oligosaccharides have a number of properties that bring them closer to simple carbohydrates (monosaccharides): they dissolve easily in water, in most cases they have a sweet taste; they can be easily obtained in the form of well-formed crystals.

Oligosaccharides are classified according to several features:

- by the number of molecules;
- by the composition of monosaccharide residues (homo-, hetero-);
- According to the nature of the glycosidic chain
- linear, branched;
- according to the structure of the molecule;
- reducing, non-reducing.

In oligosaccharide molecules, as a rule, the residues of monosaccharides are connected to each other due to the carbon of the hemiacetal hydroxyl of one molecule and the oxygen of the hemiacetal or alcohol hydroxyl of another molecule.

When a monosaccharide forms a cyclic form, a new hydroxyl appears (in glucose – near the first carbon atom, in fructose – near the 2nd) called hemiacetal or glucosidic.

In reactions, it is usually more active than others (Fig. 1.70).

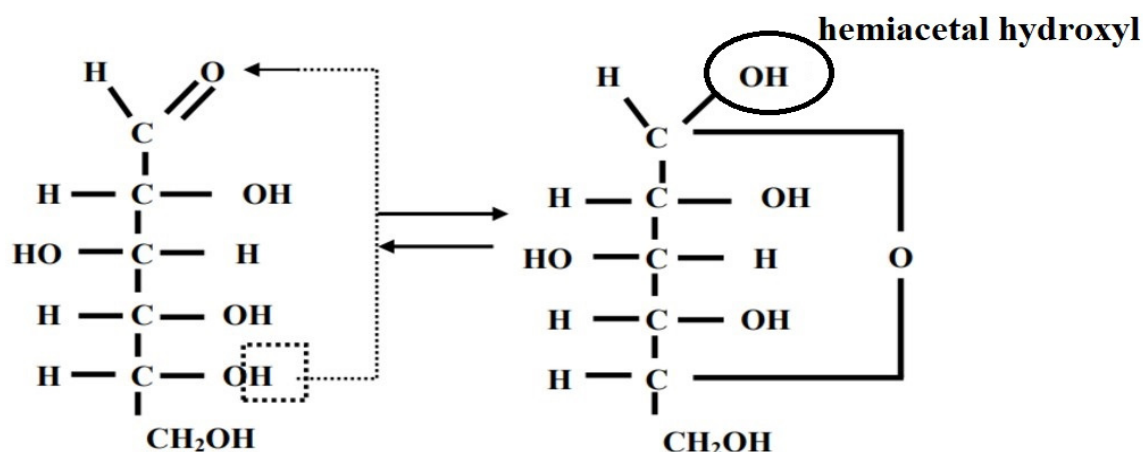
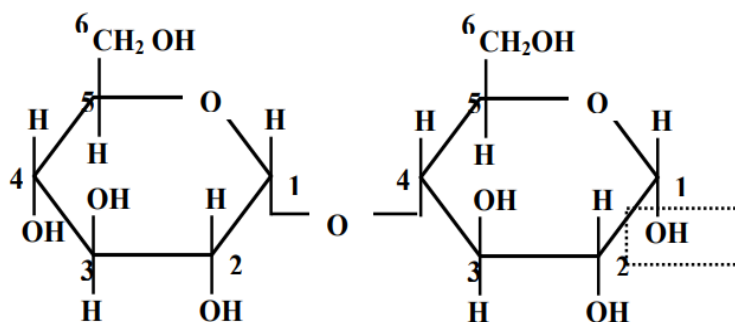


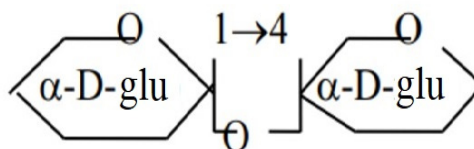
Fig. 1.70. Formation of cyclic form by monosaccharide

In reducing oligosaccharides, one monosaccharide molecule uses a hemiacetal hydroxyl to form a bond, the other uses an alcohol hydroxyl; then the hemiacetal hydroxyl remains free.

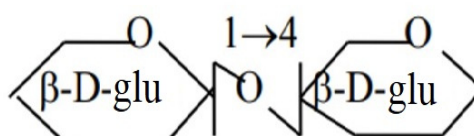


Maltose: residues of α -D-glucose molecules Maltose:

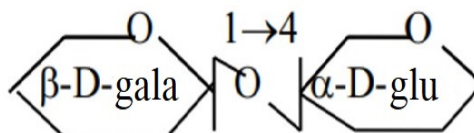
Maltose



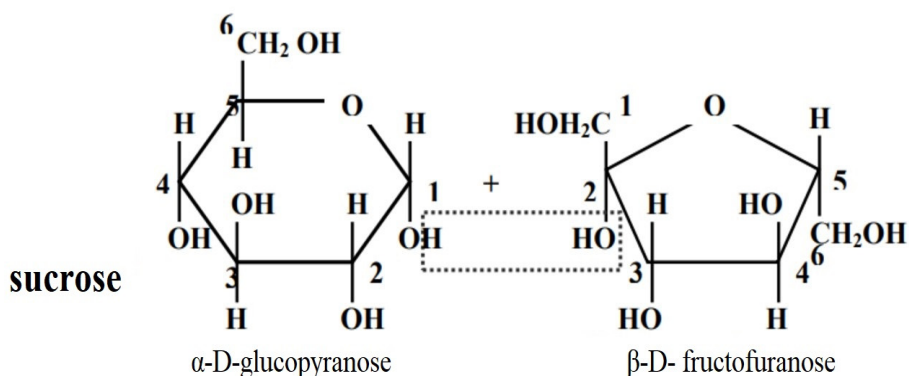
Cellobiose



Lactose



In non-reducing oligosaccharides, two adjacent monosaccharides connected by hemiacetal hydroxyls are (Fig. 1.71).



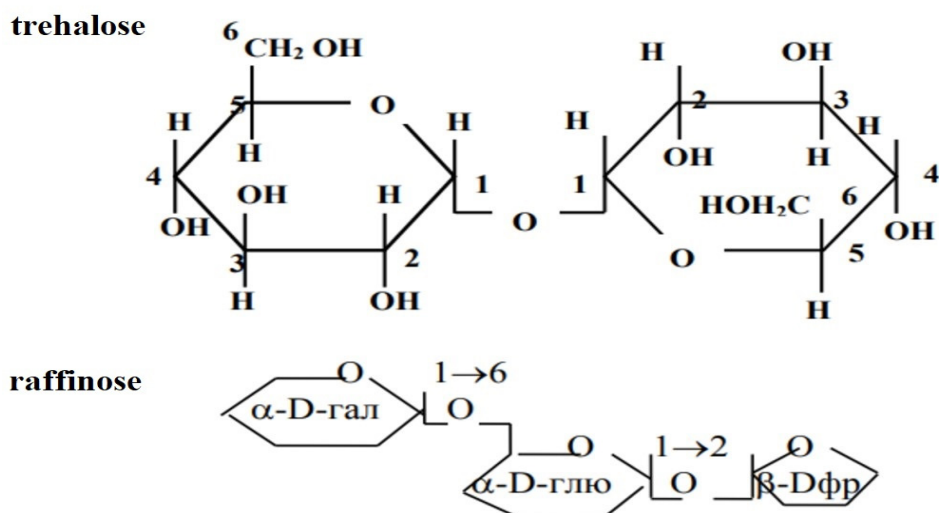


Fig. 1.71. Non-reducing oligosaccharides

The characteristics of oligosaccharides are given in Table 1.21.

Table 1.21. Characteristics of oligosaccharides

Name	Physical properties	Other information
Sucrose (beet or cane sugar) 2(alpha-D-glucopyranoside)-alpha-D-fructo-furanoside	$t_{\text{melting}} = 184-185\text{ }^{\circ}\text{C}$ $\alpha\text{D}^{20} = +66,5^{\circ}$ It dissolves well in water, the solubility increases with increasing temperature, in solutions, sweetness is detected at a concentration of 0.4%; 30% solution distinctly sweet	Among carbohydrates occupies a special place: – this is one of the main food products; – it is the output agent in the numerical biosynthesis of detergents, lactic, oxalic acids, etc. Place: in cherry beet (14-20 %), in cherry reed (14-16 %).
Trehalose (mushroom sugar) 1(alpha-D-glucopyranoside h)-alpha-D-glucopyranoside	Crystal substance $t_{\text{melting}} = 203\text{ }^{\circ}\text{C}$ $\alpha\text{D}^{20} = +197^{\circ}$	Contained in mushrooms and algae. In baker's yeast - 18% on dry matter. It is a reserve carbohydrate of the yeast cell. Trehalose is considered the quality of baker's yeast
Maltose (malt sugar) 4(alpha-D-glucopyranosido)-alpha-D-glucopyranose	It crystallizes easily, forming a crystal hydrate with one water molecule $t_{\text{melting}} = 102-103\text{ }^{\circ}\text{C}$ $\alpha\text{D}^{20} = +130,4^{\circ}$	Contained in animal and plant organisms in small quantities that are not of practical importance; is an intermediate product of the enzymatic breakdown of starch.

Table continuation 1.21.

Name	Physical properties	Other information
Lactose (milk sugar) 4(alpha-D-glucopyranose to)-alpha-D-glucopyranose	A non-hygroscopic crystalline substance $t_{\text{melting}} = 20\text{ }^{\circ}\text{C}$ $\alpha D^{20} = +52,6^{\circ}$	It is contained in cow's milk (4...6 %), it is obtained from milk whey. It participates in lactic acid fermentation (under the influence of lactic acid bacteria, it is hydrolyzed to sugars that are fermented into lactic acid), it does not participate in alcoholic fermentation. It has restorative properties.
Cellobiose 4(alpha-D-glucopyranose z)-alpha-D-glucopyranose	Crystal substance $t_{\text{melting}} = 225\text{ }^{\circ}\text{C}$ $\alpha D^{20} = +34,6^{\circ}$	It is the main structural unit of fiber (cellulose), found in free form in the sap of some trees.
Raffinose (melitriosa) alpha-D-galactopyranose do-alpha-D- glucopyranose do-alpha-D- fructofuranoside	Crystal hydrate $t_{\text{melting}} = 80\text{ }^{\circ}\text{C}$ $\alpha D^{20} = +104^{\circ}$ It does not have a sweet taste, it can increase the specific rotation of sucrose, that is why it is called plus- sugar	It is contained in cotton seeds, sugar beets. It is a companion of sucrose. It is best extracted from molasses, in which it is concentrated during the production of sugar. With complete hydrolysis, D- glucose, D-galactose, and D- fructose are formed

Questions for discussion and self-examination

1. The concept of carbohydrates? Classification of carbohydrates.
2. Describe the main properties of carbohydrates.
3. Physiological functions of carbohydrates.
4. Characteristics of oligosaccharides.
5. Isomerism of monosaccharides.

Topic 1.8. Carbohydrates: physico-chemical transformations

1.8.1. Changes in the properties of sugar and sugary substances occurring under the influence of technological factors

Sugar is one of the main types of raw materials in food technology. Sugar contains up to 99.75 % of sucrose, up to 0.03 % of ash, reducing sugars – no more than 0.05 %.

Sucrose is a disaccharide consisting of two monosaccharides - α -glucose and α -fructose, connected by glucosidic bonds. Sucrose is a disaccharide (a-D-glycopyranosyl – P-D-fructofuranoside).

Sucrose is a colorless crystalline substance with a melting point of 185–186 °C; its solutions cause the plane of polarization to rotate clockwise by +66.53 °C. Polarimetric methods for its quantitative determination are based on this property.

The main technological properties of sugar, which at the same time coincide with the functional properties of sucrose, should include:

- the ability to dissolve with the formation of solutions or syrups of different densities;
- the ability to undergo thermal transformation with the formation of caramel, as well as melanoidins;
- ability to acid and enzymatic hydrolysis;
- the ability to act as a system dehydrator;
- ability to act as a structure former, breeding material, dye.

Sucrose is well soluble in water, at 20 °C 2.039 kg of sucrose dissolves in 1 kg of water. With increasing temperature, the solubility improves and at 100 °C it is 2.4 times better than at 20 °C (Table 1.22).

Sucrose does not dissolve in alcohols, but in water-alcohol mixtures its solubility increases with an increase in the proportion of water.

Table 1.22. Solubility of sucrose at different temperatures

Temperature, °C	Solubility of sucrose	
	% by mass (% r/r*)	kg in 1 kg of water
0	64.18	1.792
10	65.58	1.905
20	67.09	2.039
30	68.70	2.195
40	70.42	2.381
50	72.25	2.604
60	74.18	2.873
70	76.22	3.205
80	78.38	3.622
90	80.61	4.157
100	82.97	4.872

* – % p/p – Brix degrees (determined by a Brix hydrometer or refractometrically)

It should be noted that the best solubility is characterized by fructose, which is able to form solutions of more than 70% concentration at 0 °C, glucose, maltose, lactose form 40% solutions at temperatures of about 10, 13 and 67 °C.

In an aqueous solution of glucose (maltose, fructose, molasses) or protein substances, sucrose will dissolve less than in water, but the total amount of dry substances may be greater than in a solution of sucrose in water. This is of great importance, especially during the co-dissolution of sugary substances.

The total solubility of sucrose and other sugars can be increased by adding invert sugar.

Boiling point. The dependence of the boiling temperature of the sucrose solution on its concentration is complex and determined by its absolute concentration in the system.

Therefore, such an important technological indicator as the boiling temperature of sucrose, depending on its concentration, can be increased by introducing other sugary substances into the system – glucose, fructose, molasses.

In the Table 1.23 and data on the boiling point of sucrose solutions of different concentrations are given.

Table 1.23. Boiling point of sucrose solutions

Sucrose content, %	Boiling temperature at atmospheric pressure, °C
10	100.1
20	100.3
30	100.6
40	101.0
50	101.8
60	103.0
70	105.0
75	107.0
80	109.4
85	113.0
90	119.6

The ability to oversaturate. From the tables shows that the increase in the boiling point depending on the concentration of sucrose is non-linear. Thus, in the concentration range of 0...50 % of sucrose, the temperature increase is only 1.8 °C, i.e. 0.032 °C for each additional percentage of concentration, and in the concentration range of 50...90 % – 17.8 °C, i.e. 0.445 ° for each additional percentage of concentration. This is important from the point of view of obtaining supersaturated sucrose solutions.

As a rule, in technological practice, supersaturated solutions are obtained in the following ways:

- cooling saturated solutions to lower temperatures;

- introducing into the saturated solution at the saturation temperature an additional substance capable of removing water, i.e. a dehydrator;
- evaporation of a saturated solution, which leads to an increase in the concentration of dry substances.

In technological practice, the speed of crystallization from saturated solutions is of great importance. The speed of crystallization in supersaturated solutions and the size of crystals can be significantly reduced with the addition of glucose, invert sugar, glucose syrups, hydrocolloids that increase viscosity.

At the same time, during supersaturation, sucrose solutions are characterized by a phase transition from solutions to a crystallized state, which, on the one hand, leads to the desired results, for example, in the formation of lipstick, and on the other hand, deteriorates the quality indicators of the finished products - saccharification of honey, formation of sugar precipitate in the process of low-temperature storage of supplies, stews, precipitation of lactose crystals in the process of cooling condensed milk or during hydration of dried whey proteins of milk, the companion of which is lactose.

The degree of crystallization depends on the occurrence of crystallization centers, the number of which depends linearly on the supersaturation coefficient and the intensity of mechanical action, such as stirring.

- the crystallization process involves two independent processes:
 - primary nucleation of crystals;
 - recrystallization of crystals, i.e. arbitrary growth at a certain speed.

The speed of the process depends on the temperature of the solution, its viscosity and the supersaturation coefficient. The rate of crystallization increases with increasing temperature, decreasing viscosity, and increasing supersaturation ratio. It was experimentally established that the rate of crystallization of pure sucrose solutions approximately doubles for every 10 °C increase in temperature.

In the invert syrup, the crystallization of sucrose is difficult due to the increased viscosity of the syrups. In general, the introduction of colloid solutions or other colloid stabilizers – starch, molasses, other polysaccharides, protein substances that increase viscosity, reduces the rate of crystallization.

Structure-shaping ability. The range of structuring for sucrose is very large and extends to structuring in solutions and structuring in a crystallized state, for example during the production of fondant masses, caramel, etc.

The structure-forming ability is based on the property of sucrose solutions, or syrups, or invert sugar to gradually change viscosity due to changes in temperature, while not changing the phase state, that is, not crystallizing. The absolute value of viscosity and its value as a function of temperature depends, first of all, on the concentration of sucrose in the solution.

The temperature effect on sugar may not lead to deep changes in its properties, but may cause deeper changes that cause destructive and polymerization processes at the same time.

Hygroscopicity of sucrose. The hygroscopicity of sucrose significantly affects the storage conditions and also affects the texture of some food products. Glucose, maltose, glucose syrups with increased reducing properties are less hygroscopic than sucrose and invert sugar and fructose.

Hygroscopic substances are recommended to be added to food products to maintain a certain level of humidity, for example in some confectionery products.

Also, the presence of hygroscopic substances has a negative effect, for example, during the manufacture of decorative semi-finished products, candies (which are not in a crystalline state).

In this case, the adsorption of moisture can cause the sugars to crystallize, releasing water that makes the mass sticky.

To prevent this effect in dry milk, juice should be prevented from exposure to high humidity by choosing the right packaging.

The glassy state of sugar and some confectionery products. By means of technological transformation of sugar from a crystalline state to a vitreous state, a significant number of food products are obtained.

The glassy state of sugar, which corresponds to its amorphous structure, is characteristic of products with a high sugar content and low water content. The amorphous structure does not appear in X-rays, and the products themselves are characterized by a significant viscosity that exceeds the value of 1013 Poise. The specified viscosity does not allow sugar to crystallize.

The vitreous body can be obtained in several ways:

- 1) by thermally melted crystalline sugar;
- 2) by rapid freezing of the solution;
- 3) rapid saturation of the solution with an increase in temperature with successive rapid cooling (in the case of "boiled" sugars);
- 4) by dehydrating the solution (lyophilization or spraying) for solutions of sucrose, lactose.

The glassy state is not stable. At certain temperatures, in the so-called "transition" zone, the viscosity drops (Fig. 1.72), and sugar can crystallize.

The disappearance of the vitreous state is accompanied by a sharp change in physical properties, and first of all – specific thermal conductivity, which can be used to determine the effect by the method of differential calorimetry.

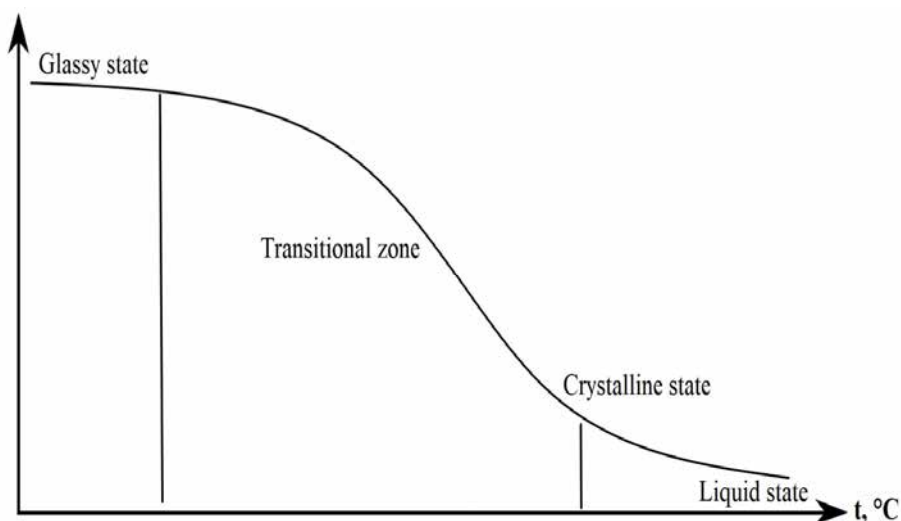


Fig. 1.72. Transition of sugar from a glassy state to a crystalline state: change in viscosity depending on temperature

The glass transition temperature decreases with increasing humidity in the system. Adding glucose to the sugar solution lowers the transition zone temperature and increases the crystallization temperature.

The table 1.24 gives the transition zone temperatures for various glassy states obtained by freezing, saturation, and dehydration. The above systems are stable only at temperatures lower than those indicated.

Table 1.24. Temperature transition zone from glassy to crystalline state

Substance	Temperature transition zone (°C)
Glycerin	-92...-83
Glucose	+20...+35
Glucose (2M solution)	-41
Saccharose	+67
Sucrose (2M solution)	-32
Lactose	>+20

Sugars that are in a glassy state are hygroscopic. Sucrose and lactose, which are in a glassy state, turn into a sticky mass as a result of crystallization, because the water that is released as a result of crystallization dissolves the outer layers of sugar. Glucose in the glassy state also tends to dissolve in adsorbed water.

Sugars in a vitreous state can be found in various food products (ice cream, skimmed milk powder, caramel, etc.).

Sweet taste and sweeteners. Sweet taste, which is carried by many sugary substances, is one of the main technological characteristics, which is dominant for justifying their use in food technology.

According to the "strength" of the sweet taste, sugars are placed in a row: sweeteners > fructose > sucrose > glycerol > glucose > galactose > glycine > lactose and maltose.

There are food additives that are superior to sucrose in terms of "power" of sweet taste.

Among other sugary substances, simple sugars, such as glucose, fructose and maltose, play a significant role, which, during the destruction of polysaccharides, have a significant impact on the characteristics and organoleptic indicators of food products.

Glucose is a monosaccharide with a molecular weight of 180.16, in nature and in products it is most often found in the form of D-glucose (component monomer of cellulose, starch, sucrose).

Glucose solutions turn the plane of polymerization to the right, and due to mutarotation, the angle of rotation from +100° for the newly obtained solutions decreases to +52.5°, which indicates the equilibrium in the solution of α - and β -stereoisomeric forms.

The key functional properties of glucose are solubility, hygroscopicity, the ability to form syrups and to be a sweetener.

The solubility of glucose in water is closely related to temperature and increases significantly with its growth. At a temperature of about 60 °C, its value exceeds the values for sucrose.

The viscosity of glucose solutions depends on its concentration and temperature. The viscosity of a saturated glucose solution increases with increasing temperature due to higher rates of its dissolution than a decrease in viscosity.

As a sweetener, glucose is worse than sucrose and is 60...75 % sweeter than sugar.

Glucose is thermally and chemically unstable and undergoes profound changes under the influence of temperature, as well as acids and alkalis, with the formation of various unsweetened and colored products.

Fructose - P-D-fructofuranose, a monosaccharide with a molecular weight of 180.16, in solution, unlike glucose, turns the plane of polarization to the left by -92.5°

Fructose is the sweetest of the monosaccharides, as its sweetness ratio, compared to sugar, is about 150 %. Well soluble in water, solubility increases with increasing temperature. Hygroscopic, which requires its preservation in a hermetic state. From a chemical point of view, fructose reduces copper-alkaline solutions, and is not oxidized by iodine in an alkaline medium, which is the basis of its definition.

Fructose is capable of intense changes in properties during heating with the formation of destruction and polymerization products. The depth of changes in fructose is indicated by the intensity of the yellow-brown color, which grows in an alkaline medium.

Maltose is a disaccharide that has reducing properties and is able to reduce copper-alkaline solutions. It is a crystal hydrate of one maltose molecule and one water molecule with a melting point of 102...103 °C. Compared to sucrose, maltose is not sweet, with a sweetness factor of 35 %. Resistant to temperature effects, well soluble in water, forms stable stable solutions. In the composition of molasses, its share is 20...35 %.

Among disaccharides, maltose plays a significant role in technological processes as a component of molasses, as well as one of the components of enzymatic and acid destruction of starch.

Maltose is capable of isomerization. It and its isomers are part of starch and glycogen.

Various changes in sugar and sugary substances occur during the production of food products.

1.8.2. Hydrolysis of disaccharides

In technological processes, **acid** and **enzymatic** hydrolysis of disaccharides are distinguished. Sucrose hydrolysis can be carried out by an invertase enzyme, for example yeast invertase in the technology of yeast dough products.

During heating of solutions of disaccharides in the presence of acids, disaccharides can break down into monomers.

Due to the change in optical activity relative to the rotation of the polarization plane, the hydrolysis process was called inversion, and the equimolecular mixture of glucose and fructose was called **invert sugar**.

Sucrose is hydrolyzed as follows (Fig. 1.73).

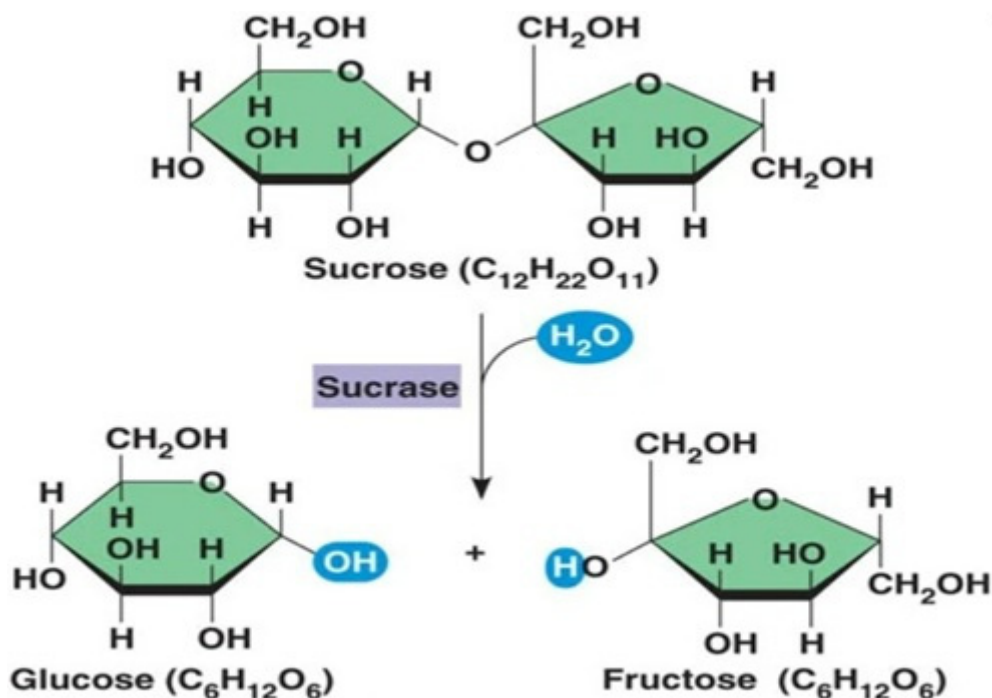


Fig. 1.73. Hydrolysis of sucrose

Inversion motivates an increase in the mass of dried invert sugars by 5.26 % of the mass of sugar, as well as an increase in the intensity of the sweet taste and solubility.

This ability to increase the concentration of solids in the solution is used in the production of syrups from sugar, especially in those cases where it is necessary to have a certain amount of solids in the solution at a lower viscosity than in the case of using sucrose. It also reduces the possibility of mold and yeast growth in some cases.

The increase in the solubility of invert sugar compared to sucrose is explained by the greater solubility of fructose (Table 1.25) and the difficulty of crystallization of glucose.

Table 1.25. Solubility of various sugars in water at a temperature of 20°C

Substance	Solubility, g/100 g of water
Saccharose	204
Fructose	375
Glucose (hydrate)	107
Maltose (hydrate)	83
Lactose (hydrate)	20

The degree and speed of inversion depend on the parameters of the technological process – the duration of the process, the temperature of hydrolysis, the concentration of sucrose, the concentration and type of acid.

In supersaturated solutions, glucose crystallizes at a much lower rate than sucrose. As the temperature increases and the processing time increases, the degree of hydrolysis increases. In systems less concentrated in terms of sugar, under other identical conditions, hydrolysis proceeds better than in more concentrated systems. Due to the fact that the hydrogen ion acts as a catalyst in the technological process, its source is of fundamental importance.

Among organic acids, oxalic acid is characterized by the greatest inverting ability, citric acid is 10 times less active, malic acid is 15 times less active, lactic acid is 17 times less active, succinic acid is 35 times less active, and acetic acid is 45 times less active.

Honey is a natural invert sugar produced by the enzyme invertase.

The use of simple sugars in the technology of food products is connected with their transformation, which results in many technological changes.

Among the main changes of sugars that take place under the influence of high temperatures, there is a change in appearance, color, taste, smell, as well as physical and chemical parameters.

These changes are united by their common feature, the concept of non-enzymatic browning.

Non-enzymatic browning is a set of complex reactions aimed at various products, with the formation of brown and black pigments that contribute to the formation of the taste and smell of finished products or semi-finished products.

Non-enzymatic browning combines such processes as the **Maillard reaction, caramelization, and the formation of melanoidins.**

According to more detailed features, the products of non-enzymatic browning are divided into products that are formed due to the predominance of the caramelization process, and products that are formed in the process of melanoid formation.

1.8.3. Caramelization of sugars

Caramelization is a thermal transformation of sugars with the formation of a vitreous body, which is accompanied by a change in color and the appearance of a whole range of new substances.

Due to caramelization in the technological process, a complete change in the structural and mechanical properties of sugar occurs with the formation of a continuous glassy mass – caramel. Many coloring substances are formed – from yellow to dark brown in color, and certain organoleptic indicators (taste, smell, color, etc.) of some types of food products are also formed.

Caramelization depends on the following factors: the type and concentration of sugar, the duration and temperature of the process, the pH of the environment, and the presence of other substances.

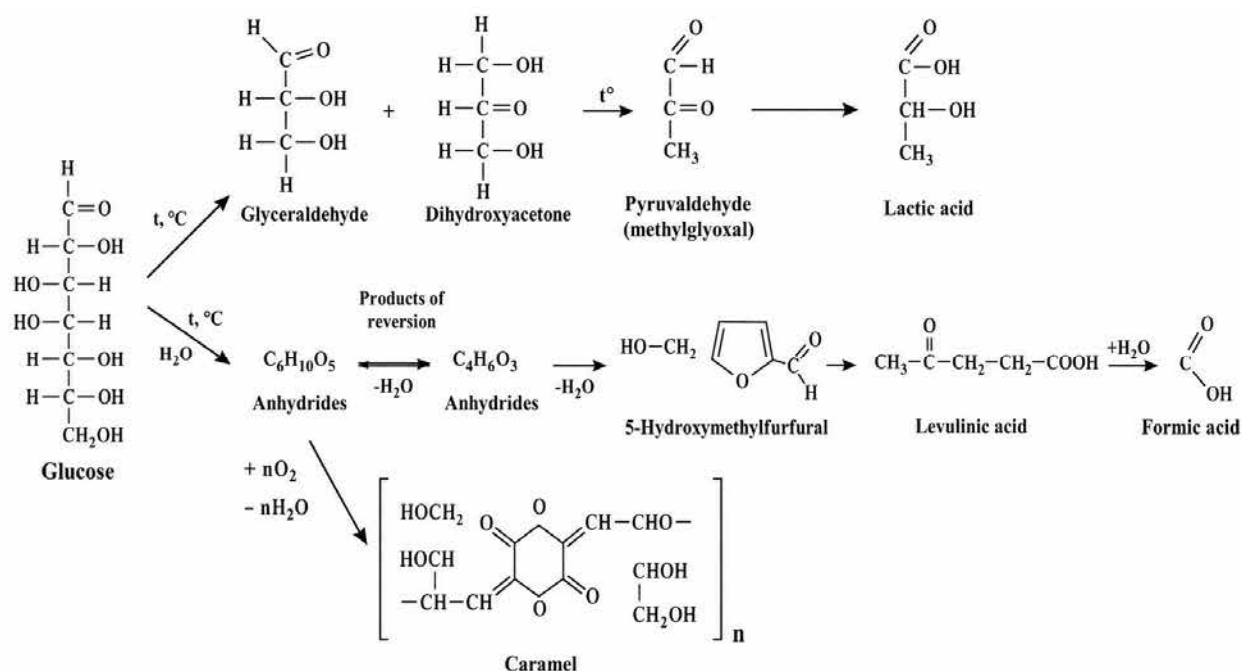


Fig.1.74. Scheme of caramelization of glucose

The intensity of the sweet taste of sugars decreases during caramelization. This is a consequence of a decrease in the share of sugars in the system due to the emergence of polymer compounds that are less sweet, as well as the destruction of sugars. Accumulation of new substances in the system due to destruction, on the other hand, dulls the sensory sensations of sweet, enriches the range of tastes and diverts the attention of consumers from sweet. An example is the consumption of sugars in the form of caramel, which does not cause the sensation of being too sweet, which is characteristic of actual sugars and honey.

Heating sugars to temperatures above $100\text{ }^\circ\text{C}$ in a neutral or weakly acidic environment leads to their dehydration with the formation of anhydrides.

Anhydrides are unsaturated products of the caramelization reaction, which have high reactivity at high temperatures.

The reactivity of anhydrides increases with an increase in the degree of dehydration, but each of them can form reversion products with unchanged sugars, that is, compounds with a higher molecular weight and more glucose residues than before the reaction.

Splitting of water during anhydridization is possible both from a single molecule of glucose or sucrose, and from compounds that are products of reversion, or polymerization and polycondensation, which is most likely during the actual course of the technological process. Several stages of anhydridization have been established for sucrose, which have a certain technological significance.

The separation of two water molecules from sucrose produces **caramelan** anhydride, which has a light straw color and is well soluble in cold water.

The separation of three molecules of sucrose from eight molecules of water produces the compound **carmelene** – a bright brown color with a ruby tint, it dissolves well in hot water and worse in cold.

More intensive dehydration of two sucrose molecules leads to the production of **carmelin**, a dark brown compound that dissolves gradually only in hot water.

With an increase in temperature or an extension of the period of processing of sugars, the formation of **humic compounds**, which are colored in black-brown color, is possible. Humic compounds are not assimilated by the body, even more - with constant consumption, they can initiate cancer diseases.

In general, it can be noted that the appearance of color depends on the value of the m:n ratio in the general formula of sugars.

In native sugars, this ratio is 1.09; upon reaching a value of 1.3, caramels begin to acquire color. In real technological processes, a value of 3.0 is achieved.

Polycondensation processes of anhydrides take place with a possible color change. The result of these processes is the formation of **caramel** – a vitreous body. This process takes place with the participation of oxygen and water. At the same time, the intensity of the sweet taste and solubility changes, a yellow-brown color appears.

The process of caramelization of sugars proceeds not only with the formation of a vitreous colored body, but also with the appearance of a group of aromatic volatile and reactive substances that arise as a result of the thermal destruction of sugars and their anhydrides.

In parallel with the formation of anhydrides, the glucose molecule is able to split between the 3rd and 4th carbon atoms with the formation of glycerol aldehyde and dioxyacetone, which upon heating are transformed into pyruvic aldehyde and lactic acid.

Due to skeletal changes, anhydrides can also form 5-oxymethylfurfural, which thermally decomposes into levulinic and formic acids.

Aromatic volatile substances that accumulate during caramelization significantly affect the sensory parameters of products.

1.8.4. The process of melanoid formation

Melanoid formation is one of the most common processes, which is accompanied by physicochemical and organoleptic changes in the components.

The reaction of melanoidin formation is a reaction of thermal condensation of carbohydrates and proteins to form melanoidins.

The substrates of the melanoidin formation reaction are primarily represented by **carbonyl compounds and reducing sugars** (polyhydroxycarbonyl compounds).

Proteins and amino acids catalyze this reaction by interfering with the process of free amino groups, especially lysine, due to the NH₂-amino group in the ε-position. Condensation between carbonyl and amino groups reduces food availability and solubility of lysine and proteins. In addition, if ascorbic acid and vitamin K are involved in the reaction, a decrease in nutritional value is observed.

Non-enzymatic browning also occurs during food storage; with increasing temperature - pasteurization, cooking, dehydration.

The effect of non-enzymatic browning on food products: the formation of a crust on bread, biscuits, etc., the specific taste and color of fried meat and potatoes, heat-treated grain, meat extracts, caramel, etc. Some compounds formed in the process of

non-enzymatic browning are able to protect lipids from oxidation, for example in fish meal.

Melanoid formation in the technological process is accompanied, as a rule, by the darkening of the mass, the appearance of a characteristic aroma, a decrease in the content of variable nitrogen, and a change in the total solubility. At the same time, rheological changes in the food system continue - viscosity increases.

Melanoidins are a heterogeneous group of high-molecular dark-colored compounds, the formation of which is accompanied by the accumulation in the food system of the products of the destruction of carbohydrates, amino acids, and their interaction products.

Melanoid formation is a multistage reaction in which many substances and their intermediates participate simultaneously. Therefore, it is impossible to determine the final products in their entirety, and the division of the process into stages is conditional (Fig. 1.75).

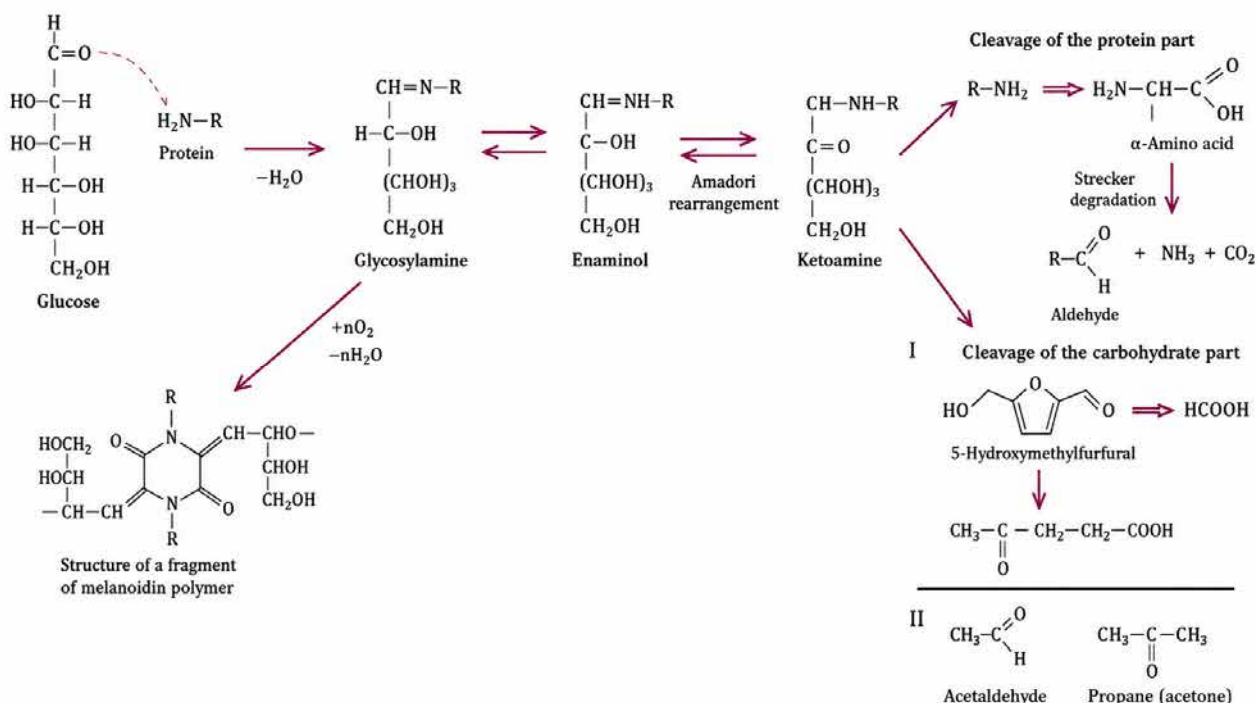


Fig. 1.75. Scheme of the process of melanoid formation

Despite the fact that the reaction of melanoid formation is objective from the point of view of the properties of substances (reduced sugars and amino acids), it is a purely technological process, because its course depends on many technological factors: temperature, duration, concentration and ratio of components, the reaction of the environment, the presence of inhibitors and initiators – and is also regulated by them.

General scheme and stages of non-enzymatic browning

The principle stages of non-enzymatic browning include:

1) formation of sugar amine complexes as a result of sugar amine condensation "Mayard condensation";

- 2) transformation of sugar-amine complexes due to Amadori (or Heinz) rearrangement;
- 3) destruction of ketosamines and formation of reactive carbonyl compounds;
- 4) destruction according to Steker;
- 5) formation of melanoidins.

Destruction according to Steker. Aldoses form aldosylamines, and ketoses form ketosylamines.

The Schiff alkalis formed in the second stage are very reactive and, at high temperatures, are capable of polymerization and polycondensation reactions with the formation of colored products or of decomposition into acetaldehyde and aminoacetone (substances capable of entering into the melanoid formation reaction due to the active carbonyl group).

In the case of participation in the aldose reaction, Schiff bases are rapidly isomerized into N-substituted aldosylamine.

This reaction is most characteristic for glucose, and the least for polysaccharides. Maillard condensation can be carried out under the influence of all reducing sugars that have a free carbonyl - aldoses, ketoses, uronic acids, reducing disaccharides. Pentoses are more reactive than hexoses; aldoses - more than ketoses.

A large share of α -amino nitrogen in the system, that is, free amino acids, the presence of a significant number of peptides, the presence of low molecular weight proteins in the system activate the course of the sucroamine condensation reaction. This is less characteristic of higher molecular weight proteins.

The intensity of the reaction depends on the method of heat treatment – in the process of hydrothermal treatment, other things being equal, it is less intense than during frying and baking, that is, processes that go with the evaporation of moisture, and due to this, the concentration of reacting components increases.

The reaction is inhibited by low pH values due to the formation of unreactive NH^+ ionized groups. At the same time, at the II stage, the reaction is accelerated by H^+ ions (acid catalysis).

The reaction is inhibited by low pH values due to the formation of ionized NH_3 groups, which are unreactive. At the same time, at the II stage, the reaction is accelerated by H ions.

Maillard condensation is a reaction between free carbonyl and variable groups with the formation of glucosamines (carbonylamines) in the first stage and Schiff bases in the second stage.

The analysis of the dependences "I" and "II" (Fig. 1.76) shows that at low substrate concentrations the reaction proceeds completely and at a high speed, therefore the resulting (dashed) indicates the accumulation of Schiff bases. When a certain amount of Schiff compounds is formed, the reaction rate decreases.

The formation of glycosylamine is a mutually reversible reaction. For example, in very acidic environments, sugar and amino acids are able to regenerate completely.

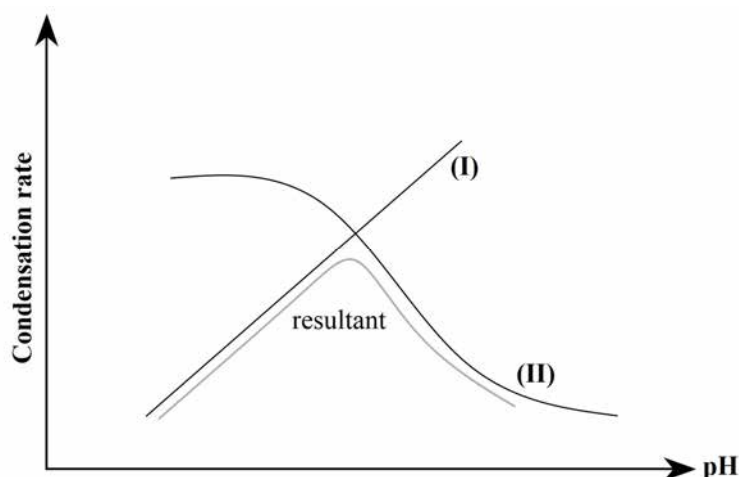


Fig. 1.76. Maillard condensation: rate as a function of pH

Amadori (or Heinz) rearrangement is a chemical transformation of sugar amine complexes, which, depending on the constituent parts, is called the Amadori (from aldosylamines) or Heinz (from ketosylamines) rearrangement.

As a result of the Amadori (or Heinz) rearrangement:

- 1) ketosamines are formed from aldosylamines;
- 2) aldosesamines are formed from ketosylamines.

Ketosamine is formed by Amadori rearrangement from aldosylamines, while ketosylamines are converted to aldosesamines by Heinz transformations. These reactions are catalyzed by carboxyl groups of amino acids. Thus, the amino acid acts as a catalyst in the "glucose - amino acid" condensation reaction (for example, glycine) with the formation of the corresponding ketosamine and its transformation into the form of D-fructosoglycine.

The destruction of ketosamines and the formation of reactive carbonyl compounds is carried out due to:

- enolization in positions 1 and 2 (carbon atom) with the formation of unsaturated carbonyls, which are precursors of the appearance of brown non-enzymatic compounds;
- enolization in position 2-3 (carbon atom) with the formation of reductants (the reaction proceeds well in an alkaline medium and is observed in food products with a pH of about 7.0).

Sometimes the process of destruction of ketosamines is classified as a process of oxidative deamination and decarboxylation to an aldehyde or ketone. Ketosamines are very unstable, especially at high temperatures typical of food manufacturing processes, which is the reason for their decomposition. Depending on the type of amino acid that entered the sucroamine condensation reaction, the final aldehyde can be from leucine – 2-methylbutanal, methionine – methional, isoleucine – 3-methylbutanal, phenylalanine – phenylethanal.

In technological processes, a heterogeneous mixture of aldehydes is formed from a mixture of amino acids or proteins, which effectively determine the aroma. In parallel, the sugar component of the reaction, similar to the caramelization reaction, is

anhydridized and decomposes sequentially into 5-oxymethylfurfural, formic and levulinic acids. At the same time, aldehydes are formed: acetyl, diacetyl.

In a mixture with products of protein destruction:

- a composition of volatile substances with a strong aroma is formed, which is perceived as the aroma of fried, baked, baked products, including bread, coffee, cocoa, roasted malt, etc.

- a group of unsaturated, highly reactive substances is formed, which can potentially form polymers of unknown dimensions at high temperatures.

Strecker degradation. α -dicarbonyl compounds, which are formed during the degradation of ketosamines, can react with the amino acid, leading to its degradation. An increase in temperature to values that are characteristic of food preparation technology significantly initiates this process.

As a result of Steker's degradation, carbon anhydride, aldehyde, which contain one less carbon atom than the initial acid, and ammonia are formed.

In general, the melanoid reaction can be divided into two stages:

- 1) formation and accumulation of reactive carbonyl compounds formed from reducing sugars;

- 2) formation of brown polymers.

Reactive compounds are almost always present in food products, but their number can significantly increase under certain circumstances, in particular, temperature regimes.

Depending on the activity, compounds can be classified as follows: saturated ketones and aldehydes, unsaturated aldehydes and ketones, α - and β -unsaturated aldehydes and ketones; reducing dicarbonyl compounds; dicarbonyl unsaturated compounds.

Formation of brown polymers. Carbonyl compounds formed at the first stage of browning are chemically unstable and therefore actively capable of destruction or polymerization. Thus, substances with a lower molecular weight (volatile, which have a smell) or with a large molecular weight - more than 50,000, which are estimated as pigments, are formed from them. The formation of polymers is partly a consequence of aldol condensation of ketosamines or their derivatives and condensation of aldosesamines.

These unsaturated polymers can contain up to 5 % nitrogen. These compounds are insoluble in water, sometimes have reducing properties, can participate in reactions with proteins and Maillard condensation.

Due to the presence of a significant amount of reactive substances, intensively colored heterocyclic polymers – **melanoidins** – are formed as a result of the condensation reaction of aldehydes, as well as aldehyde-amine condensation with the participation of products of destruction of sugar and protein components and during the course of active oxidation.

It should be noted that melanoid formation is a process that reduces the biological value of products due to the destruction of protein or amino acid components of food.

In the presence of antioxidants (hydrogen peroxide, ascorbic acid), melanoid formation is less intense.

The nature of reducing sugars. Pentoses, or more precisely riboses, are the most reactive sugars. Hexoses (glucose, fructose), reducing disaccharides (lactose, maltose) and sucrose, which does not have a free reducing group and therefore does not affect non-enzymatic browning, follow decreasing reactivity. Exceptions are acidic products, in which sucrose is hydrolyzed sequentially to glucose and fructose, or neutral sugar solutions, where inversion is always present at temperatures above 130°C.

Temperature. The activation energy of various stages of the non-enzymatic browning process is: disappearance of variable nitrogen – 26 kcal/mol, formation of glycosamine – 3...9 kcal/mol, cleavage of ketosamine – 24 kcal/mol, formation of pigments – 20...43 kcal/mol mole. The given values of the activation energy are sufficiently high. At the same time, the reaction rate of the variable zot disappearance stage increases 20,000 times with a temperature change from 0 to 70°C. Thus, at low temperatures, the browning process can slow down, and at elevated temperatures, it can be noticeably accelerated, even in the absence of variable kztalizers in the system.

Water activity. Water plays a key role as a non-enzymatic browning factor. For most products, the rate of browning is maximum in the interval $a_w = 0.55...0.75$. Products dehydrated to the water content, when it is in monomolecular form, are more resistant to browning if their surface is constantly moistened (products packed in a container through which water vapor does not pass) or if the storage takes place at moderate temperatures (below 25 °C). A partial loss of reducing sugars (and available lysine) can be detected at lower values, that is, at those values that are necessary for the formation of pigments.

pH value. The effects of the influence of pH values are complex, since each reaction that affects browning has its own pH-optimal action: for Maillard condensation, pH=6...8; for Amadori rearrangement reactions pH=7.0; for degradation of ketosamines through enolization pH=5.5; for aerobic and anaerobic degradation of ascorbic acid, the pH values are shifted to an even more acidic zone.

Depending on the pH values, the reaction mechanism follows the following directions:

- food products with a pH value of 6...8 (milk, eggs, etc.) are most affected by the Maillard reaction. A decrease in pH values increases the rate of browning of products due to dehydration and negatively changes their organoleptic characteristics;
- in products that have natural pH values of 2.5...3.5 and are poor in amine compounds (concentrates and fruit juices), the Maillard condensation reaction takes place very slowly on its own, and the browning is associated with the degradation reactions of ascorbic acid and fructose.

1.8.5. Fermentation of carbohydrates

Fermentation processes of monosaccharides are widely used in food technology (in the production of bread, beer, kvass, alcohol, wine, etc.). Fermentation is the process of breaking down monosaccharides under the action of microorganisms and some other factors. There are alcoholic, lactic, butyric and citric acid fermentations.

Alcoholic fermentation takes place under the influence of microorganisms and plays an important role in the production of alcohol, wine, and bakery products. Along with the main products obtained during alcoholic fermentation, alcohol and carbon dioxide, as a result of fermentation such compounds as glycerol, succinic acid, acetic acid, isoamyl and isopropyl alcohols and others are formed. These products significantly affect the taste and aroma of food products.

Lactic acid fermentation occurs during the production of kefir and other lactic sour products, cheese, sauerkraut. Two groups of lactic acid bacteria are known. The first of them includes homofermentative bacteria that produce only lactic acid.

Lactic acid bacteria of the second group (heterofermentative bacteria) produce, in addition to lactic acid, acetic acid, as well as ethyl alcohol (often in fairly significant quantities), carbon dioxide, formic acid and other products. The ratio between these products depends on many conditions (temperature, pH of the medium, etc.). Most often, this is due to the joint activity of lactic acid bacteria with yeast. This kind of common "ferment" is often created artificially and is widely used in baking bread, in the production of bread kvass and a number of lactic acid products (cheese, kefir, kislyak, koumiss, etc.).

Lactic acid fermentation is widely used in the production of lactic acid, which is used in a number of branches of the food industry. As a result of butyric acid fermentation, butyric acid is formed. This process occurs during long-term storage of food products.

Butyric acid has a bitter aftertaste. Accumulation of this acid in products worsens their taste.

Citric acid fermentation occurs under the action of mold fungi. Citric acid is produced industrially by fermentation of a sucrose solution with the fungus *Aspergillus niger*.

Questions for discussion and self-examination

- 1. What changes occur with carbohydrates during the technological process.*
- 2. Describe the hydrolysis of carbohydrates. For what purpose is hydrolysis of carbohydrates used in food production technology?*
- 3. Define the process of caramelization of sugars. Intermediate and final products of the process.*
- 4. Maillard reaction.*
- 5. Factors affecting the course of the reaction of melanoid formation.*
- 6. Features of carbohydrate fermentation types.*

SECTION 2. POLYSACCHARIDES, PHENOLIC COMPOUNDS, FOOD ACIDS, MINERALS, ENZYMES: CHARACTERISTICS, COMPOSITION, PROPERTIES AND THEIR CHANGES DURING THE TECHNOLOGICAL PROCESS

Topic 2.1. Polysaccharides: structure, characteristics

Higher polysaccharides are high molecular weight substances that are slightly soluble or insoluble in water and tasteless. These include the most important carbohydrates included in food products: starch, fiber, and pectin substances.

Polysaccharides are also called glycans (from the word glucose), and private names are formed from the name of the original monosaccharide, replacing the suffix *osa* with the suffix *an*, for example, fructan, galactans, etc.

Unlike monosaccharides and oligosaccharides, glycans are either insoluble in water or give very viscous solutions, do not have a sweet taste, are difficult to separate from tissues, and often depolymerize and oxidize. The most important representatives of glucans are starch and cellulose.

Depending on the features of the chemical structure, polysaccharides can be divided according to various classification features (Table 2.1).

Table 2.1. Classification of polysaccharides by structure

Characteristic	Main representatives
The structure of the polymer chain	
Linear	Alginates, carrageenans, modified cellulose, furcelleran, pectins
Ramified	Galactomannans (guar gum and locust bean gum), xanthans, gum arabic, gum ghatti, caraya gum, tragacanth
The nature of monomer residues	
Homoglycans,	Modified cellulose, modified starches
Heteroglycans	Alginates, carrageenans, galactomannans, pectins
Triheteroglycans	Xanthans, caraway gum, gellan gum
Tetraheteroglycans	Gum Arabic
Pentaheteroglycans	Ghatti gum, tragacanth
Charge	
Neutral	Derived cellulose, amylopectins, galactomannans Alginates, carrageenans, pectins, xanthans, tragacanth, caraya gum,
Anionic (acidic)	gum arabic, ghatti gum

2.1.1. Characteristics of starch, structure of starch grains

Starch is a vegetable high-molecular polysaccharide.

By chemical nature, starch is a polymer of glucose (α -D-glycosidic residue). Its chemical formula is $(C_6H_{10}O_5)_n$. The molecular weight of starch molecules is very large and is within 104...108. This polysaccharide is built from two constituent parts - linear amylose and branched amylopectin.

Amylose is a long, usually unbranched chain in which D-glucopyranose residues are connected by $\alpha(1-4)$ bonds. The molecular weight of amylose is from 105 to 106.

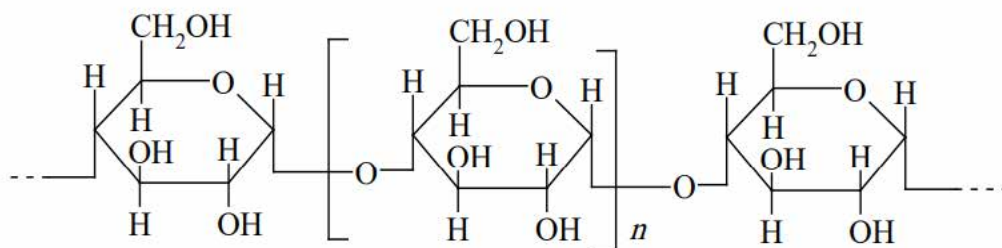


Fig. 2.1. Fragment of the amylose molecule

In native starch granules, amylose chains are coiled into a spiral with 6-10 glucosidic residues on each turn (Fig. 2.2). Because to this structure, the size of the molecules decreases. Amylose easily dissolves in dilute alkali, in individual organic compounds. It is able to form complexes with polar and non-polar organic compounds, in particular with long-chain fatty acids. Amylose jelly is an opaque white mass, irreversible at normal temperatures.

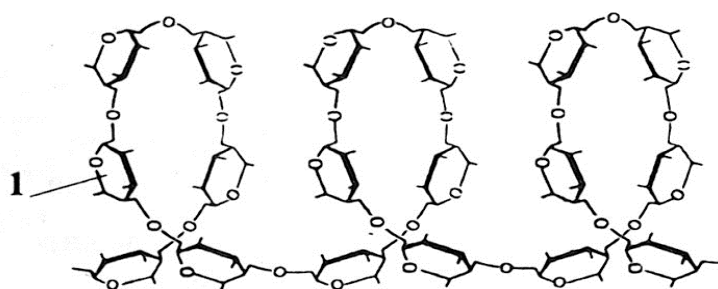


Fig. 2.2. Single helix formed by glucose residues of amylose in space; 1 - amylose molecule

The iodine solution turns amylose blue, due to the formation of a complex "inclusion compound" (clathrate): iodine molecules enter the channel of the amylose spiral.

Amylose is characterized by a transition to its original granular state, which is called "retrogradation". The mechanism of the transition of this polysaccharide into the crystalline state is that elongated linear amylose molecules are more freely oriented relative to other soluble amylose molecules than much more compact branched amylopectin molecules. Therefore, retrogradation is almost exclusively associated with the amylose fraction.

Amylopectin consists of highly branched chains, which are also built from α -D-glucopyranose. But in them, in addition to $\alpha(1-4)$ -type bonds, there are $\alpha(1-6)$ -bonds at the branching points (their 4...5% of the total number of glucosidic bonds), which are located approximately through 20 glucose residues (Fig. 2.3).

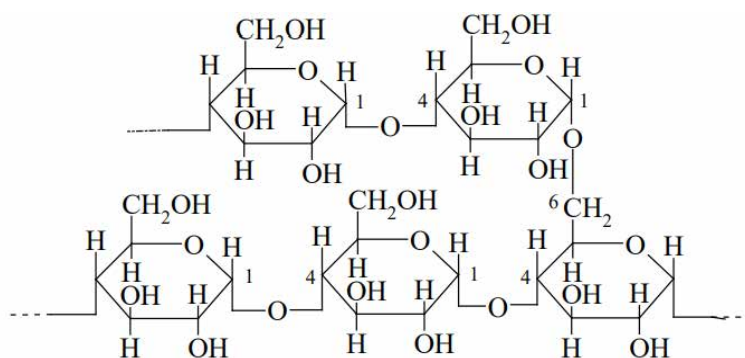


Fig. 2.3. The structure of the amylopectin molecule

The molecular weight of amylopectin can reach from 107 and higher. Solutions of amylopectin give a blue-violet color with iodine, which determines the formation of both complex and adsorption compounds.

Due to the low strength of compounds of starch polysaccharides with iodine, they easily disintegrate during heating or addition of alkali, while the blue color disappears.

Starch in plant cells is deposited in the form of grains (granules). In different plants, they differ in size, shape, and layer structure.

The ratio of amylose and amylopectin in different plant species is different (Table 2.2).

Table 2.2. The ratio of amylose and amylopectin in the starch of various starch carriers

Type of starch carrier	Amylose, %	Amylopectin, %
Potato	23	77
Wheat	20	80
Fig	15...35	65...85
Corn is waxy	0	100
Sorghum	25	75
Oat	26	74
Pea	66	34
Bananas	17	83
Apples	100	0

At the same time, they are identical in their basic chemical structure (Fig. 2.4).

According to this model, there is a "growth point" in the central part of the grain, around which growth rings of hydrogen-bonded starch polysaccharides – amylose and amylopectin – are concentrated. These layers differ in density, crystallinity, and resistance to chemical and enzymatic actions. They form a structural complex of granules, which consists of crystalline and amorphous parts. The degree of crystallinity of starch grains is within 14...42% and depends on the ratio of amylose and amylopectin content. Short chains in the amylopectin molecule form double helices that form crystalline lamellae (crystallites). Free double helices and crystallites create so-called half-crystals. The

remaining amylose molecules and long amylopectin chains form the amorphous part of starch grains.

In the process of amylopectin synthesis and its crystallization, a small amount of phosphate remains bound to the hydroxyl group of the sixth carbon atom. It is characteristic of amylose to capture lipids during the formation of spirals.

The boundary layer of the starch grain, according to most researchers, is made of amylopectin.

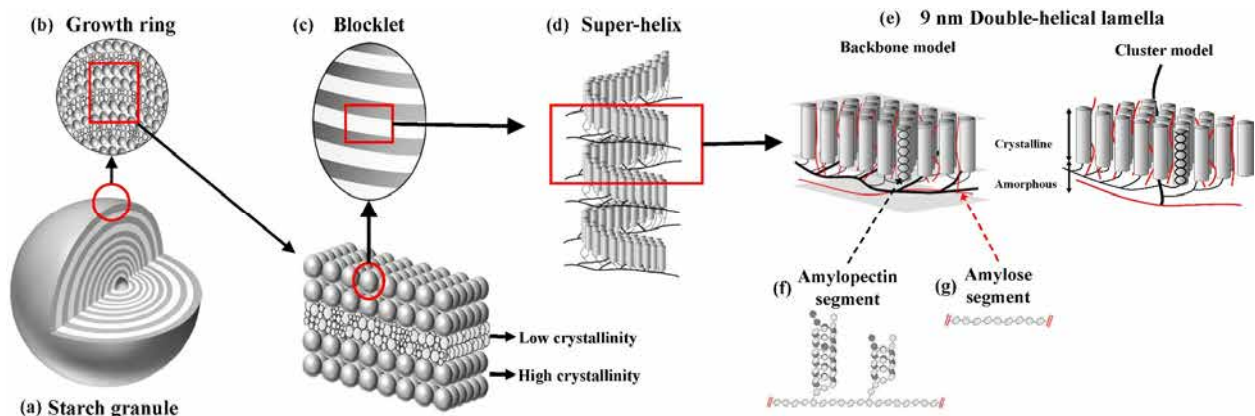


Fig. 2.4. Model of starch grain formation

2.1.2. Modified types of starch. Properties, characteristics

Unlike native plant starches, modified starches are products of fractionation, destruction and various modifications of native plant starches, which are mainly a mixture of two fractions of homoglucans (glucose polymers) of linear and branched structure – amylose and amylopectin.

Features of the chemical structure and properties of these fractions, as well as their ratio in native starch, which depend on the type of plant source (potatoes, rice, corn, etc.), determine the main technological property of starch – the ability to dissolve when heated in water to form viscous solutions (paste).

However, the properties of the resulting paste often do not meet the necessary technological requirements: corn starches form a weak, rubbery paste and undesirable gels during heat treatment.

The process of syneresis is also typical for the paste formed by native starches – volume reduction with the release of a liquid phase as a result of involuntary compaction of the structural network.

Processing methods (physical, chemical, biological) of native starches allow to significantly change their structure, which is reflected in the solubility and properties of the paste.

Reactive centers in polymer starch molecules are:

- hydroxyl groups of glucose structural units, the activity of which in relation to chemical reagents varies in the series: OH near C₆ > OH near C₂ > OH near C₃;
- α-glycosidic bonds connecting glucose structural units into polymer chains;
- terminal residues of D-glucopyranoses, which have reducing properties.

Various types of modified starches can be obtained by changes occurring in native starches (Table 2.3).

Table 2.3. Types of starch modification

Properties	Advantages
Resistant	
Low degree of attack by enzymes and assimilation by the body	Increases the stability of foam, increases the viscosity of whipped masses
Porous	
High absorption capacity due to the porous structure	It is used in baking technologies
Swelling	
Ability to thicken in cold water	Eliminates the need for heat treatment (convenience and energy saving)
Hydrolyzed	
Decrease in viscosity and increase in strength of slurry	Improvement of texture with increasing starch concentration
Enzymatic conversion	
Change in viscosity, jelly strength and sweetness	Change in texture and rheological properties
Oxidized	
The presence of carbonyl and carboxyl groups, which increase transparency and reduce retrogradation	Improving the adhesive characteristics of glazes, obtaining soft, stable glazes at a high concentration
Stabilized	
Prevention of compression of granules, reduction of pasteurization temperature	Stability during cooling and freezing/thawing, extension of shelf life
Split (heat treatment)	
Strengthening of granules and delay of swelling, reduction of viscosity	Increasing the resistance of starch to the action of acids, temperature and deformation
Cross-linked	
Strengthening of granules and delay of swelling, reduction of viscosity	Increasing the resistance of starch to the action of acids, temperature and deformation

Swelling starches. Starches that can dissolve in cold water are obtained through physical transformations that do not cause significant destruction of starch molecules. It is obtained by heating a starch suspension under conditions that ensure rapid pasteurization and subsequent drying of the paste. Starches that swell in cold water are obtained by heat treatment of native corn starch in 75...90% ethanol at a temperature of 150...175 °C for 2.0 hours, or by drying the starch suspension in a spray dryer. Both native and chemically modified starches can be used to obtain

soluble and swelling starches. The obtained swelling starches retain the properties achieved by chemical modification, for example, they show stability in an acidic environment, stability during freezing.

Split starches are products that, as a result of physical or chemical actions, have shorter (compared to native starches) molecular chains. This group includes dextrin, products of acid or enzymatic hydrolysis, as well as oxidized starches.

Dextrin is obtained by dry heating native starches in the presence of acid catalysts or without them.

Hydrolyzed starches are obtained by treating starch suspensions with solutions of acids or amylase hydrolytic enzymes. The composition and properties of oxidized starches are determined by the choice of oxidizers. Like acids, oxidizing agents lead to the formation of starches with shorter molecular chains.

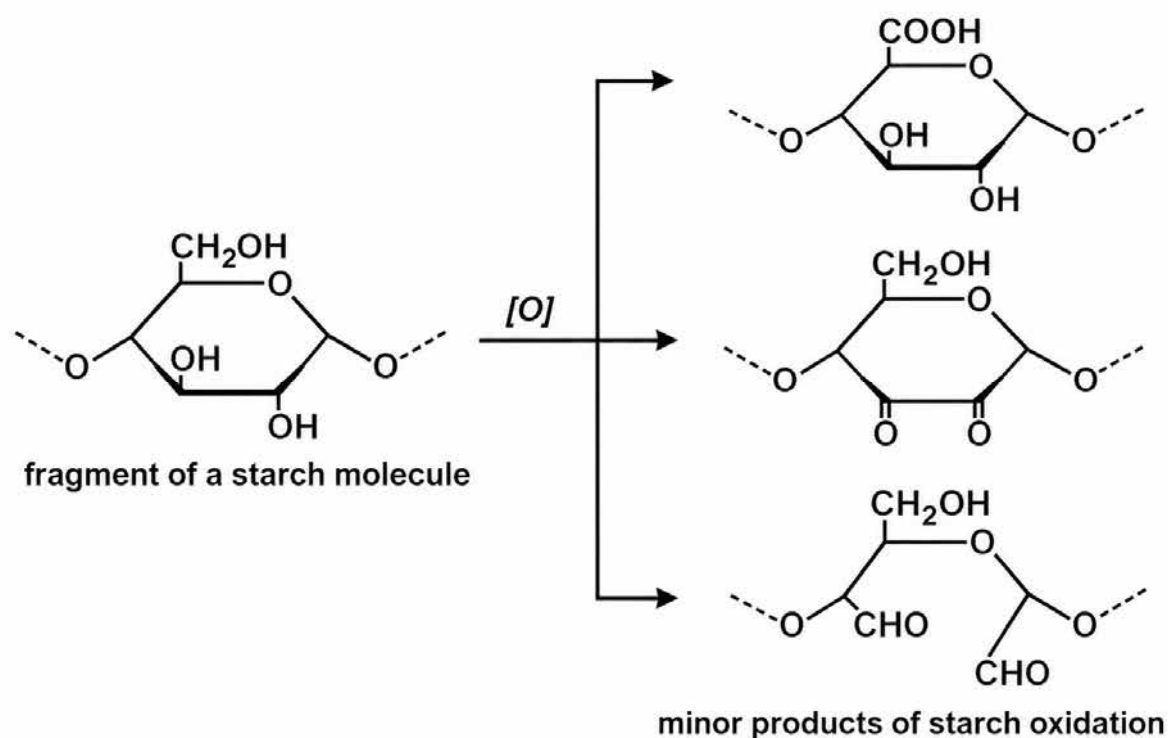


Fig. 2.5. Formation of starches with shorter molecular chains

Diluted solutions of highly oxidized starches retain transparency during long-term storage.

Stabilized starches are products of chemical modification with monofunctional reagents with the formation of derivatives with an ether or ester bond based on hydroxyl groups. The main types of modified starches of this group, as well as their properties, are listed in the table 2.4.

Stitched starches. Cross-linking of individual starch molecules among themselves occurs as a result of the interaction of their hydroxyl groups with bifunctional reagents. For food purposes, mainly three types of intermolecularly cross-linked starches are used – distarch esters of phosphoric and adipic acids, as well as distarch malglycerols:

Table 2.4. Esterified and esterified food starches

Ethers- and esterified starches	Broadcast groups	Main characteristics
Esthers		
Acetylated	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{C}-\text{CH}_3 \end{array}$	Increased transparency and stability of the paste at low temperatures, easier heat treatment
Phosphorylated	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{P}-\text{ONa} \\ \\ \text{OH} \end{array}$	Increased transparency and stability of the paste, resistance to freezing and thawing
Esterified with octenyl succinic acid	$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\text{C}-\text{CH}-\text{CH}_2-\text{C}-\text{ONa} \\ \\ \text{CH}=\text{CH}-(\text{CH}_2)_7-\text{CH}_3 \end{array}$	Emulsifying ability and stabilizing
Ethers		
Hydroxypropylated	$\begin{array}{c} -\text{CH}_2-\text{CH}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	Increased transparency and stability of the paste, resistance to freezing and thawing, easier heat treatment

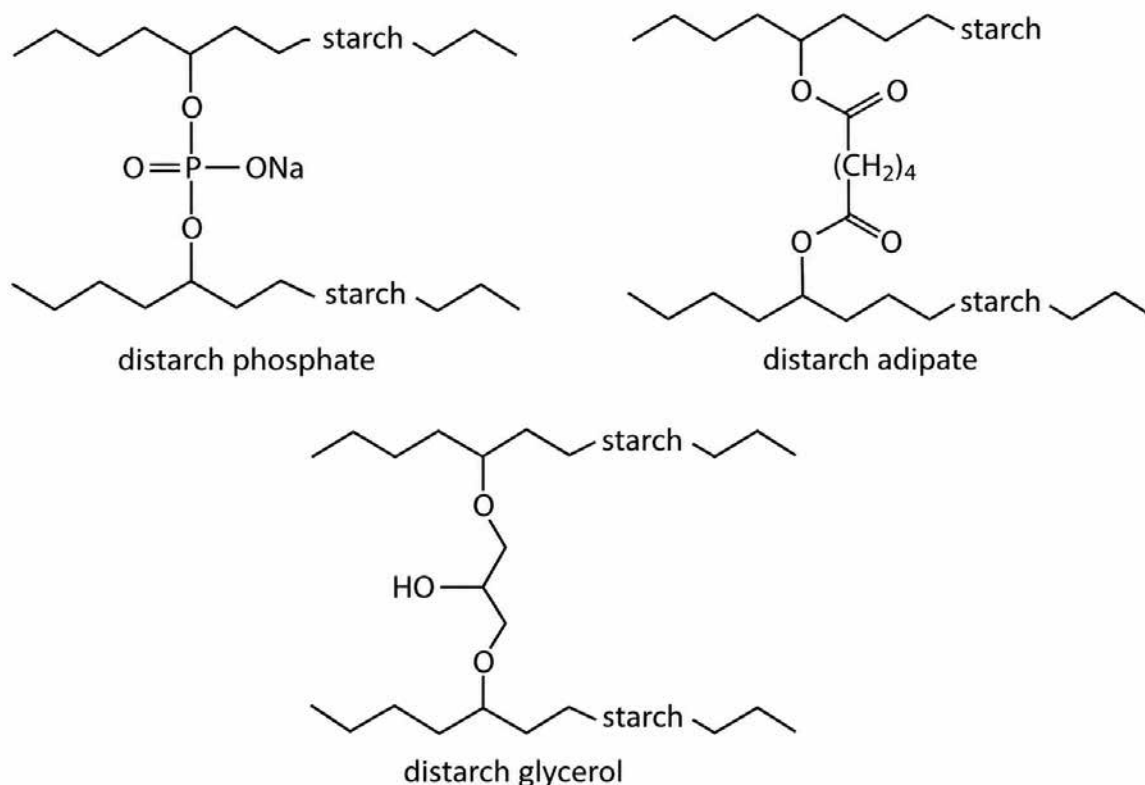


Fig. 2.6. Types of intermolecular cross-linked starches

Starches of this subgroup have a reduced rate of swelling and pasteurization, which creates the effect of prolonged action.

The paste formed by cross-linked starches is more viscous, has a "short" texture, is resistant to high temperatures, long-term heating, low pH, and mechanical loads.

Resistance to acidification and physical actions is proportional to the number of cross-links. Due to these properties, cross-linked starches are effective in technologies that include long-term heat treatment, intensive mechanical actions, as well as in technologies that require prolongation of the processes of swelling of starch granules, increase in viscosity and texture formation.

Starch derivatives

Complex esters of starch are obtained during the interaction of reactive groups of starch polysaccharides (reducing terminal, alcoholic at C₂, C₃ and C₆) with appropriate chemical reagents.

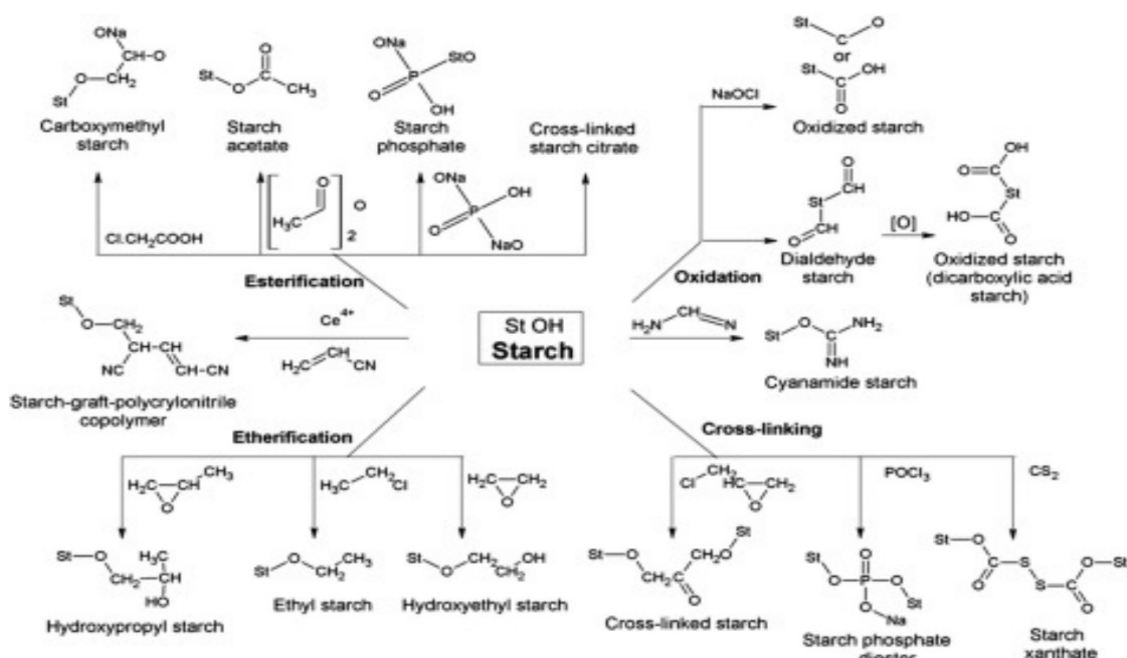


Fig. 2.7. Reactions leading to starch modification

The ability of these groups to undergo substitution reactions with various organic and inorganic compounds is used to produce a number of modified starches called "crosslinked", due to the introduction of a crosslink or bridge between two adjacent polysaccharide chains.

Due to the change in the chemical structure, such properties of pasteurized products as viscosity, stability, film-forming ability, resistance to retrogradation, mechanical and thermal effects are noticeably increased.

Substituted starches include: monostarch phosphates, distarch phosphates, acetylated, oxyalkylated and cross-linked starches.

Monostarch phosphates are esters in which one hydroxyl group of a glucose residue is esterified with one of the acid groups of a phosphoric acid residue and its salts. Monostarch phosphates are prepared by heating starch with water-soluble

phosphates, salts of ortho-, pyro- or metaphosphoric acid. Starch grades A and B are distinguished by the processing method.

Monostarch phosphates form stable pastes with increased transparency, resistance to freezing and thawing. They have the maximum viscosity at a temperature of 65 °C. After reaching the maximum, the viscosity of the paste drops sharply.

Starch grade A is used for the production of flour confectionery products, in particular biscuit semi-finished products, cookies, wafer semi-finished products; grade B – for stabilization and thickening of butter creams, as well as the production of other semi-finished products that are stored in chilled and frozen conditions.

Distarch phosphates are ethers in which the hydroxides of glucose residues of various chains interacted with two acid groups of phosphoric acid and its salts.

For their production, sodium trimetaphosphate, phosphorus chloride, phosphorus pentachloride or phosphorus thiochloride are used. Distarch phosphates form stable pastes that are resistant to heat, mechanical impact and the action of acids. Pastes are characterized by low transparency and a non-stringent, short-drop consistency. Pastes of these starches have a maximum viscosity at a temperature of 75 °C, which greatly increases upon cooling.

These starches increase the quality of decorative semi-finished products, give baked products a shiny surface.

Acetylated starches. Glacial acetic acid, acetic anhydride and other reagents are used to prepare these types of starch esters. During their production, not only the formation of a complex ester occurs, but also the destructive splitting of starch.

The pasteurization temperature of pastes of the specified starches is lower, and the viscosity is higher than that of the raw materials. They retain their properties at low pH values, high temperatures, and mechanical action. This type of starch products is well preserved during freezing and thawing. Crosslinks increase the resistance of pastes to high temperatures, mixing and low pH values.

Acetylated starches are used in the manufacture of baked goods.

Oxyalkylated starches. In industrial conditions, two types of starch esters of this type are produced - oxyethyl and oxypropyl starches. Starch is subjected to esterification at a temperature lower than its pasteurization point, using ethylene oxide or propylene oxide. The reaction is carried out in an alkaline environment.

The introduction of oxyalkyl groups into starch, even with a low degree of substitution, lowers the temperature of starch pasteurization, increases the rate of swelling and dispersion of grains during heating, increases the transparency of the paste, reduces its gelatinization ability, and increases resistance to retrogradation, to the action of acids, weak oxidants.

Oxyalkylated starches are used to prepare fillings, thicken creams, and improve the consistency of baked goods.

2.1.3. Characteristics of cellulose and its derivatives

Cellulose and its derivatives include products of mechanical and chemical modification and depolymerization of natural cellulose, which is a linear polymer consisting of D-glucopyranose residues connected by β -1,4-glycosidic bonds.

The presence of a β -glycosidic bond leads to the formation of linear molecules with zones of crystallinity (highly oriented areas) that include separate amorphous (unoriented) areas at the level of secondary and tertiary structures (conformation of polymer chains, packing of chains in fibers).

Cellulose comes in two modifications:

- microcrystalline cellulose
- powdered cellulose extracted from vegetable raw materials (wood, cotton, etc.).

The main technological functions of cellulose are emulsifier and texturizer.

Chemical modification of cellulose molecules leads to changes in properties and, as a result, to changes in functions in food systems.

The availability and reactivity of the hydroxyl groups of β -D-glucopyranose residues plays a major role in the formation of cellulose derivatives.

The structure and technological functions of food cellulose esters are presented in the table 2.5.

Table 2.5. Modified cellulose and their technological functions

Name	X	Y
Methyl cellulose	-CH ₃	-H
Ethyl cellulose	-CH ₂ CH ₃	-H
Hydroxypropyl cellulose	-CH ₂ CH(OH)CH ₃	-H
Hydroxypropyl methylcellulose	-CH ₂ CH(OH)CH ₃	-CH ₃
Methylethyl cellulose	-CH ₃	-CH ₂ CH ₃
Carboxymethyl cellulose (sodium salt)	-CH ₂ COONa	-H
Ethylhydroxy-ethylcellulose	-CH ₂ CH ₃	-CH ₂ CH ₂ OH

By combining the initial reagents, mixed cellulose derivatives are obtained, for example, methyl ethyl cellulose, methyl hydroxypropyl cellulose, etc.

Cellulose and its derivatives: microcrystalline cellulose, methyl cellulose, carboxymethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, methyl ethyl cellulose.

Methylcellulose is soluble in cold water, and turns into a gel in warm water. The solubility of methylcellulose decreases with increasing temperature. It practically does not dissolve in water at a temperature close to the boiling point.

Gelation in methylcellulose solutions is caused mainly by the hydrophobic interaction of nonpolar groups of macromolecules.

Carboxymethylcellulose is obtained from pure cotton cellulose. It adsorbs water in a 50-fold amount, forming colloidal systems.

Microcrystalline cellulose is partially acid-hydrolyzed cellulose, differs from natural cellulose by a shortened molecular chain and the absence of associative bonds.

Aqueous dispersions of microcrystalline cellulose are gel-like at a concentration of about 1 %. Moreover, with an increase in the concentration of dispersion systems

(about 1.2...1.5 %), their pseudoplasticity becomes more noticeable. The viscosity of the systems increases over time, especially after 18 hours of storage.

2.1.4. Pectins and inulin

Pectins are a group of high-molecular heteroglycans that are part of the cell walls of vegetables and fruits, and through side chains are connected to hemicelluloses, for example, galactan, and then to cellulose fibers.

In such a bound form, called "protopectin", they are insoluble in water.

The term "pectin substances" includes: hydratopectin (soluble pectin), protopectin (pectin insoluble in water), pectin acids and pectinates, pectic acids and pectates.

By chemical nature, pectins are heteropolysaccharides, the basis of which are rhamnogalacturonans.

The main chain of the polymer molecule is formed by derivatives of polygalacturonic (pectic) acid (polyuronides), in which the residues of D-galacturonic acid are connected by a 1,4- α -glycosidic bond.

The main chain of polygalacturonic acid in solution has the form of a spiral containing three molecules of galacturonic acid in one turn.

Molecules of L-rhamnose (6-deoxy-L-mannopyranose) are incorporated into the chain of polygalacturonic acid unevenly through 1,2- α -glycosidic bonds, which gives the polymer molecule a zigzag character (Fig. 2.8).

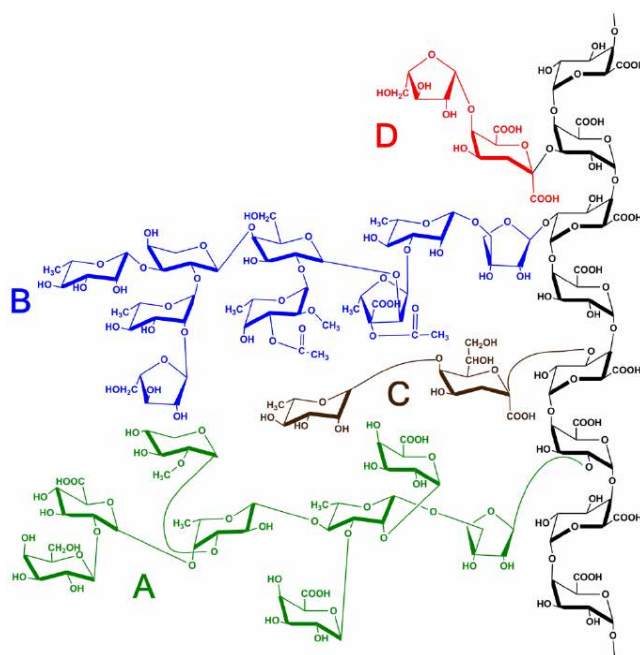


Fig. 2.8. Schematic representation of the rhamnogalacturonan fragment

The number of substituted carboxyl groups determines the degree of esterification of pectin. If more than 50% of the carboxyl groups contain residues of ethyl alcohol, it is highly esterified (high-comethoxylated) pectin, if the degree of esterification is below 50 %, it is low-esterified.

Pectin is formed from protopectin under the action of acids, alkalis or the enzyme protopectinase.

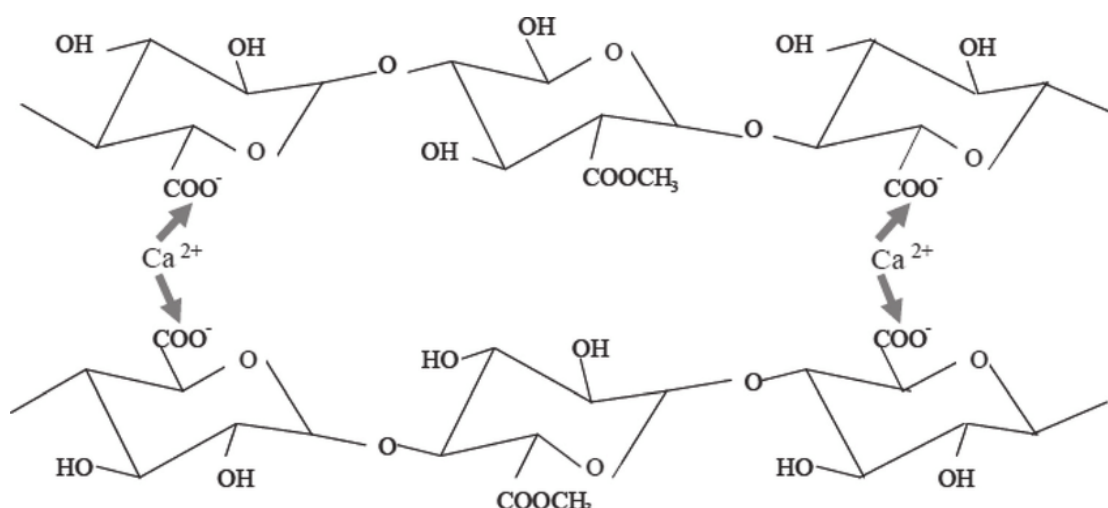


Fig. 2.9. Mechanism of formation of jellies

Pectin substances as gelatinizers are widely used in the production of marmalade, pastille, jelly and jam, as well as in bread baking and cheese making.

In food production, the source of pectin substances is apples or lemons. Phytopolysaccharides also include slimes and gums.

Gums are polysaccharides that are released in the form of viscous solutions and form a glassy mass when the integrity of the bark of many trees and the shell of plants is disturbed.

The property of forming gum is very widespread in plants. The most famous gum-bearing plants belong to the legume, rose family, etc.

Gums are heteropolysaccharides, which consist of several monosaccharides, among which there may be one or more uronic acids. Due to increased viscosity, stickiness, swelling and other valuable properties, gums are widely used in food production as emulsifiers, thickeners, binders and stabilizers.

Mucilages are polysaccharides similar to gums, but found in intact plants. The source of mucus is bark, roots, leaves, seeds, etc. Rye and flax grains contain a significant amount of mucus, from where they are extracted with water. Mucus and gums are practically indistinguishable by chemical structure, but it is noted that among mucilages there are more polysaccharides with a relatively simple structure.

There are many neutral hetero- and homopolysaccharides in mucus. Mucilages swell in water and form viscous solutions. The mucilages of vegetable plants are hydrophilic polysaccharides, chemically, neutral mucilages are similar to hemicellulose, and acidic mucilages are similar to gums. Vegetable plants with a large amount of mucus are very useful for preparing dietary dishes that treat gastritis and stomach ulcers.

The structure of seaweed polysaccharides is significantly different from the polysaccharides of terrestrial plant organisms.

Although the fiber that takes part in the construction of cell walls of algae is similar to ordinary fiber, the bulk of these walls and the intercellular substance are the so-called slimes of algae - agar, carrageenan, alginic acid, etc.

Agar and carrageenan are obtained on an industrial scale from many types of red algae. Agar is a mixture of polysaccharides agarose and agarpectin. Agarose is made of D-galactose and 3,6-anhydro-L-galactose. Alginic acid is obtained from brown algae.

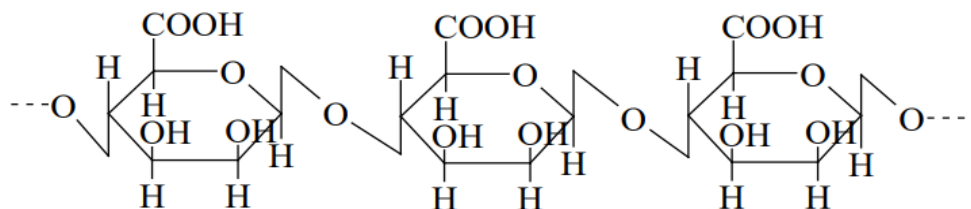


Fig. 2.10. Fragment of alginic acid molecule

Algae polysaccharides are widely used in the food industry. The connective tissue of animal organisms contains a significant amount of acidic mucopolysaccharides. These are linear polymers with molecules that are built from residues of amino sugars and uronic acids. The acidic properties of many of them are due to the presence of carboxyl groups and the presence of sulfuric acid residues.

Acidic mucopolysaccharides form complexes with proteins in the connective tissue. Such polysaccharides include hyaluronic acid. Complete acid hydrolysis of this polysaccharide gives glucosamine, acetic acid, and carbon monoxide as a result of decarboxylation of uronic acid.

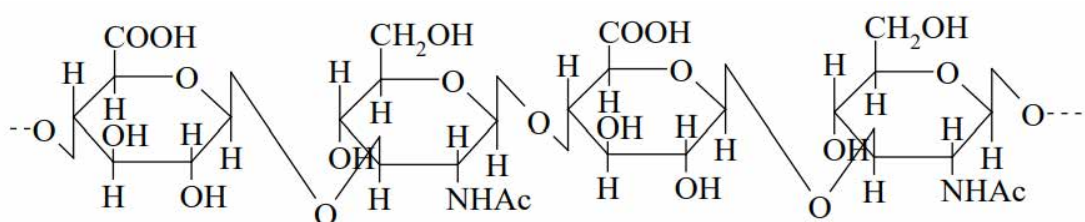


Fig. 2.11. A fragment of a hyaluronic acid molecule

An important property of hyaluronic acid is the formation of high viscosity solutions. This property is strongly influenced by the ionic strength and pH of the solution.

Glycogen – animal starch, is a reserve polysaccharide in the body of humans and animals, it is the most important source of energy.

Glycogen is contained in all cells of a living organism, but most of it is in the liver (up to 20 % of raw mass) and in muscles (up to 4 %). It is also found in yeast and higher fungi.

Glycogen can be isolated from animal tissues by the action of a solution of trichloroacetic acid in the cold ($w = 5\ldots 10\%$), or with a solution of KOH = 60 %) at a temperature of 100 °C, followed by precipitation with ethanol. Glycogen is easily hydrolyzed by acids to glucose.

Glycogen is a white amorphous powder, well soluble even in cold water, in which it forms an opalescent substance. The glycogen solution rotates the plane of light polarization to the right, its specific angle of rotation is $+196^\circ$.

The glycogen molecule is built from α -D-glucopyranose residues connected mainly by α -(1 $\rightarrow$ 4) glycosidic bonds. About 7...9 % of bonds are α -(1 $\rightarrow$ 6)-glycosidic bonds and about 0.5 ... 1 % are α -(1 $\rightarrow$ 3)-glycosidic bonds.

Glycogen is similar in structure to amylopectin, but its molecules are even more branched. The outer chains of molecules are longer than the inner chains. The total number of glucose residues in a glycogen molecule is higher than in amylopectin molecules.

The molecular weight of glycogen reaches many millions of units, and the degree of polymerization is 2500-25000. With iodine, glycogen solutions give a color from wine-red to red-brown, depending on the origin of glycogen.

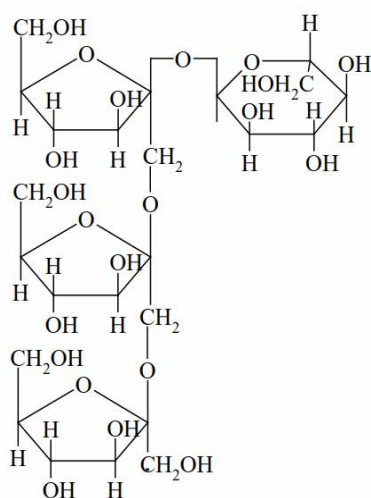
In the body of animals and humans, glycogen is synthesized from glucose and accumulates in tissues, and in the period between eating, it is broken down with the participation of enzymes. However, the amount of glycogen that can be stored in tissues is limited.

After storing 50...60 g of glycogen per kilogram of tissue, fat, not glycogen, begins to be synthesized from glucose. From this time, obesity of the body begins. During starvation, increased muscle work, lack of vitamins, etc., there is a sharp decrease in glycogen content, and with a large amount of carbohydrates supplied with food, the amount of glycogen can increase.

In addition to the liver and muscles, glycogen is deposited in small amounts in all tissues and organs.

Inulin. Reserve polysaccharides include inulin. This polysaccharide consists of β -D-fructofuranose residues connected by a 2,1-glycosidic bond, and one glucopyranose residue is placed at one end of the chain and in the middle.

Its empirical formula is $(C_6H_{10}O_5)_n$, the molecular weight of inulin does not exceed 5000-6000 conventional units with a chain length of 38-45 hexose units.



Inulin solutions rotate the plane of polarized light to the left, the angle of specific rotation is -39° . Inulin is a hygroscopic compound, easily soluble in hot water and difficult in cold water. It is contained in dahlia tubers (10...12 %), chicory roots (10 %), Jerusalem artichokes, artichokes, evening primrose and other substances. The solution of inulin is not colored by iodine.

Fig. 2.12. Fragment of inulin molecule

Fiber (cellulose) consists of β -D-glucopyranose residues connected by a 1,4-glycosidic bond:

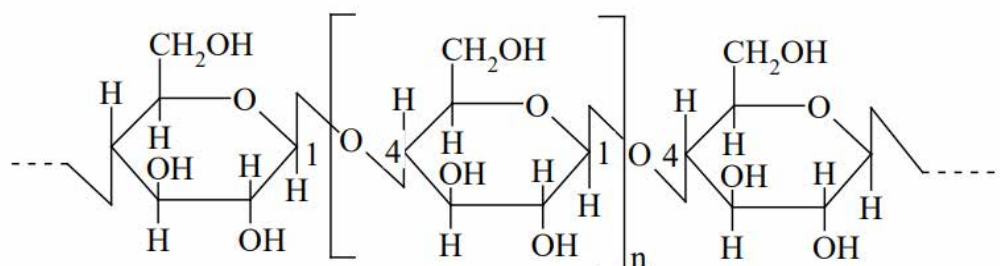


Fig. 2.13. Fragment of a fiber molecule

Fiber has a molecular weight of 100,000 to 1 million. It does not dissolve in water. Due to its stability, it is the most widespread biopolymer in the world.

A characteristic feature of fiber, which mainly determines its mechanical, physicochemical and chemical properties, is the linear conformation of its molecules, which is strengthened by intramolecular hydrogen bonds.

Linear fiber macromolecules, arranged in approximately parallel bundles, form structures regular in three dimensions due to additional intermolecular hydrogen bonds, which is characteristic of crystals.

In the fiber, amorphous fibers are located between the crystalline fragments, the presence of which is due to the high mechanical strength and insolubility of the fibers.

Swelling and reactivity are also associated with amorphous fragments that are more easily permeable to chemical reagents. Fiber plays the role of a supporting material and is a component of plant cell membranes. Fiber has high mechanical strength and is broken down by a special cellulase enzyme in the body of herbivores.

Enzymes of the human gastrointestinal tract do not break down fiber, so it is classified as ballast substances or dietary fibers. Fiber increases the secretion of bile, which contributes to better removal of cholesterol from the body. This property is used in medical nutrition for diseases of the liver, gall bladder, and atherosclerosis. It is prescribed for excessive fullness and diabetes due to its ability to cause a feeling of satiety.

Fiber is a fibrous substance, strong, colorless, odorless, does not stain with iodine, does not dissolve in water and organic solvents.

It is dissolved in some solvents (for example, Schweitzer's reagent). Hemicelluloses are heteropolysaccharides with a relatively low molecular weight.

They have a more or less linear structure of molecules, but do not form fibrillar structures and together with pectin substances, which are built mainly from residues of uronic acids, play the role of material – cement in the plant cell wall. Hemicelluloses include such heteropolysaccharides as glucomannans, galactomannans, xylans, which contain residues of mannose, galactose, arabinose, xylose, glucose and other monosaccharides in their side chains.

Hemicelluloses are widely used for the production of fodder and food products. Hemicelluloses belong to a group of dietary fibers that are necessary for normal

digestion. They affect lipid metabolism, play the role of enterosorbents, reduce cholesterol content, absorb microflora, heavy metal salts.

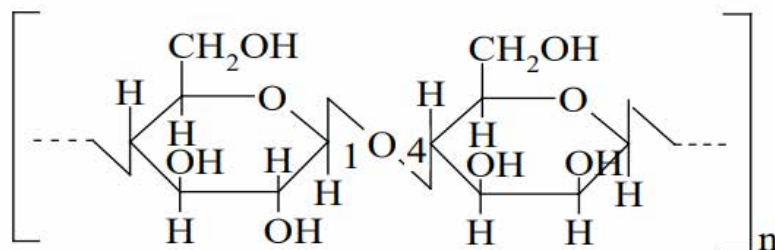


Fig. 2.14. Fragment of the hemicellulose molecule of glucomannan

Questions for discussion and self-examination

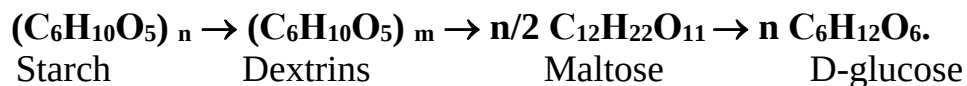
1. Characteristics of the structure and properties of polysaccharides that are part of starch.
2. Characteristics of differences in the structure of different types of starch.
3. Types of starches, their physical and chemical properties.
4. Modifications of starch, practical application.
5. Characteristics of inulin and pectin.

Topic 2.2. Physicochemical Properties of Polysaccharides.

2.2.1. The main properties of starch

Water-holding capacity of starch. Native starch is practically insoluble in cold water, but due to its hydrophilicity, it absorbs up to 30 % of moisture to its own weight, slightly increasing in volume. Starch grains bind water mainly by adsorption, and only a small part of it is bound by microcapillaries. The speed and amount of water absorption depend on the state of the starch grain. Whole grains of starch absorb a maximum of 0.3...0.4 g/g of water per dry substance, and damaged ones - 2...3 g/g of water.

Starch hydrolysis. During heating with water in an acidic environment, starch undergoes hydrolysis according to the scheme:



The breakdown of starch under the action of enzymes is called amylolysis.

α -amylase catalyzes the breaking of α -1,4-glucosidic bonds of this biopolymer with the formation of low-molecular branched oligosaccharides, a small amount of glucose and maltose. Acting on a whole starch grain, α -amylase attacks it, loosening the surface and forming channels and grooves, that is, it seems to split the grain into parts.

Schematically, the effect of α -amylase on starch is shown in Fig. 2.15.

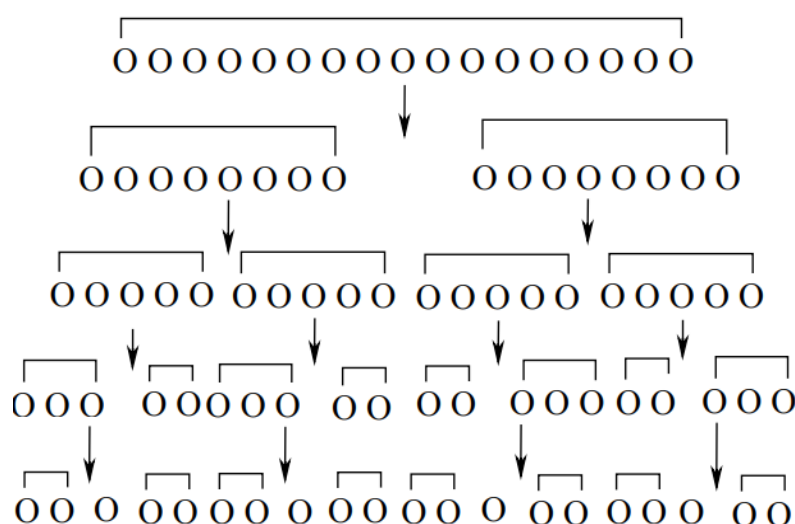


Fig. 2.15. Scheme of action of α -amylase on amylose

Under the action of this enzyme, mainly dextrans are formed.

For malt and mushroom α -amylases, optimal pH values are within 4.5...5.5 and temperature 55...65 °C. Bacterial α -amylases show maximum activity at pH 6.0...7.0 and temperatures 65...90 °C.

β -amylase is an enzyme of final action, showing affinity to the second β -1,4-bond from the non-reducing end of the linear chain of amylose and amylopectin.

Unlike α -amylase, β -amylase practically does not hydrolyze native starch.

Clayterized starch is hydrolyzed by it with the formation of maltose in the β -configuration. If amylose is subject to hydrolysis, then the hydrolysis goes completely to maltose.

In the case of hydrolysis of amylopectin, the splitting process takes place to a much lesser extent. It stops at the penultimate β -1,4 bond, which borders the β -1,6 bond. 54...58% of maltose accumulates in the hydrolyzate, the rest consists of high molecular weight dextrans that contain a significant amount of β -1,6-links – the so-called β -dextrans (Fig. 2.16).

Optimal conditions for the action of β -amylase: pH 4.2; temperature 50 °C. Calcium ions inhibit the action of the enzyme.

Neither α - nor β -amylase alone can completely hydrolyze starch. Under the simultaneous action of both these enzymes, starch is hydrolyzed by 95%.

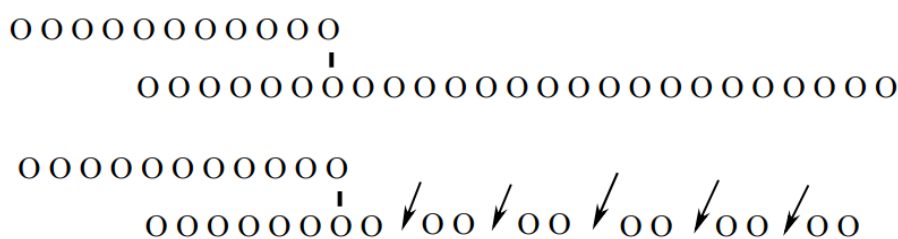


Fig.2.16. Scheme of action of β -amylase on amylose

Amyloglucosidase (glucoamylase) cleaves α -1,4-, α -1,6-glycosidic bonds in starch. Moreover, the rate of hydrolysis of α -1,4-bonds is 15 times greater than that of α -1,6-bonds. The only product of hydrolysis at all stages is α -glucose.

Depending on the optimal pH values, acidic (pH 3.5...5.6) and neutral glucoamylases are distinguished. The optimal temperature of action of glucoamylases varies between 45...60 °C.

The degree of hydrolysis of starch by amylases can be assessed by the color of its solution with iodine. At the first stages of hydrolysis, dextrans are obtained, which differ little from starch in terms of molecular size and properties. With iodine, they give a blue or purple color. In the process of further hydrolysis, the molecular weight of dextrans decreases, they begin to turn dark brown from iodine, then red, and finally stop reacting with iodine. According to the properties, the following types of dextrans are distinguished, which are listed in the (Table 2.6).

Table 2.6. Types of dextrans formed during starch hydrolysis

Dextrans	Molecular weight	Color with iodine	Solubility	Method of deposition
Amylodextrans	10 000	Purple-blue	In 25% alcohol	40% alcohol
Erythrodextrans	6 000	Red-brown	In 55% alcohol	65% alcohol
Acrodextrans	3 000	They are not colored	In 70% alcohol	Alcoholic solution
Maltodextrans	from 700 and below	They are not colored	—	—

Starch pyrolysis. As a result of heat treatment of dry starch, complex transformations occur, which are represented by a number of chemical reactions. At the first stages (up to 130 °C), it loses all the capillary and part of the bound moisture. A further increase in temperature leads to acceleration of the splitting of polysaccharide molecules, irreversible separation of water, changes in the structure of carbohydrates due to the formation of new α - and β -bonds, i.e., a recombination reaction takes place. The first step of such transformations is the formation of levoglucosan (Fig. 2.17).

Pasteurization of starch. When starch is heated in water, a wheatpaste is formed - a dispersion of swollen starch grains in water and dissolved fractions of amylose and amylopectin.

Swelling and pasteurization is one of the most important properties of starch, which depends on the yield, volume, and consistency of products based on it. It swells, absorbing a large amount of solvent and significantly increasing in volume.

During the heating of starch suspension to 50...60 °C, limited and reverse absorption of water by starch grains occurs. The grains become transparent. During the removal of water by careful drying, the properties of starch do not change: the shape and layering of the grains are preserved, as well as their double refraction of polarized light.

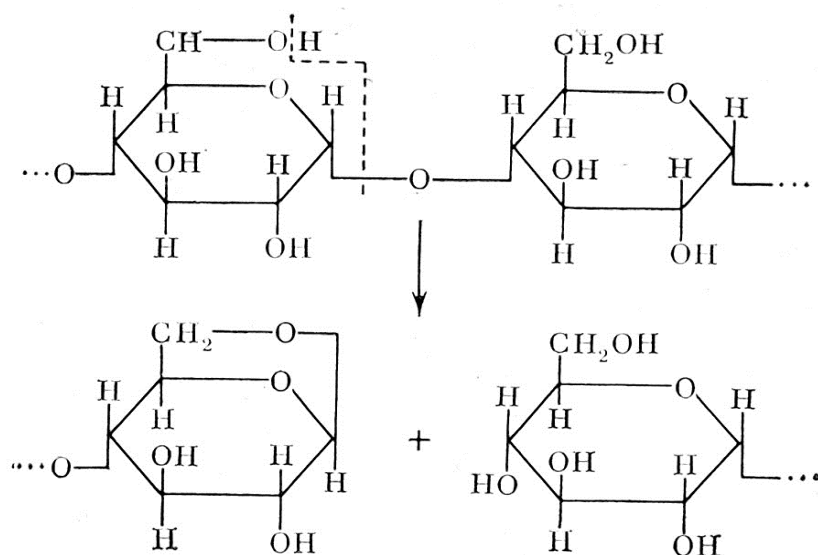


Fig. 2.17. Mechanism of formation of levoglucosan

Further heating to temperatures of 80...90 °C leads to irreversible strong swelling, which is accompanied by a several-fold increase in grain volume, loss of layering, and the transition of the low-molecular fraction of amylose into solution.

Heating above 100 °C causes disintegration of grains. At the same time, the wheatpaste is a solution of polysaccharides (amylose and amylopectin) in which fragments of destroyed grains are dispersed.

The degree of swelling depends on the temperature of the environment and the ratio of water and starch.

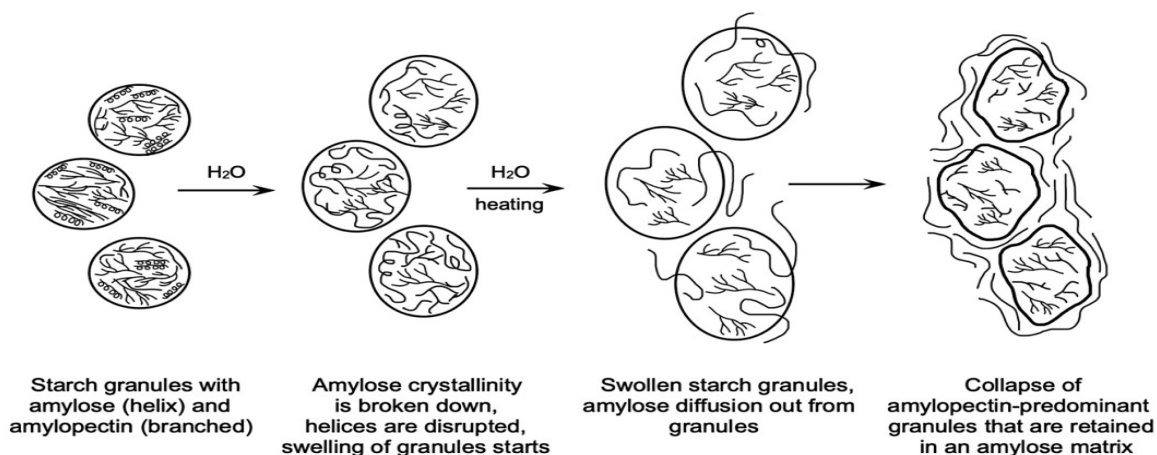


Fig. 2.18. Starch gelatinization scheme

Due to the differences in temperature intervals of pasteurization, the properties of starches of different types differ significantly. Thus, the temperatures at the beginning and end of starch pasteurization differ by 5...15 °C, which is due to both the size and structure of grains and the composition of starch polysaccharides.

Sucrose has a great hydration capacity, so in the three-component system starch-water-sucrose, it will bind water molecules, preventing them from adsorbing on the surface and swelling of starch grains.

An increase in the concentration of sucrose helps to slow down the course of pasteurization of starch. As the concentration increases, the viscosity of the wheatpastes increases, but the strength of the gelatins formed by starch decreases.

The effect of other sugars, such as D-glucose, is less than that of sucrose, since the number of water molecules bound by the hydroxyl group of this disaccharide is much larger.

The viscosity of starch wheatpastes decreases with decreasing pH.

This regularity is explained by the hydrolytic action of H^+ ions on starch polysaccharides. Modified starches are used to manufacture a range of products with a low pH value.

Acids and sugars are present in multicomponent starch-containing systems (often once). In this case, the effect of acid is prevented to some extent by the high concentration of sugar, which inhibits the swelling of starch grains. Addition of a significant amount of sucrose to acidified wheatpastes slows down hydrolysis, which occurs due to its high hydration capacity, and because of this, insufficient binding of water by starch grains.

Sodium chloride, even in small concentrations, reduces the viscosity of starch wheatpaste.

Most of the **surface-active substances** increase the temperature of reaching the maximum viscosity, but these substances stabilize the wheatpaste during storage.

Proteins are either natural companions of starch in natural systems, or they are added in the form of milk and eggs. They have a stabilizing effect on starch pastes.

The amount of water in the system also affects the starch pasteurization process. For complete pasteurization of starch grains, a starch:water ratio of 1:10 is required. In the dough preparation during the baking of bakery products, the process of pasteurization is significantly different, because the water in the system is three times less than required.

The process of pasteurization in the dough preparation contributes to the formation of a dry and elastic pulp in the products.

2.2.2. Properties of starch pastes

Transparency of wheatpastes. The transparency property of pasteurized starch pastes is used to identify and characterize starches. Thus, wheatpastes from tuber cultures have a transparent, colorless jelly-like consistency, from cereals – opaque milky-white paste-like consistency. Corn amylopectin starch paste is closer in properties to potato starch. The transparency of starch pastes depends on the presence of other substances. Yes, sugar significantly increases this indicator. Surface-active substances significantly increase the transparency of wheatpastes. And food emulsifiers, such as glycerin monostearate, make wheatpastes opaque. Protein substances, which are present together with starch in many food products, reduce the transparency of wheatpastes.

Drag-forming ability of wheatpastes. Starch pastes in concentrations starting from 4% are able to form gelatin over a period of time. Potato starch or other tuberous starches are used to obtain a jelly-like consistency, and corn or other grain starches are used to make viscous paste-like masses. During storage or freezing in the

jelly, water is removed and the structure of the jelly itself is compacted. Amylopectin starches, in particular waxy corn, or modified starches are used to obtain syneresis-resistant jelly.

The presence of a "raw grain" flavor in the wheatpastes. The organoleptic quality indicators of decorative semi-finished products made from starch-containing raw materials depend on the taste characteristics of starch. The "starchy" taste or "raw grain" taste is caused by the non-carbohydrate components of the starch granules. This flavor is weakened during cooking and can be completely masked by other flavors. The less pronounced starchy taste of tuber and amylopectin starches may be the result of their lower lipid content.

Film-forming ability of wheatpastes. Starch pastes, especially rich in amylose, form strong films with low oxygen permeability. For this, a method of extruding starch with softeners, plasticizers at temperatures between 150...200 °C and using approximately 30% of the plasticizer by weight of the polymer is used. There is a method of obtaining starch films from hot water solutions at elevated temperature (150 °C) and pressure. Dispersion of starch polysaccharides takes place quickly and completely. Films obtained from starch are amorphous, the degree of crystallization varies depending on the conditions of film formation. The mechanical properties of amylopectin films are more fragile than those of amylose.

Retrogradation of wheatpastes. Starch pastes undergo aging during storage or cooling (retrogradation is a process that consists in the transition of amylose and amylopectin from a hydrated, pasteurized state to a crystalline state. That is, in the process of aging over time, amylose and amylopectin lose hydrogen bonds with water molecules. Water from Polysaccharides of the starch grain are attracted, form hydrogen bonds between themselves, and are compacted, which leads to their acquisition of a crystalline structure inherent in native starch grains.

In baked semi-finished products, in which only the surface layers of starch grains are pasteurized, the retrogradation process occurs quickly. It is known that amylopectin solutions retrograde much more slowly than amylose. Retrogradation of polysaccharides can be partially stopped by heating.

During the freezing and thawing of starch pastes, the consistency changes, liquid delamination from the jelly is observed. However, the property of swollen starch grains to form a spongy structure of coacervates during freezing and thawing in an aqueous environment is undesirable, if starch-containing semi-finished products and products are allowed to be stored in a frozen state. You can prevent these negative phenomena with the help of certain measures. So, for the production of confectionery products, you can use waxy corn starch containing 100% amylopectin, or starch male phosphates (monoamylorthophosphoric ester).

The decisive factor for the preparation of a dispersion stable under freezing and thawing conditions is that the starch grains must be completely dispersed by intensive homogenization and immediately frozen at a temperature lower than -20 °C. The thawing temperature should change rapidly from -2 to +1 °C. These conditions are also used to determine the behavior of starch during freezing and thawing.

2.2.3. Properties of pectin substances

Under the influence of hot water, weak hydrogen bonds can be broken, anhydride bonds can also be destroyed, hydrolysis of ether bonds is possible.

Pectins dissolve in cold and warm water and form solutions of 4...5 % concentration. The solutions have an acidic reaction (pH 2.9...3.2), are viscous. Pectins do not dissolve in most organic solvents. Precipitate with lower alcohols.

Pectins are sensitive to the action of acids and alkalis, in the presence of sugar in an acidic environment they form jelly. The gelling properties of pectin are more significant, the more methoxyl groups in its molecule. Optimum conditions for the formation of strong gelatin from highly esterified pectin: pectin - 0.5...1.0%, sugar – 60 %, pH – 2.6...3.1.

Low-esterified pectins form gels under the action of metal salts with a valency of 2 and higher. Calcium salts are often used for this.

Complexing ability. One of the most important properties of pectin substances is the ability to complex formation, which is based on the interaction of pectin molecules with ions of heavy and radioactive metals. This property gives reason to recommend pectin for inclusion in the diet of people who are in an environment contaminated with radionuclides and in contact with heavy metals.

Long-lived isotopes of cesium (Cs^{137}), strontium (Sr^{90}), yttrium (I^{91}), etc. are especially dangerous for the human body. Excretion of pectin in relation to the administered dose of cesium is 8.4%, strontium – 52.6 %.

The complex-forming properties of pectin substances (Fig. 2.19) depend on the content of free carboxyl groups, that is, on the degree of esterification of carboxyl groups with methanol. The degree of esterification determines the linear charge density of the macromolecule, and, as a result, the strength and method of binding cations.

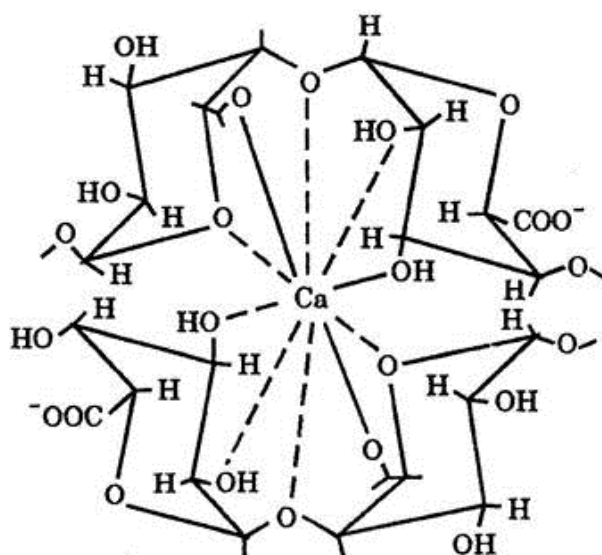


Fig. 2.19. Model of complex formation of pectin "egg lattice"

With a high degree of esterification of pectin (more than 90%), free carboxyl groups, which include C_6 atoms, are significantly distant from each other. At the same time, calcium or strontium salts of pectin acid dissociate almost completely

with a decrease in the degree of esterification, i.e., with an increase in the charge of the macromolecule, the connection of pectin substances with cations increases, and the stability constant of pects increases. At a degree of esterification of 40%, a change in conformation occurs, which leads to the aggregation of pectin macromolecules and the formation of a strong weak bond.

The complex-forming ability does not depend on the molecular weight of pectin and is determined by the cation exchange selectivity coefficient, which is a characteristic of the saturation of pectin substances with a divalent cation. The specified coefficient for Cu^{2+} , Pb^{2+} , Co^{2+} , Sr^{2+} , Ca^{2+} is equal to: 3300, 2580, 241, 120, 121, respectively.

Studies of the sorption capacity of pectic acid have shown that cations are placed in the following order by complexing ability or "activity": $\text{Mn}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Cd}^{2+}$. This sequence is explained by the fact that cations of divalent manganese, copper, cobalt, and nickel, in addition to compounds of the $\text{R}(\text{COO})_2\text{Me}$ type, form compounds of a different type due to interaction (except for carboxyl) with oxy groups of macromolecules or due to the formation of a salt of the type $\text{R}(\text{COO})\text{Me}(\text{OOCCH}_3)$.

The complexing ability of pectin depends on the pH of the environment. At different pH values, pectin substances have different values of complexing ability. The optimal pH value of the environment at which maximum complex formation occurs is individual for each type of pectin and depends on the type of raw material.

The combined effect of pectin and heavy metal salts significantly affects the complex-forming ability. A simultaneous decrease in the concentration of pectin in the solution with an increase in the concentration of a heavy metal in it leads to a significant increase in the binding constant.

Due to its complexing ability with respect to metals, pectin is an indispensable substance in the production of prophylactic and therapeutic nutrition products. The optimal preventive dose of pectin is no more than 2...4 g per day for people who are in contact with heavy metals. For those people who are in conditions of radioactive contamination, a daily rate of pectin of at least 15...16 g is recommended.

Questions for discussion and self-examination

- 1. Technological differences in the processes of swelling, solubility and pasteurization, their practical application.*
- 2. Viscosity of starch pastes, its role in forming the structure of food products.*
- 3. The solubility of starch polysaccharides, the influence of technological factors on it.*
- 4. Enzymatic hydrolysis of starch, practical significance of the process.*

Topic 2.3. Phenolic compounds of food products and food raw materials

2.3.1. Phenolic compounds. Information

Phenolic compounds are the most widespread class of biologically active substances of plant origin. In 1989, Harborne introduced the term "phenols", which unites a group of identified chemical compounds in the molecule of which there is an aromatic ring connected to one or more hydroxyl groups.

Biosynthesis of phenolic compounds in a plant cell occurs in protoplasm, in particular, in chloroplasts. However, the main mass of water-soluble phenols is concentrated in vacuoles, which are limited from the cytoplasm by a protein-lipid membrane – the tonoplast, which regulates the participation of substances contained in vacuoles in cell metabolism.

All phenolic compounds are active metabolites of cellular metabolism and play an important role in various physiological functions of plants, fruits, potatoes and vegetables – respiration, growth, resistance to infectious diseases.

The important biological role of phenolic compounds is evidenced by their distribution in plant tissue. Different organs and tissues of plants, fruits and vegetables differ not only in the quantitative content of phenols, but also in their qualitative composition.

Aromatic rings are not synthesized in the body of humans and animals, but come together with plant food and are included in the composition of many vital phenolic compounds – adrenaline, thyroxine, serotonin, etc.

2.3.2. Classification and nomenclature of phenolic compounds

To date, more than 2,000 phenolic compounds are known, which differ significantly in their properties, which is why it is difficult to classify them.

Today there are several types of classification.

J. B. Harborne and N.W. Simmonds suggests classifying phenolic compounds into groups depending on the number of carbon atoms in the molecule (Table 2.7).

Table 2.7. Classification of phenolic compounds depending on the number of carbon atoms in the molecule

Structure	Compound class
C ₆	Simple phenols
C ₆ – C ₁	Phenolic acids, alcohols and aldehydes
C ₆ – C ₂	Acetophenones and phenylacetic acids
C ₆ – C ₃	Hydroxycinnamic acids, coumarins, chromones
C ₆ – C ₁ – C ₆	Benzophenones, xanthenes
C ₆ – C ₂ – C ₆	Stilbeny
C ₆ – C ₃ – C ₆	Flavonoids
Quinones:	
C ₆ , C ₁₀ , C ₁₄	Benzoquinones, Naphthoquinones, Anthraquinones
C ₃₀	Biflavonoids
(C ₆ – C ₃) ₂	Lignans, neolignans
(C ₆ – C ₃) _n	Polymers (lignin)
Tannins	Oligomers or polymers

Conventionally, phenolic compounds are divided into three main groups:

- Monomeric;
- Dimeric;
- Polymeric.

2.3.3. Monomeric compounds

Monomeric phenolic compounds contain one aromatic ring and are divided into three subgroups.

1. Compounds of the C₆ series consisting of an aromatic ring without carbon side chains. These include phenol, hydroquinone, pyrocatechin and its derivatives, guaiacol, phloroglucin, pyrogallol (Fig. 2.20).

Phenol is an organic compound, which under normal conditions is a white or colorless crystalline substance with a sweet smell, moderately soluble in water. In the presence of impurities or under the influence of light or air, phenol crystals gradually turn pink.

At a temperature from 0 to 65 °C, phenol dissolves in water to a limited extent, and above 65.3 °C it is miscible in any proportions. It dissolves well in alcohols, benzene, chloroform, ethers.

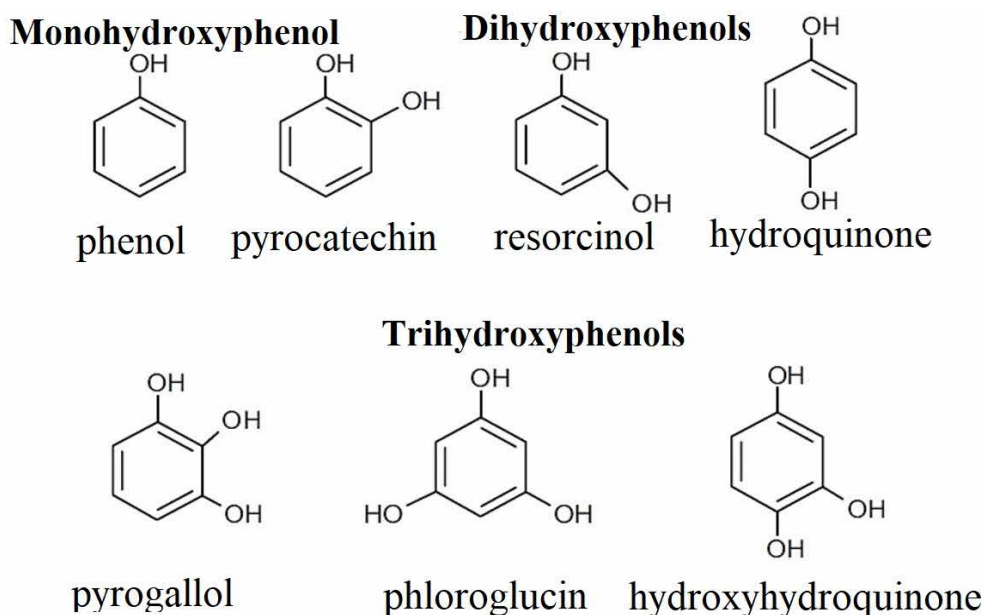


Fig. 2.20. Phenolic compounds of the C₆ series

When phenols are oxidized, quinones (benzoquinones) are formed. They are not found in the free state in plants, but their derivatives are widespread. For example, benzoquinone derivatives are electron carriers of the electron transport chain of photosynthesis and respiration – plastoquinone and ubiquinone (Fig. 2.21).

Pyrocatechin is an organic compound in the form of colorless crystals that darken to brown under the influence of light and air.

Pyrocatechin is found in tea leaves, onion husks, etc.

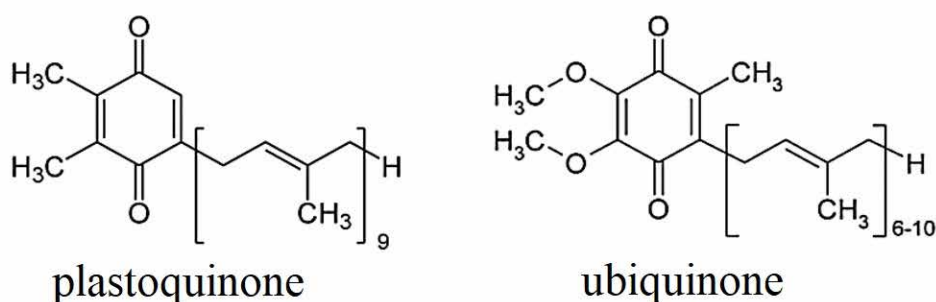


Fig. 2.21. Structural formulas of benzoquinone derivatives

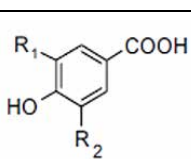
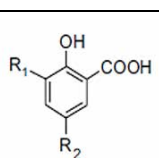
Phloroglucin is found in the peel of onions, in the form of glycosides – in the peel of citrus fruits.

2. Compounds with the basic structure of the C₆-C₁ series, which include a group of phenolic acids and their derivatives – protocatechuic, vanillic, gallic, salicylic, oxybenzoic and other acids (Table 2.8).

Phenolic acids are derivatives of aromatic hydrocarbons, in the molecules of which the hydrogen atoms of the benzene nucleus are replaced by carboxyl (–COOH) and hydroxyl (–OH) groups. They are sometimes considered as aromatic acids, in the molecules of which the hydrogen atom of the benzene nucleus is replaced by hydroxyl groups. Phenolic acids simultaneously have the properties of carboxylic acids and phenols. In addition, they are characterized by properties due to the presence of both types of functional groups and a benzene nucleus in the molecule.

Phenolic acids are solid crystalline substances. Compounds that have one phenolic hydroxyl in their composition are relatively poorly soluble in cold water, but dissolve well in hot water and many organic solvents. As the number of phenolic hydroxyls increases, the solubility of phenolic acids increases.

Table 2.8. Derivatives of benzoic acid

	Acid	R ₁	R ₂
	n-Hydroxybenzoic acid	-H	-H
	Protocatechuic acid	-OH	-H
	Gallic acid	-OH	-OH
	Vanillic acid	-OCH ₃	-H
	Lilac acid	-OCH ₃	-OCH ₃
	Salicylic acid	-H	-H
	Gentisic acid	-H	-OH
	o-Pyrocatechuic acid	-OH	-H

2-Oxybenzoic acid or **salicylic acid** is a typical phenolic acid, sometimes called oxybenzoic acid.

Salicylic acid is widely used in the food industry, in canning, as a reagent for colorimetric determination in solutions of ferrum and copper, as an acid-base

indicator in luminescence analysis (at pH=2.5...4.6 and in the presence of acid with blue luminescence appears), etc.

Salicylic acid is well soluble in ethanol, diethyl ether and other polar organic solvents, poorly soluble in water.

In nature, this acid is found in plants – mainly in the form of a methyl ether glycoside (in particular, salicylic acid was first isolated from the bark of the *Salix* L. willow, where the name comes from), and free salicylic acid, together with salicylic aldehyde, is contained in small amounts in the ether oil secreted from the flowers of some types of spirea.

3,4,5-Trioxybenzoic or **gallic acid** is a phenolic acid containing one carboxyl (--COOH) and three hydroxyl (--OH) groups in its molecule.

Gallic acid forms a crystal hydrate with a water molecule – colorless crystals that darken in the light. It is well soluble in boiling water, alcohol, worse in ether, poorly in cold water; has an astringent taste.

Gallic acid is also found in the following plants: badan, wine grapes (seeds), common walnut, blackberry, golden root, Indian gooseberry (fruit), mango (peel, leaves), raspberry.

It has anti-inflammatory, antimicrobial, antiviral properties and is an antioxidant.

Lilac acid is a 3,5-dimethyl ester of gallic acid. It is a gray-beige or pale brown powder, slightly soluble in water and chloroform, but well soluble in ethanol and diethyl ether (Fig. 2.22).

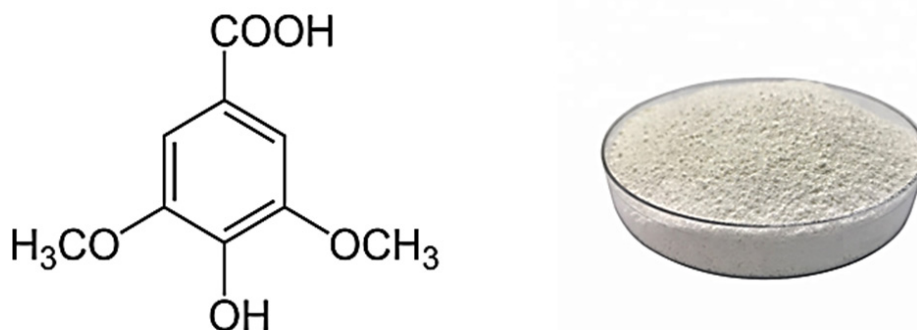


Fig. 2.22. Lilac acid

Lilic acid is found in various parts of many plants, including grapes, plums, pears, various citrus fruits, as well as mushrooms and baker's yeast.

Oxybenzoic acids are widely distributed in plants. They are usually present in them in a bound state and are released during hydrolysis. Vanillic and lilac acids in the form of esters are part of minin.

Derivatives of phenolic acids – aldehydes and alcohols – were found in plants. Especially famous vanillin is vanillic aldehyde. It has a very pleasant smell and is found in the fruits and branches of the vanilla tree in the form of a glycoside – glucovanillin. Glycoside and vanillin itself are widely used in the confectionery industry.

Phenolic acids can be connected by ester bonds with sugars, more often with glucose. Glycogalin was isolated from a number of plants (rhubarb, eucalyptus), in which the carboxyl group of gallic acid is linked to the glycosidic hydroxyl of glucose.

3. Compounds with the basic structure of the C₆–C₃ series, consisting of an aromatic ring and a three-carbon side chain; are divided into cinnamic acids, coumarins and derivatives of the latter: isocoumarins, furocoumarins (Fig. 2.23).

Hydroxycinnamic acids are widespread in plants. Usually they are in a bound state, and in a free state, except for coffee, they are rarely found.

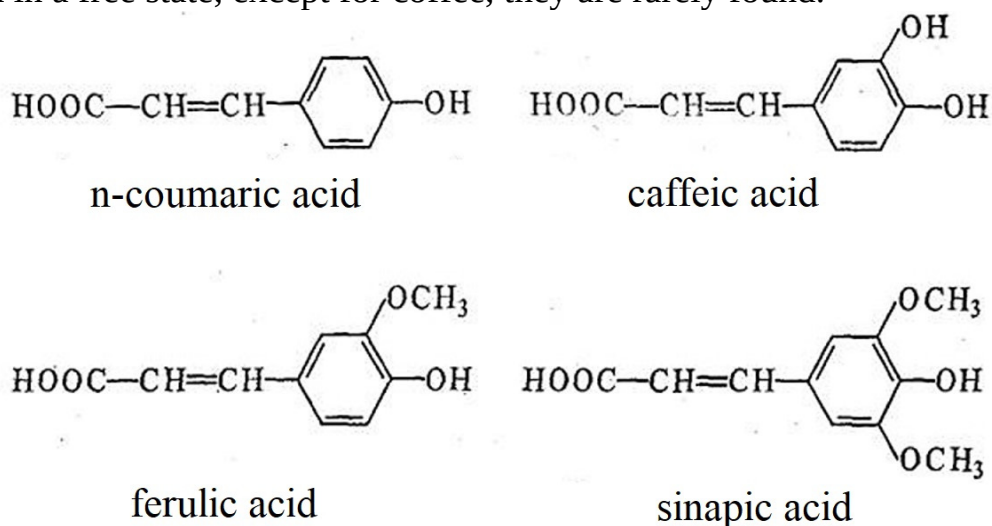


Fig. 2.23. Phenolic compounds of the C₆–C₃ series

Hydroxycinnamic acids are characterized by cis-trans isomerism. In the solution, an equilibrium is established between the trans and cis forms. Ultraviolet shifts this equilibrium towards the formation of cis-forms.

Cis-isomers of hydroxycinnamic acids are activators of plant growth processes, and trans-isomers do not have such properties.

In the biogenesis of hydroxycinnamic acid, the main precursor is the amino acid phenylalanine, from which cinnamic acid is synthesized through deamination with the participation of the enzyme phenylalanine deaminase in the plant, and through hydroxylation and methylation, some hydroxy and methyl derivatives are formed.

Two stereoisomers of o-hydroxycinnamic acid are known: one has a trans-configuration and is called coumaric acid, the other has a cis-configuration and is called **coumaric acid** (Fig. 2.24). Only coumaric acid can exist in a free state, for example in various types of aloe. Coumaric acid is cyclized into coumarin lactone, found in many plants.

Caffeic acid (3,4-dihydroxycinnamic acid), which is very common in nature, often forms dimers (pseudodepsides). For example, chlorogenic acid is a pseudodepside of caffeic and quinic acids.

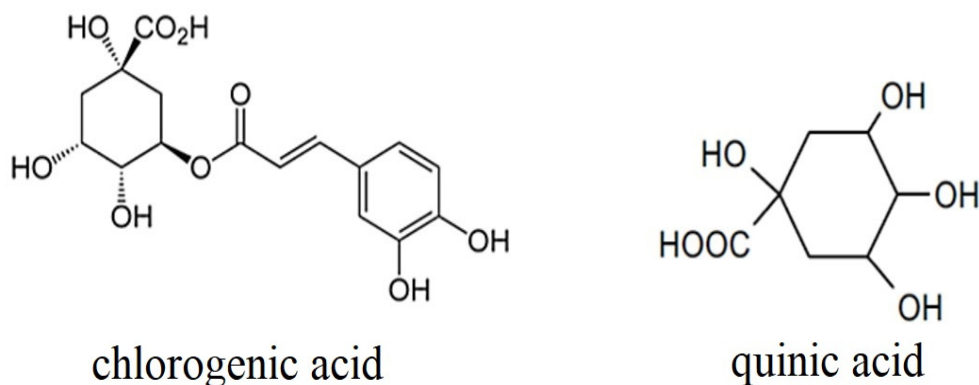


Fig. 2.24. Stereoisomers of o-hydroxycinnamic acid

Of the tripeptides of caffeic acid, isochlorogenic acid and cynarin should be noted.

Caffeic acid is present in almost all plants, as it is an intermediate product of lignin biosynthesis. It is one of the main hydroxycinnamic acids present in wine.

Caffeic acid has weak bacteriostatic properties, exhibits anti-inflammatory, hepatoprotective and immunotropic effects. Methyl esters of caffeic acid – ferulic and sinapic acids – are found in higher plants.

The complex ester of caffeic and quinic acids is chlorogenic acid, which is widely present in plants, especially in sunflower seeds and coffee beans.

It is the presence of chlorogenic acid in sunflower seeds that determines the acquisition of a dark color by proteins obtained from defatted seeds and added to bakery products to increase biological value.

Chlorogenic acid is an important intermediate compound in the biosynthesis of phenols. It is widely distributed in the plant world, in particular found in apples, pears, eggplants, artichokes, etc.

The total content of caffeic and chlorogenic acids in coffee beans is up to 6%.

Daily consumption of coffee provides 0.5...1 g of chlorogenic acid to the human body. At the same time, increased concentrations of homocysteine (cytotoxic effect) can be observed in the body, which is probably due to the high content of chlorogenic acid.

Numerous studies of the mechanisms of action of caffeic acid at the cellular, tissue, and whole organism levels have proven that under in vitro conditions, caffeic and chlorogenic acids are highly effective antioxidants.

Ferulic acid occurs in plants in a free state and in the composition of esters; has choleric, antimicrobial, antimycosis, hepatoprotective effect, inhibits erythrocyte aggregation. Widespread in the Umbrella family.

Of the **alicyclic acids**, henna and **shikimic acid** sometimes accumulate in plants in significant quantities.

Shikimic acid was first isolated from star anise fruits. It plays an important role in the biosynthesis of aromatic amino acids, cinnamic acids, flavonoids and other phenolic compounds.

Hydroxycinnamic alcohols are found in plants – derivatives of the corresponding acids: coumaric – coumaric alcohol, ferulic – coniferyl, sinapic – sinapic. Alcohols usually do not accumulate, but, apparently, are used in the formation of lignin, of which they are monomers.

Hydroxycinnamic acids can form esters with organic acids of the aliphatic series. Thus, caffeic acid forms esters with malic and tartaric acids. The first ester is called phaseolinic acid, which is present in bean leaves. The second is cicoric acid. It is found in chicory leaves.

Esters of hydroxycinnamic acids and sugars, more often glucose, are common in plants. Hydroxycinnamic acids are part of polysaccharides and proteins. For example, ferulic acid is found in the xylans of wheat flour and in the polysaccharides of pineapples.

Coumarins are lactones formed when the cycle is closed between the hydroxyl and carboxyl groups in the hydroxycinnamic acid molecule. At the same time, the side chain of the acid should be in the cis-form, and the hydroxyl should be in the ortho-position.

Coumarin is a colorless crystalline substance with a pleasant smell of freshly cut hay. In the free state, coumarin is not found in plants. It is usually contained in the form of glycosides (flowers and leaves of burkun). In herbaceous plants, there is a glycoside in the cell sap that contains ortho-coumaric acid. During wilting, plant tissues are damaged, the permeability of membranes is disturbed. Glycosides from cell juice come into contact with cytoplasmic enzymes. Sugars are cleaved from glycosides, and coumaric acid after trans-cis isomerization forms lactone-coumarin. At the same time, the withering grass acquires the smell of hay.

Hydroxylated coumarins are often found in plants as part of glycosides. For example, esculetin from the fruit of the horse chestnut and scopoletin from the roots of Japanese scopolia (Fig. 2.25). Both of these coumarins have P-vitamin activity and are used in medicine as agents that strengthen capillary walls.

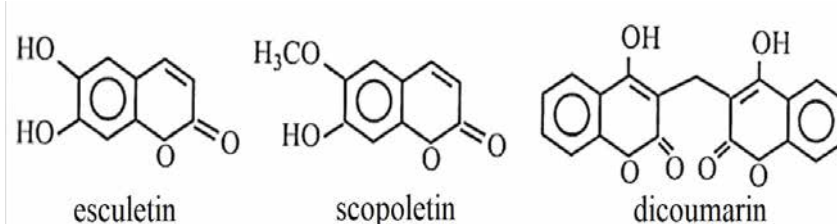


Fig. 2.25. Structural formulas of hydroxylated coumarins

Dicoumarin, which prevents blood clotting, was found in the white burdock root. This and other dicoumarins are used as drugs that prevent the formation of blood clots.

2.3.4. Dimeric compounds

Dimeric phenolic compounds include flavonoids and isoflavonoids.

Flavonoids are biologically active substances based on a diphenylpropane fragment with the general formula $C_6-C_3-C_6$. The name comes from the Latin word flavus - yellow, because the first isolated flavonoids had a yellow color.

The flavonoid molecule consists of two phenolic residues (rings A and B) connected by a propane link (Fig. 2.26), so they can be considered as derivatives of phenylpropanoids.

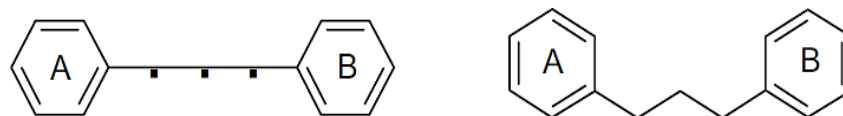


Fig. 2.26. Flavonoid molecule

Examples of the most common flavonoids contained in food products are given in the Table 2.9

Table 29. Plant sources of flavonoids

Class of flavonoids	Name	Substitutes	Natural source
Flavone	Apigenin routine Tangeretin	5,7 – OH 5,7,3',4'-OH, 3-O- rutinosis 5,6,7,8,4'-OCH ₃	parsley, celery buckwheat, citrus fruits citrus fruits
Flavanone	Naringin Naringenin	5,4'-OH 5,7,4'-OH	citrus fruits orange peel
Flavonol	Kaempferol Quercetin	3,5,7,4'-OH 3,5,7,3',4'-OH	broccoli, tea onions, broccoli, apples, berries
Flavanonol	Taxifolin Genistein	3,5,7,3',4'-OH 5,7,4'-OH	fruits soybeans
Isoflavone	Daidzein Puerarin (-)-Epicatechin	4'-OH, 7-O-glucose 7,4'-OH, 8-C- glucose 3,5,7,3',4'- OH	soybeans kudzu tea
Catechin	(-)-Epigallocatechin (-)-Epigallocatechin gallate	3,5,7,3',4',5'- OH 5,7,3',4',5'-OH, 3- gallat	tea
Anthocyanidin	Cyanidine Delphinidin	3,5,7,3',4'- OH 3,5,7,3',4',5'- OH	cherries, strawberries dark fruits

Flavonoids have different positions of phenolic radicals in the propane fragment. According to this feature, they are divided into three main groups:

- euflavonoids;
- isoflavonoids;
- neoflavonoids.

Group I – euflavonoids, or flavonoids, or true flavonoids, in which ring B is attached to the C-3 position of the propane chain (Fig. 2.27).

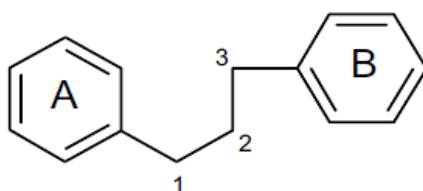
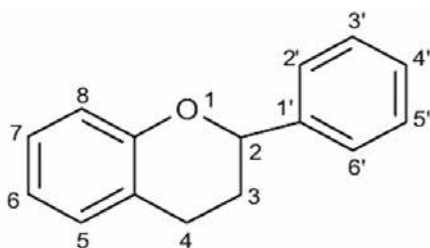
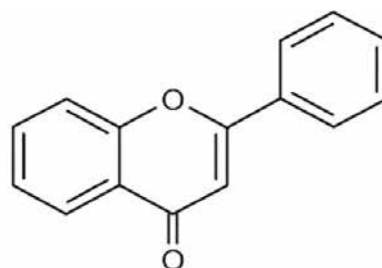


Fig. 2.27. Structural formulas of euflavonoids

If a pyran heterocycle condenses with the A ring, a flavan (phenylbenzopyran) is formed. The oxidized flavan contains γ -pyrone molecules (Fig. 2.28).



flavan

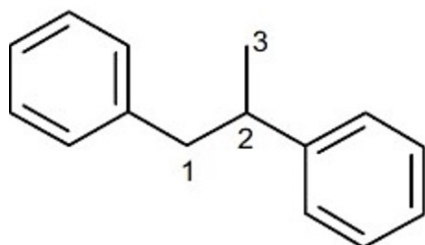


flavone

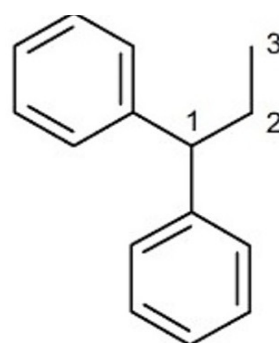
Fig. 2.28. Structural formulas of euflavonoids

Group 2 – isoflavonoids, ring B is attached to the second carbon atom of the propane fragment.

Group 3 – neoflavonoids, containing ring B in the C-1 position of the propane chain (Fig. 2.29).



isoflavonoids



neoflavonoids

Fig. 2.29. Structural formulas of groups of dimeric compounds

Classification of euflavonoids

According to the degree of oxidation of the propane fragment and the size of the heterocycle, euflavonoids can be divided into 10 classes (Fig. 2.30).

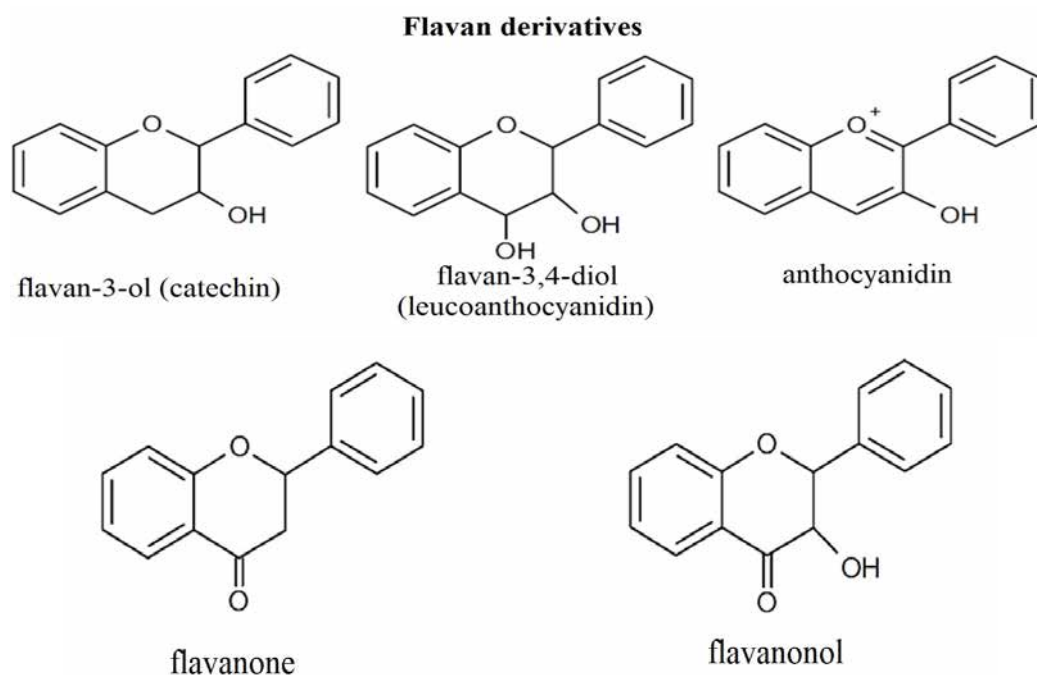


Fig. 2.30. Classes of euflavonoids

Catechins are colorless crystalline substances. Unlike most other flavonoids, they do not form glucosides. They are characterized by acylation of the hydroxyl group (formation of halo ethers at the C₃ atom).

Catechins are the most abundant flavonoids identified in more than 200 plant species. There are about 18 of their isomers.

The general concept comes from the word "catechu". This word is used to refer to the extract of acacia trees, which is widely used as a food additive, binder, tannin and dye. It is extracted from several species of acacia, but especially from the *Senegalia catechu* tree by boiling the wood in water and evaporating the resulting extract.

The leader in the content of catechins are tea leaves and shoots (up to 30% by weight of dry matter), in which epicatechin (EC), epicatechin-3-gallate (ECG), epigallocatechin (ECG), epigallocatechin-3-gallate (ECG) are found), catechin and galocatechin (GK). The largest content (65% of the total content) consists of ECG. So, a glass of green tea contains 100-200 mg of ECG. Other catechins are present in small amounts. Black and oolong tea contain less catechins than green tea, which is due to the special treatment of tea leaves after harvesting.

Catechins are found in large quantities in many fruits and berries (apples, quinces, apricots, peaches, plums, cherries, strawberries, currants, raspberries, horseradish, etc.). They are also found in dark chocolate.

Tannin is the general name of isomers of one of the catechins, which is present in white, yellow and green tea in a higher concentration than in black, which is associated with oxidation processes during the fermentation of black tea.

Oxidative transformations of catechins play an important role in the production of cocoa, tea, and wine. This is due to the fact that the oxidation products of catechins

have a characteristic pleasant, slightly astringent taste and color. Catechins have the highest vitamin activity compared to all other groups of flavonoid compounds.

Catechins are well soluble in water, have a weak astringent taste, are easily oxidized in the light, when heated, especially in an alkaline environment (Fig. 2.31) under the action of oxidizing enzymes (phenoloxidase and peroxidase).

Catechins have high biological activity. They destroy free radicals, thereby preventing the aging of the body and contributing to the prevention of cancer. They are also able to absorb cholesterol, reducing the risk of atherosclerosis, thrombosis, heart attacks and strokes.

Catechins contribute to the prevention of diabetes, as they help the body regulate blood sugar levels. They regulate the permeability of capillaries and increase the elasticity of their walls, and also help the body use ascorbic acid (vitamin C) more efficiently. Therefore, catechins are used in the treatment of diseases associated with capillary dysfunction, edema of vascular origin, etc.

Catechins are able to bind metals such as lead, chromium, tin, cadmium and remove them from the body.

Being strong antioxidants, catechins help speed up metabolism and increase energy expenditure, as well as prevent the absorption of fats by the body.

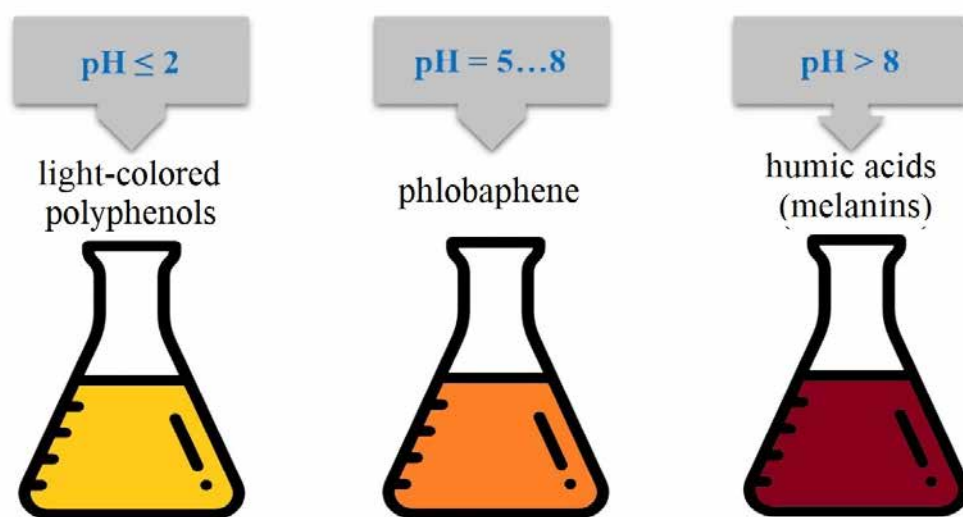


Fig. 2.31. Dependence of the color of catechin solutions from the pH of the medium

Leucoanthocyanins are products of further oxidation of catechins. They are found in fruits and vegetables together with catechins, but their content is much higher. According to scientists, it is leucoanthocyanins that are responsible for the unwanted color change of fruits during the canning process (Fig. 2.32).

Like catechins, leucoanthocyanins are easily oxidized and form polymerization products in the form of condensed tannins.

Leucoanthocyanins change color depending on temperature. So, at 135 °C they are yellow, at 165 °C – wine-red, above 225 °C – blue-gray, at 260 °C – black. When heated, they turn into leucoanthocyanidins.

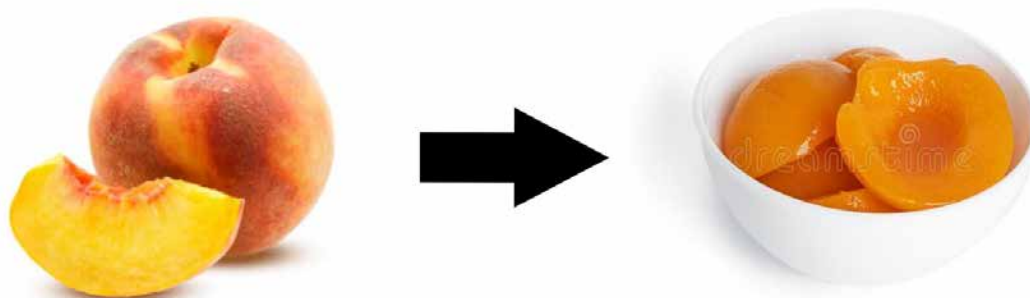


Fig. 2.32. Changes in food products during canning under the influence of leucoanthocyanins

Leukoanthocyanidins are compounds structurally similar to catechins, often accompany them and are derivatives of flavan-3,4-diol. They contain three asymmetric carbon atoms (C_2 , C_3 and C_4) and, therefore, each of the leucoanthocyanidins can be represented by 8 isomers and 4 racemates.

Leukoanthocyanidins are labile compounds that are easily oxidized to the corresponding anthocyanidins when heated with acids. This reaction is used to detect leucoanthocyanidins in plants. Like catechins, they exist in the free (not bound to sugars) state, but unlike them, they do not form galloyl esters.

The following compounds are best known in nature: leucocyanidin ($R = OH$, $R_1 = H$), leucopelargonidin ($R = R_1 = H$) and leucodelphinidin ($R = R_1 = OH$). Leukoanthocyanidins are very widespread in plants. They are usually accompanied by oligo- and polymeric forms, which also complicates their isolation and identification. Leukoanthocyanidins, like catechins, reduce the permeability of capillary walls (P-vitamin action).

Leukoanthocyanidins play an important role in the formation of the color of white table wines (brown).

Anthocyanins (from the Greek "anthos" (flower) and "cyanos" (azure, blue)) are the most important plant pigments (Fig. 2.33, Table 10).

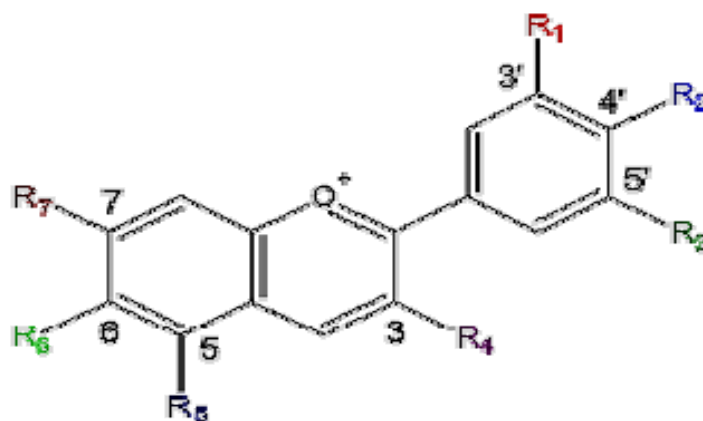


Fig. 2.33. Structure of anthocyanins

Table 2.10. Structure of anthocyanins

Aglycones	Substitutes in clauses						
	R ₁	R ₂	R ₃	R ₄	R ₅	R ₆	R ₇
Aurantidin	-H	-OH	-H	-OH	-OH	-OH	-OH
Cyanidin	-OH	-OH	-H	-OH	-OH	-H	-OH
Delphinidin	-OH	-OH	-OH	-OH	-OH	-H	-OH
Europinidin	-OCH ₃	-OH	-OH	-OH	-OCH ₃	-H	-OH
Luteolinidin	-OH	-OH	-H	-H	-OH	-H	-OH
Pelargonidin	-H	-OH	-H	-OH	-OH	-H	-OH
Malvidin	-OCH ₃	-OH	-OCH ₃	-OH	-OH	-H	-OH
Peonidin	-OCH ₃	-OH	-H	-OH	-OH	-H	-OH
Petunidin	-OH	-OH	-OCH ₃	-OH	-OH	-H	-OH
Rosinidin	-OCH ₃	-OH	-H	-OH	-OH	-H	-OCH ₃

Anthocyanins color flower petals, fruits, and sometimes leaves in blue, blue, pink, red, purple colors with various shades and transitions. They are also called plant chameleons. All anthocyanins are present in plants in the form of glycosides. During hydrolysis, anthocyanins are broken down into glucose and a colored aglycon called **anthocyanidin**. Anthocyanins dissolve in water and are contained in cell juice.

Enin, keracyanin, and betanin are representatives of anthocyanins.

Enin is contained in the juice of red grapes. During hydrolysis, it breaks down into glucose and the anthocyanidin malvidin (Fig. 2.34). Enin is a red food dye obtained from waste from the primary stages of winemaking and juice production (grape pomace). It is used in the confectionery industry, in liquor production, and also for coloring soft drinks.

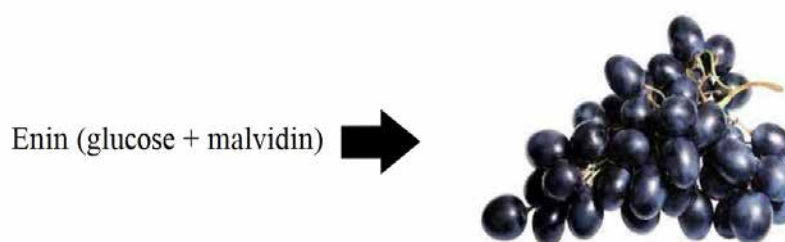


Fig. 2.34. Enin as a representative of anthocyanins

Keratanin is found in cherries. It contains glucose, rhamnose and cyanidin, which is also an aglycon of anthocyanins of black currants, raspberries, lingonberries, and plums (Fig. 2.35).

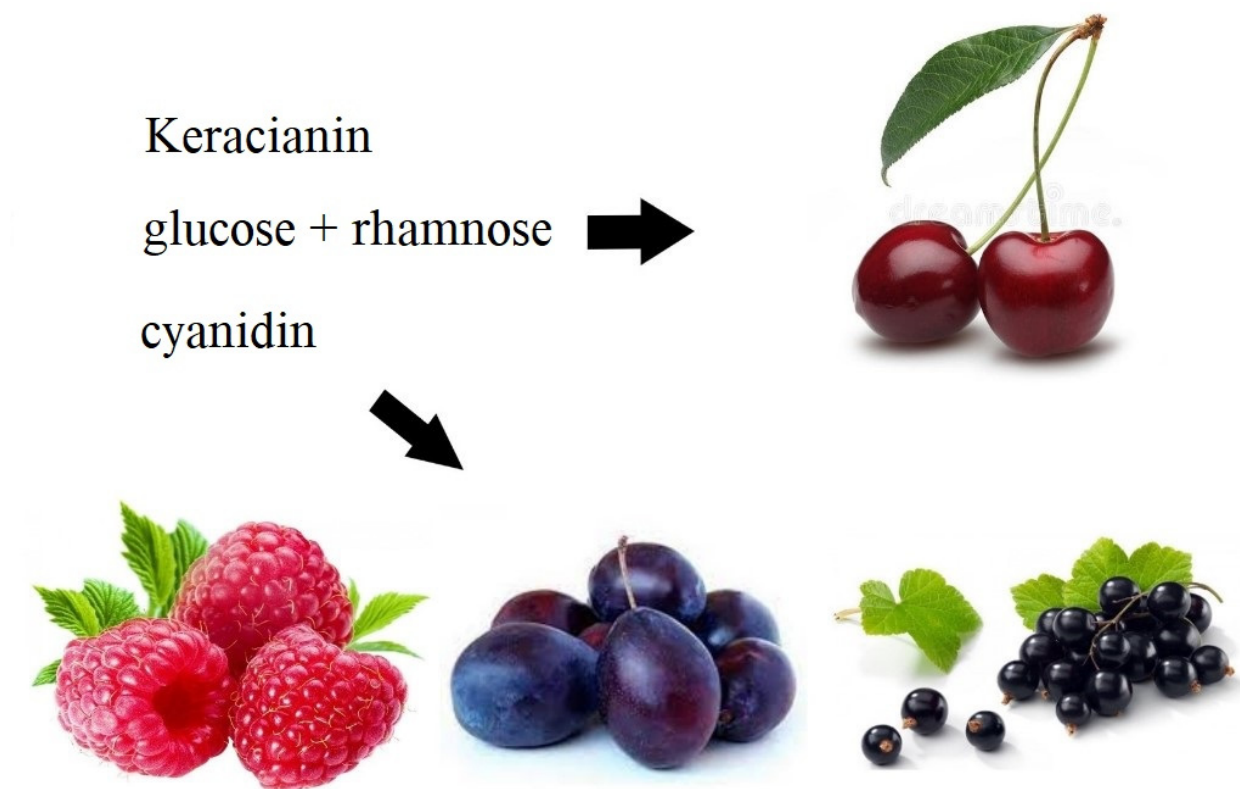


Fig. 2.35. Keracianin as a representative of anthocyanins

Betanin is found in beet roots. It consists of glucose and nitrogen-containing aglycon betacyanin (Fig. 2.36).

Betanin prevents the formation and growth of cancer cells, promotes the assimilation of proteins, improves fat metabolism, and prevents the development of atherosclerosis.

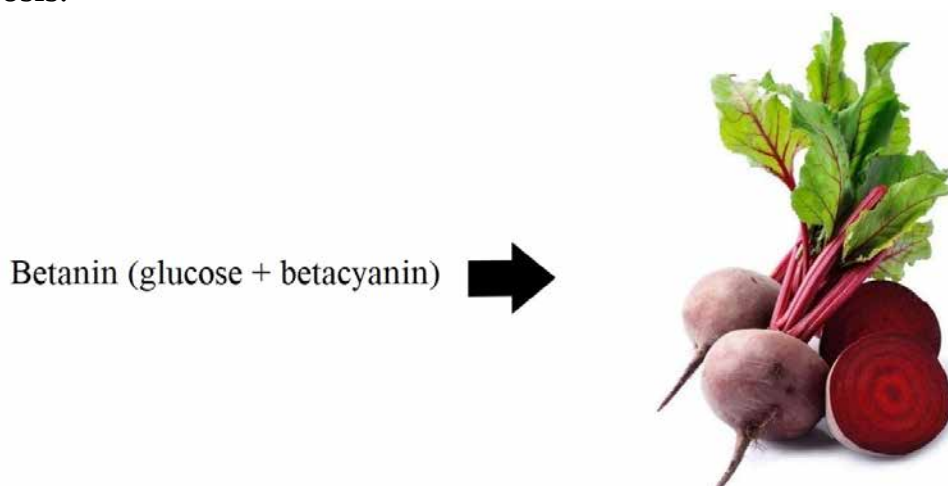


Fig. 2.36. Betanin as a representative of anthocyanins

A feature of the structure of anthocyanidins is the presence of tetravalent oxygen (oxonium) and free positive valence in the heterocyclic ring.

Nowadays, more than 20 anthocyanidins are known, among which four are the most common: pelargonidin, cyanidin, delphinidin and malvidin (a methylated derivative of delphinidin).

Anthocyanidins are more often glycosylated near C-3, less often in other positions. If glycosides are formed by joining two sugars, then this happens near C-3 and C-5.

Glucose, galactose, rhamnose, xylose, rarely arabinose are found as monosaccharides in anthocyanins, and rutinose, sophorose, and sambubiose are most often found as disaccharides. Sometimes anthocyanins contain branched trisaccharides.

What color anthocyanins will color the plant depends on many factors. First of all, the color is determined by the structure and concentration of anthocyanins (increases under conditions of stress). The concentration of anthocyanins in cell juice can vary in a wide range – from 0.01 to 15%. For example, common blue corn contains 0.05% of the anthocyanin cyanine, and dark purple corn contains 13-14%, and the same applies to other plants.

The pH of the cell juice is also an important factor affecting the color of anthocyanins. This is due to the fact that anthocyanin molecules have a free valency. Usually, in an acidic environment, anthocyanins have a red color of various intensity and shades, and in an alkaline environment, they are blue.

Such changes in the color of anthocyanins can be observed by adding acid or alkali to the colored juice of currants, cherries, table beets or red cabbage. In nature, sharp changes in the pH of cell juice do not occur, so this factor does not play a major role in the coloring of anthocyanins. But you can notice that some pink and red flowers turn blue when they fade, which indicates a change in pH in the dying cells.

The red cabbage epidermis cells contain rubrobrasil chloride pigment. In some intensively colored cells, its content is so high that at low temperatures, the pigment is released in the form of crystals.

At a medium pH value of 2.4...4, cabbage has a purple color, 4...6 – purple, 6...7 – blue, 7...8 – green.

However, the pH in the vacuoles can vary from 4 to 6 and, therefore, the appearance of a blue color in most cases cannot be explained by the influence of the pH of the medium. Thus, the ability of anthocyanins to chelate with metal ions is of great importance in the coloring of flowers and fruits.

Complexes of anthocyanins with aluminum, iron, magnesium, molybdenum, tungsten ions, stabilized by co-pigments (mainly flavones and flavonols), are called metalloanthocyanins (Fig. 2.37).

Flavanones are compounds with an unstable dihydro- γ -pyrone ring, which is easily opened under the action of acids and alkalis, resulting in the formation of chalcones. They are optically active substances with an asymmetric C₂ carbon atom, so they have two optical isomers and a racemate. In plants, they are usually found in the form of left-rotating forms.

Flavanonols are also unstable compounds, which is why they do not accumulate in significant quantities in plants, being reduced to leucoanthocyanidins, contain two asymmetric carbon atoms (C₂ and C₃), therefore occur in the form of four isomers and two racemates. They exist, as a rule, in the form of aglycones. Flavanones and flavanonols are colorless phenolic compounds. They are rich in citrus fruits, which contain naringenin, hesperidin and eridictol.

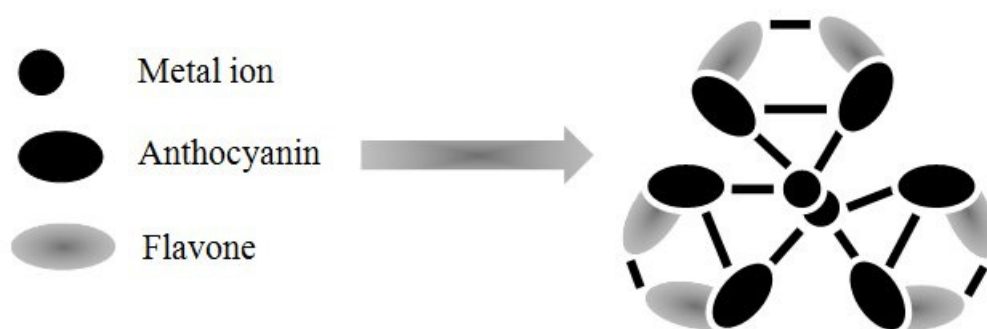
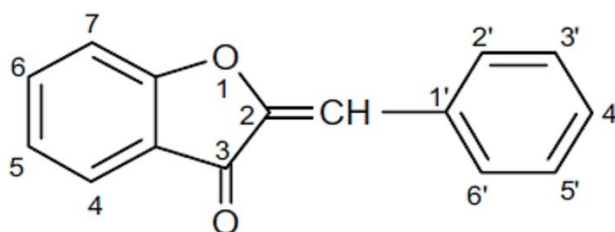


Fig.2.37. Scheme of formation of metalloanthocyanin from six molecules of anthocyanin, flavone and two metal ions (a). Spatial structure of isolated protocyanin from cornflower petals (b)

Flavones are the most widespread group of flavonoids, which includes both unsubstituted and substituted compounds, as well as condensed systems (for example, hepatoprotective flavolignans). These are pigments that have a yellow color and are found in many fruits and vegetables. Flavones are precursors of anthocyanins.

Flavonols belong to a large group of compounds, and in 50% of them aglycones are represented by kaempferol and quercetin. Their diversity is due to the presence of methoxy- (1–8 methoxyl groups), mono-, dimethyldioxy- and glycosylated derivatives. Flavones and flavonols are present in the form of both O- and C-glycosides. Flavonols differ from flavones by the presence of a hydroxyl group, and they also have strong bactericidal properties. Most often, fruits and vegetables contain quercetin, kaempferol, rutin and myricetin from flavonols. Quercetin is the most common flavonol, which gives the peel of onions and sea buckthorn a golden color.

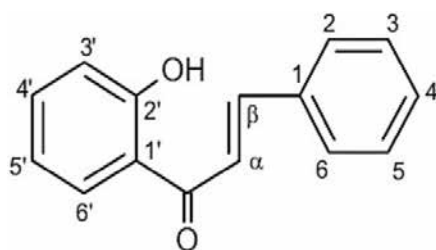
Class of aurones that have a five-membered heterocycle can be seen as derivatives of 2-benzylidenecoumarone.



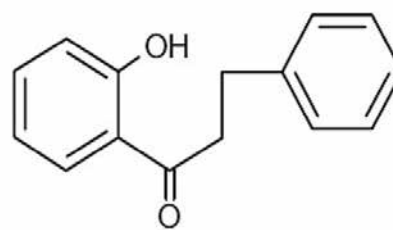
Auron

Aurones are bright yellow compounds that can be formed from the corresponding chalcones under the action of the plant enzyme chalconase. These compounds are most often found in the form of 6,3',4'-trihydroxy-, 4,6,3',4'- and 6,7,3',4'-tetrahydroxy derivatives with a carbohydrate substituent at C₆, and the majority belong to O-glycosides.

Flavonoids with an open propane fragment are called chalcones and dihydrochalcones.



Halkon



Dihydrochalcone

Chalcones exist in plants in the form of aglycones and glycosides and differ in the number of substituents in ring B. Usually 5,7-dihydroxy-substituted, 5,6,7- and 5,7,8-hydroxy- and/or methoxy-derivatives are found. Chalcones are characterized by ease of isomerization reactions into dihydrochalcones and flavanones.

Dihydrochalcones are relatively rare in plants, they exist in the form of aglycones, glycosides, methoxy and pyran derivatives. In an acidic environment, chalcones and dihydrochalcones are transformed into flavanones.

Classification of isoflavonoids

The classification of isoflavonoids is based on the degree of oxidation of the propane fragment and the nature of the heterocycle. Isoflavonoids are divided into simple and condensed. Simple isoflavonoids include isoflavans, isoflavanones, isoflavones, isochalcones; to condensed ones – coumestans, pterocarpanes, rotenoids, etc.

Classification of neoflavonoids

Among neoflavonoids there are subclasses of flavan, flavone, and chalcone. As a result of substitution of C-4 position instead of γ -pyrone in the group there are compounds with an α -pyrone heterocycle (Fig. 2.38).

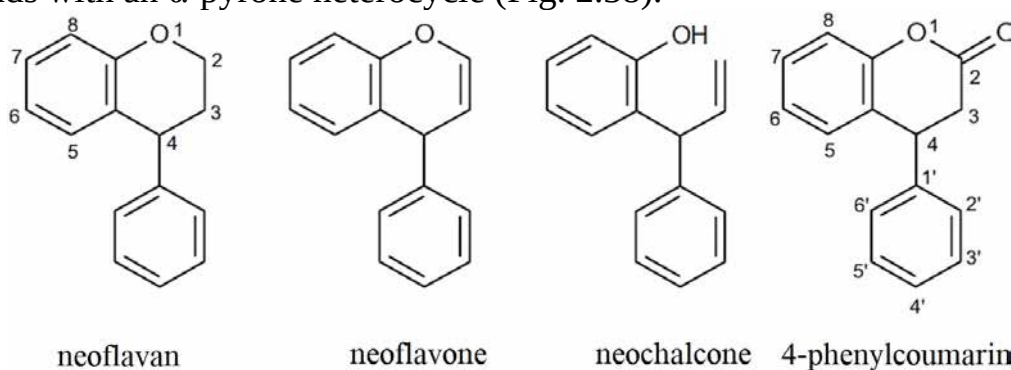


Fig. 2.38. Structural formulas of neoflavonoids

Flavonoids contain reactive phenolic radicals and a carbonyl group in the molecule. Thanks to this, they participate in various metabolic processes, which determines their biological activity.

All natural flavonoids are low-toxic, they exhibit a wide range of physiological effects on the human body: they participate in redox processes, immune reactions, cause anti-inflammatory, sensitizing, antitumor, radioprotective effects. Most flavonoids, especially catechins, have a high level of antioxidant activity.

2.3.5. Polymer compounds

Polymeric phenolic compounds include tannins (tannins), lignins, melanins, and humic acids.

Tannins are polymeric phenolic compounds that accumulate in the bark and wood of oak, eucalyptus, chestnut, sorrel rhizomes, many fruits (quince, apples, persimmons, grapes), tea leaves, etc.

Tannins can cause poisoning, but their bitter taste prevents herbivores from eating plants with high tannin content.

Natural tannins, as a rule, are poorly identified, they are a complex mixture of closely related compounds with a molecular weight of 500-5000, sometimes up to 20000. Most tannins are polyphenolic compounds with protein-binding properties, which is not characteristic of most polyphenols. The formation of tannin-protein complexes is associated with changes in the pH of the environment. In cells, tannins are localized in vacuoles in a dissolved state. When the tonoplast is damaged, tannins are oxidized under the action of cytoplasmic enzymes and turn into insoluble phlobafens – brownish-red amorphous compounds.

According to their structure, tannins are classified into two groups: **hydrolyzed** and **condensed** (proanthocyanidins).

Hydrolyzed (halotannins, ellagotannins) - decompose under the conditions of acid or enzymatic hydrolysis. Halotannins and ellagotannins are complex esters of gallic and ellagic acid and glucose.

Condensed tannins do not disintegrate under the action of acids, but form water-insoluble polymerization products of catechins, leucoanthocyanids and other reduced forms of flavonoids. Depolymerization products of condensed tannins are mainly cyanidin or delphinidin, which is why they can be classified as procyanidins or prodelphinidins.

Tannins participate in oxidation-reduction reactions, are oxygen carriers in plants. The ability to easily give up electrons and protons makes them active neutralizers of free radicals. Tanning substances prevent the development of uncontrolled self-oxidation of lipids and the accumulation of toxic lipid peroxides and epoxides.

Lignin is found in lignified plant tissues along with cellulose and hemicellulose.

Lignin is not an individual compound with a strictly defined composition. It encrusts cellulose fibrils and thereby participates in the creation of supporting elements of plant tissues. The nature of the relationship between lignin and the carbon components of wood has not yet been established.

By its chemical nature, lignin is a three-dimensional polymer of phenolic nature. During the oxidation of nitrobenzene in an alkaline environment, lignin is split with the formation of aromatic aldehydes: vanillin, lilac aldehyde and n-oxybenzaldehyde.

Melanins are phenolic polymers, the structure of which has not been fully elucidated. They are painted black or brown-black.

2.3.6. Chemical and biotechnological properties of phenolic compounds

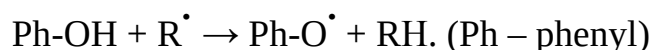
The chemical properties of phenolic compounds are largely determined by the presence of benzene rings, hydroxyl groups, and carbon side radicals in the molecule. Among the most important chemical properties: **ether formation, oxidation, polymerization, condensation.**

One of the most important functions of these substances is participation in redox processes.

Derivatives of phenolic compounds in the form of ubiquinones are hydrogen (electron) carriers in the normal respiratory chain localized in mitochondria. They are embedded in it in the area between flavoproteins and the cytochrome system.

The antioxidant activity of flavonoids (as polyatomic phenols of plant origin) consists in the rapid capture of the unpaired electron of radicals that are formed in the processes of lipid oxidation of cell membranes (more precisely, the unsaturated higher carboxylic acids that are part of them). The formed new radical of the phenoxyl type has little activity in the further transfer of radicals along the chain (break of the chain).

This is due to its delocalization in the molecule and steric shielding. Stable phenoxyl radicals are formed. In this way, the chain of oxidation and deterioration of fats is interrupted. The flavonoid molecule Ph-OH is a reducing agent (electron donor) in relation to the radical R. and changes to the radical (oxidized) form Ph-O:



The greater the number of OH groups in the flavonoid structure, the higher its ability to oxidize (antioxidant activity). In addition, the presence of a carbonyl group and double bonds affect antioxidant activity. Thus, studies of the antioxidant activity of quercetin showed: first, oxidation of OH groups of ring B occurs (sequential separation of two electrons from each OH group), then oxidation of the hydroxyl group in ring C, and finally oxidation of OH groups of ring A.

Studies of the antioxidant activity of flavonoids are carried out using electrochemistry methods (voltammograms are made, the number of peaks corresponds to the number of active centers). It was shown that the most active in redox reactions are flavonoids, which contain OH groups in the B and C rings, as well as the C₂-C₃ double bond. The transformation of the pyrocatechin group in the B ring (two hydroxyl groups in the ortho position) into a pyrogallol group (three OH groups) leads to an increase in antioxidant activity, and a decrease in the number of OH groups in the B ring to one - to a decrease.

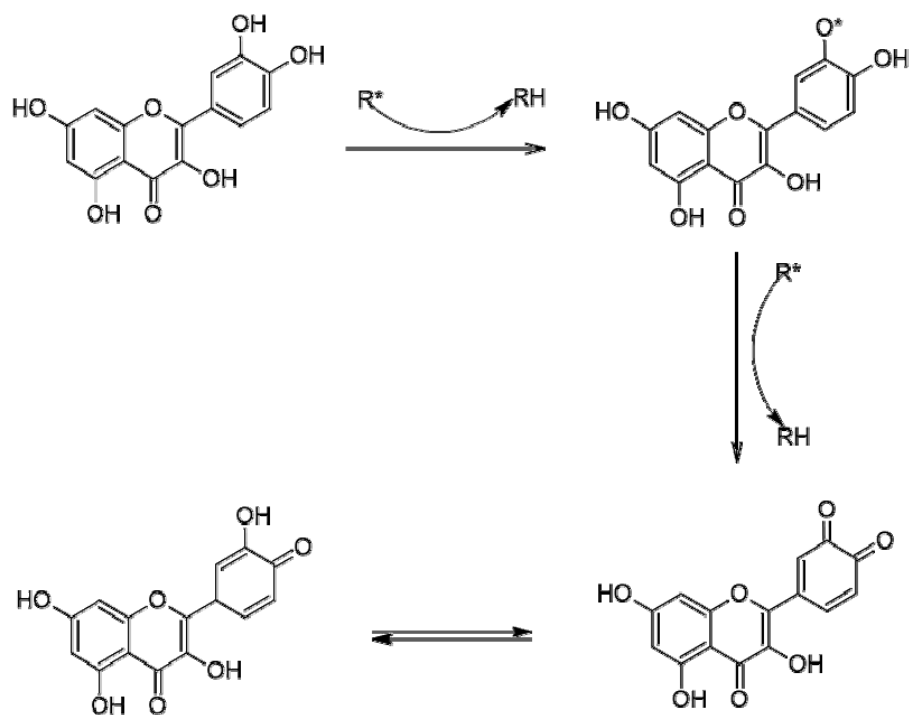


Fig. 2.39. Stabilization of the quercetin radical

Questions for discussion and self-examination

1. Describe phenolic compounds.
2. Name the main classifications of phenolic compounds.
3. Describe the monomeric compounds of the C_6 series.
4. Describe the monomeric compounds of the C_6-C_1 series.
5. Describe the monomeric compounds of the C_6-C_3 series.
6. What are dimeric compounds?
7. Describe flavonoids.
8. Describe the following compounds: catechins, anthocyanins, flavones.
9. To which compounds are tannins classified?
10. Describe the chemical and biological properties of phenolic compounds.

Topic 2.4. Food acids

2.4.1. Food acids. Concept

Food acids are a group of substances of organic and inorganic nature that are diverse in their properties.

The composition and peculiarities of the structure of food acids are different and depend on the specifics of the food object, as well as on the nature of acid formation.

Non-volatile mono- and tricarboxylic acids, saturated and unsaturated, including hydroxy and oxo acids, are found in most plant objects.

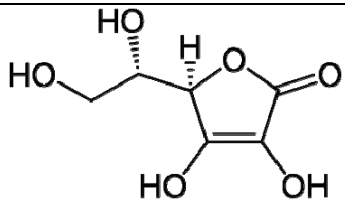
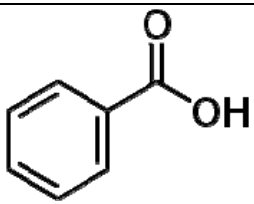
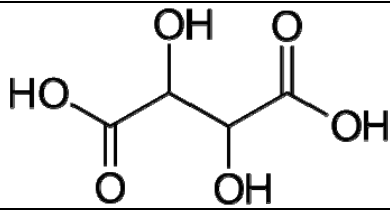
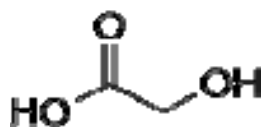
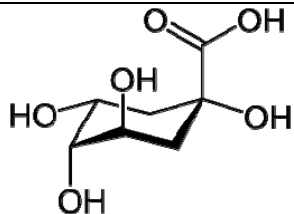
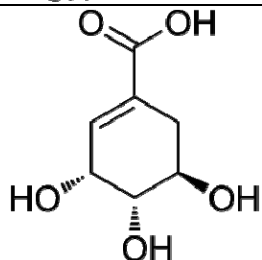
Volatile acids - formic and acetic – can be isolated in the products of fruit processing. The acidity of milk and dairy products is formed both due to lactic acid,

which is formed as a result of biochemical transformations of milk lactose, and due to other acids and acid salts contained in milk, as well as acid groups of casein.

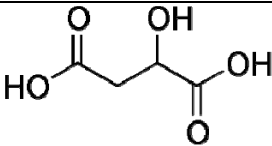
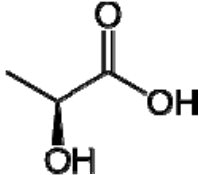
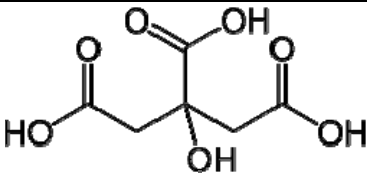
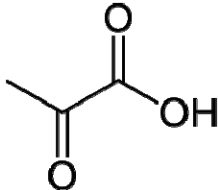
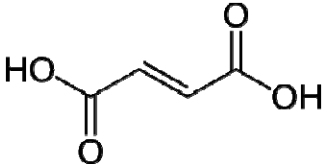
The group of organic food acids also includes amino acids, which are part of proteins, and higher carboxylic acids, which are structural components of lipids.

The names and formulas of some acids, which are most often found in food products, are given in Table 2.11.

Table 2.11. Basic food acids

Acid name (salt name)	Formula
1	2
Ascorbic acid (Ascorbate)	
Aspartic acid (Aspartate)	$\text{HOOC}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{COOH}$
Benzoic acid (Benzoate)	
Tartaric acid (Tartrate)	
Glycolic acid (Glycolate)	
Quinic acid (Quinate)	
Shikimic acid (Shikimate)	

Continuation of Table 2.11

1	2
Malic acid (Malate)	
Succinic acid (Succinate)	$\text{HOOC-CH}_2\text{-CH}_2\text{-COOH}$
Glyceric acid (Glycerate)	$\text{CH}_2\text{OHCHOHCOOH}$
Lactic acid (Lactate)	
Hydrochloric acid (Chloride)	HCl
Sulfuric acid (Sulfate)	H_2SO_4
Orthophosphate acid (Orthophosphate)	H_3PO_4
Citric acid (Citrate)	
Isocitric acid (Isocitrate)	$\begin{array}{c} \text{CH}_2\text{—COOH} \\ \\ \text{CH—COOH} \\ \\ \text{CH(OH)—COOH} \end{array}$
Formic acid (Formate)	HCOOH
Pyruvic acid (Pyruvate)	
Pyroglutamic acid (Pyroglutamate)	
Acetic acid (Acetate)	$\text{CH}_3\text{-COOH}$
Fumaric acid (Fumarate)	
Oxalic acid (oxalate)	HOOC-COOH

The main sources of food acids are vegetable raw materials and products of their processing. Organic food acids are contained in most plants - berries, fruits, vegetables, including root crops, leafy greens. Together with carbohydrates and aromatic compounds, they form the taste and aroma of fruits and, as a result, of their processing products.

The main food acids of fruits, berries and vegetables are presented in the Table. 2.12.

Table 2.12. Main food acids of selected fruits, berries and vegetables

Plant raw materials	Basic acids
Fruits, berries	
Apricots	Malic acid, citric acid
Avocado	Tartaric acid
Quince	Malic acid (no citric acid)
Pineapples	Citric acid, malic acid
Oranges	Citric acid, malic acid, oxalic acid
Orange peel	Malic acid, citric acid, oxalic acid
Bananas	Malic acid, citric acid, tartaric acid
Grape	Malic acid and tartaric acid (3:2), citric acid, oxalic acid
Cherry	Malic acid, citric acid, tartaric acid, succinic acid, quinic acid, shikimic acid, glyceric acid, glycolic acid
Grapefruit	
Pears	Citric acid, tartaric acid, malic acid, oxalic acid
Blackberry	Malic acid, citric acid, tartaric acid, oxalic acid
Strawberry	Isocitric acid, malic acid, shikimic acid, quinic acid
Cranberry	Citric acid, malic acid, shikimic acid, succinic acid, glyceric acid, glycolic acid, aspartic acid
Gooseberry	
Lemons	Citric acid, malic acid, benzoic acid
Lemons	Citric acid, malic acid, shikimic acid, quinic acid
Peaches	Citric acid, malic acid, tartaric acid, oxalic acid
Plums	Citric acid, malic acid, tartaric acid, oxalic acid
Currant	Malic acid, citric acid
Dates	Malic acid, tartaric acid, oxalic acid
Blueberries	Citric acid, tartaric acid, malic acid, succinic acid
Apples	Citric acid, malic acid, acetic acid Citric acid, malic acid, glyceric acid, glycolic acid, succinic acid, glucuronic acid, galacturonic acid, quinic acid, glutamic acid, aspartic acid Malic acid, quinic acid, α -ketoglutaric acid, oxaloacetic acid, citric acid, pyruvic acid, fumaric acid, lactic acid, succinic acid
Vegetables	
Beans	Citric acid, malic acid
Broccoli	Malic acid and citric acid (3:2), oxalic acid, succinic acid
Mushrooms	Ketostearic acid, fumaric acid, allantoinic acid
Pea	Malic acid
Potato	Malic acid, citric acid, oxalic acid, phosphoric acid, pyroglutamic acid
Carrot	Malic acid, citric acid, isocitric acid, succinic acid, fumaric acid
Tomatoes	Citric acid, malic acid, oxalic acid, succinic acid, glycolic acid, tartaric acid
Rhubarb	Malic acid, citric acid, oxalic acid

The concentrations of individual organic acids in different fruits and berries are not the same.

Citrus fruits contain mainly citric acid and small amounts of malic acid. The content of malic acid in oranges is 10...25 %, in tangerines – up to 20 %, in grapefruits and lemons – up to 5 % in relation to total acidity. Unlike the fruit, the peel of oranges contains a significant (approximately 0.1 %) amount of oxalic acid.

Citric acid is also the main acid in the acid spectrum of pineapples, where its content is 85%. The share of malic acid in these fruits is about 1 %.

The dominant acid in stone fruits is malic acid, the content of which in their acid spectrum ranges from 50 to 90 %.

In sour varieties of apples, malic acid makes up more than 90 % of the total acidity, in cherries its concentration reaches 85...90 %, in plums (depending on the variety) – from 35 to 90 %. Other acids in these fruits include citric acid and quinic acid.

More than 90 % of the acidity is accounted by malic acid, citric acid and quinic acid in such fruits as peaches and apricots, and the ratio of malic acid and citric acid can vary in a wide range, which in some cases is associated with a change in the content of these acids in fruits in maturation process. It has been established, for example, that when peaches ripen, the amount of malic acid in them increases significantly, and the amount of citric acid decreases. Unlike other fruits, tartaric acid is the main component in grapes, which makes up 50-60 % of the total acidity. The rest is malic acid (25-30 %) and citric acid (up to 10 %). In the process of grape ripening, the content of malic acid decreases more intensively than that of tartaric acid.

In most types of berries, with the exception of grapes, gooseberries, blueberries and blackberries, citric acid predominates. Thus, in strawberries its share is 70...90 %, in currants – 85...90 %. The content of malic acid in these berries is 10...15 %. Blackberries contain 65-85 % isolitric acid, and gooseberries contain 45% malic and citric acids and 5-10 % shikimic acid.

A certain amount of acids in fruits and berries can be found in the form of salts. Their content, for example, in lemons, is up to 3%, and in certain types of pears – 20...30 %.

Unlike most organic acids in the composition of fruits and berries, lactic acid is formed, obviously, only by microbiological means.

The acid spectrum of vegetables is mainly represented by the same organic acids, the ratio of which varies widely. Along with the already known, vegetables contain succinic acid, fumaric acid, pyroglutamic acid and some other acids of different structure.

A distinctive feature of tomatoes is the presence of inorganic acids in them - orthophosphate acid, sulfuric acid and hydrochloric acid.

In milk and dairy products, the main organic acid is lactic acid, the formation of which is associated with biochemical transformation milk sugar – lactose under the action of lactic acid bacteria.

With the participation of homofermentative lactic acid bacteria in this process, lactic acid is practically the only product of the reaction. In the case of heterofermentative aroma-forming lactic acid bacteria, acetic acid and propionic acid

appear along with lactic acid, as well as other fermentation products - ethanol, ethyl ethanoate.

It has been established that food acids are characterized by a positive biological effect. So, benzoic acid has an antiseptic effect, uronic acids and their derivatives remove metabolic products from the body, salts of heavy metals, radionuclides, cholesterol, citric and some other acids reduce the risk of synthesis of carcinogenic nitrosamines in the body, and therefore the risk of developing oncological pathologies.

Organic acids of berries and fruits stimulate the secretion of juice in the gastrointestinal tract and thus improve digestion, reduce the risk of developing many gastrointestinal diseases. For different acids, some other effects have been found.

In connection with the effective biological action, the direction of using organic acids as food additives and during the production of functional food products, including beverages, was formed.

In addition, the value of food acids in human nutrition is determined by their energy value and participation in metabolism. The main biological function of organic acids included in food is related to their participation in digestion processes.

2.4.2. Properties of food acids

The sour taste of a food product is caused by Hydrogen ions, which are formed as a result of electrolytic dissociation of acids and acid salts contained in this product. The activity of Hydrogen ions (active acidity) is characterized by the pH indicator (negative decimal logarithm of the concentration of Hydrogen ions). The pH values for some liquid food products are given in Table 2.13

Table 2.13. pH values for some liquid food products

Foodstuff	pH value
Orange juice	3.2...3.5
Pineapple juice	3.6
Grape juice	3.2
Grapefruit juice	3.1
Banana nectar	3.66
Beer	4.2...4.6
Milk	6.6...6.8
Condensed milk	6.1...6.4
Yogurt	4.0...4.3
Cocoa (drink)	6.3...6.4

Almost all food acids are weak electrolytes, dissociate slightly in aqueous solutions. In addition, there may be buffer substances in the food system, in the presence of which the activity of Hydrogen ions will remain approximately the same due to the dissociation equilibrium of weak electrolytes. An example of such a system is milk.

In this regard, the total concentration of acidic substances in a food product is determined by the indicator of potential, total or titrated (alkaline) acidity.

For different products, this value is expressed by different indicators. For example, in juices, the total acidity is determined in g per 1 liter, in milk – in degrees Turner.

Food acids in the composition of food raw materials and products perform various functions related to the quality of food objects.

As part of a complex of taste-aromatic substances, they participate in the formation of taste and aroma. It is the taste, together with the smell and appearance, that exerts the main influence on the consumer's choice of this or that product in comparison with such indicators as its composition and nutritional value. A change in taste and aroma is often a sign of spoilage of a food product or the presence of foreign substances in its composition.

The main taste sensation caused by the presence of acids in the product is a sour taste, which is generally proportional to the concentration of H^+ ions (taking into account differences in the activity of substances that cause the same taste perception). For example, the limit concentration (minimum concentration of a flavoring substance perceived by the senses), which allows you to feel a sour taste, is 0.017 % for citric acid, 0.03 % for acetic acid.

For organic acids, the perception of sour taste is also affected by the anion of the molecule. Depending on the nature of the latter, combined taste sensations may occur, for example, citric acid has a sweet-sour taste, and picric acid has a sour-bitter taste. A change in taste sensations also occurs in the presence of salts of organic acids. Yes, ammonium salts give the product a salty taste.

It is natural that the presence of several organic acids in the composition of the product in combination with tasteful organic substances of other classes cause the formation of original taste sensations, often peculiar to only one, specific type of food products.

The quality of a food product is an integral characteristic that includes, in addition to organoleptic properties (taste, color, aroma), indicators characterizing its colloidal, chemical and microbiological stability.

The formation of product quality is carried out at all stages of the technological process of its production. At the same time, many technological indicators that ensure the creation of a high-quality product depend on the active acidity (pH) of the food system.

In general, the pH value affects the following technological processes parameters:

- formation of taste and aroma components characteristic of a specific type of product;
- colloidal stability of a polydisperse food system (for example, the colloidal state of milk proteins or a complex of protein-tannin compounds in beer);
- thermal stability of the food system (for example, the thermal stability of protein substances of dairy products, which depends on the state of equilibrium between ionized and colloidally distributed calcium orthophosphate);
- biological stability (for example, beer and juices);
- activity of enzymes;
- growth conditions of beneficial microflora and its influence on ripening

processes (for example, beer or cheese).

The presence of food acids in the product may be the result of the intentional introduction of acid into the food system during the technological process to adjust its pH.

In this case, food acids are used as technological food additives.

In general, three main purposes of adding acids to the food system can be distinguished:

- provision of certain organoleptic properties (taste, color, aroma) characteristic of a specific product;
- influence on colloidal properties, which lead to the formation of a consistency characteristic of a specific product;
- increased stability, which ensures the preservation of product quality over a certain period of time.

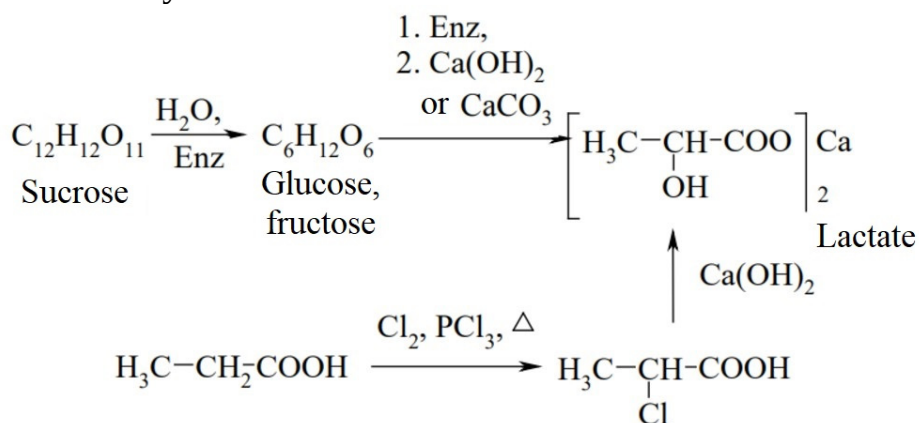
2.4.3. Characteristics of food acids

Acetic acid is the most famous food acid and is produced in the form of an essence containing 70-80 % acid. In everyday life, vinegar essence diluted with water is used, which was called table vinegar. Using vinegar to preserve food is one of the oldest methods of preservation. Depending on the raw material from which acetic acid is obtained, a distinction is made between wine vinegar, fruit vinegar, apple vinegar, alcohol vinegar, and synthetic acetic acid. Acetic acid is obtained by acetic acid fermentation of alcohol or synthetically. Salts and esters of this acid are called acetates. Potassium and sodium acetates (E461 and E462) are used as food additives.

Together with acetic acid and acetates, diacetates of sodium and potassium are used. These substances consist of acetic acid and acetates in a molar ratio of 1:1. Acetic acid is a colorless liquid, miscible with water in all respects. Sodium diacetate is a white crystalline powder, soluble in water, with a strong odor of acetic acid.

Acetic acid has no legal restrictions; its action is based mainly on lowering the pH of the preservative product, is manifested at a content above 0.5 % and is directed mainly against bacteria. The main field of use is canned vegetables and pickled products. It is used in mayonnaise, sauces, during pickling of fish products and vegetables, berries and fruits. Acetic acid is also widely used as a flavor additive.

Lactic acid is produced in two forms that differ in concentration: a 40 % solution and a concentrate containing at least 70 % acid. Obtained by lactic acid fermentation of carbohydrates:



Its salts and esters are called lactates. As a food additive, E 270 is used in the production of soft drinks, caramel masses, and fermented milk products. Lactic acid has limitations for use in baby food products.

Citric acid is a product of citric acid fermentation of sugars.

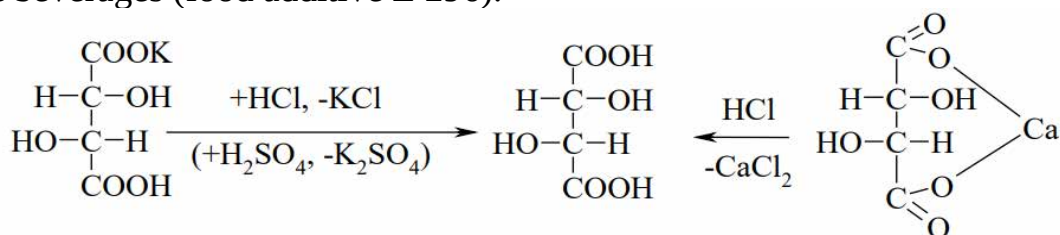
Synthetically, citric acid is produced from ketene and anhydride of 2-hydroxybutanoic acid (oxaloacetic acid) through alcoholanhydridolactone.

It has the mildest taste compared to other food acids and does not irritate the mucous membranes of the digestive tract.

Salts and esters of citric acid are citrates. It is used in the confectionery industry, in the production of soft drinks and some types of canned fish (food additive E 330). Citric acid softens the sweet taste, gives a fresher shade and brings it closer to the pleasant sour-sweet taste of fruits and berries.

But at the same time, it removes calcium from the body, worsens blood coagulation, so it is recommended to replace it with succinic acid.

Malic acid has a weaker sour taste than citric acid and tartaric acid. For industrial use, this acid is obtained synthetically from maleic acid, in connection with which purity criteria include restrictions on the content of toxic maleic acid impurities in it. Salts and esters of malic acid are called malates. Malic acid exhibits the chemical properties of oxyacids. When heated to 100 °C, it turns into an anhydride. It is used in confectionery production and in the production of non-alcoholic beverages (food additive E 296).

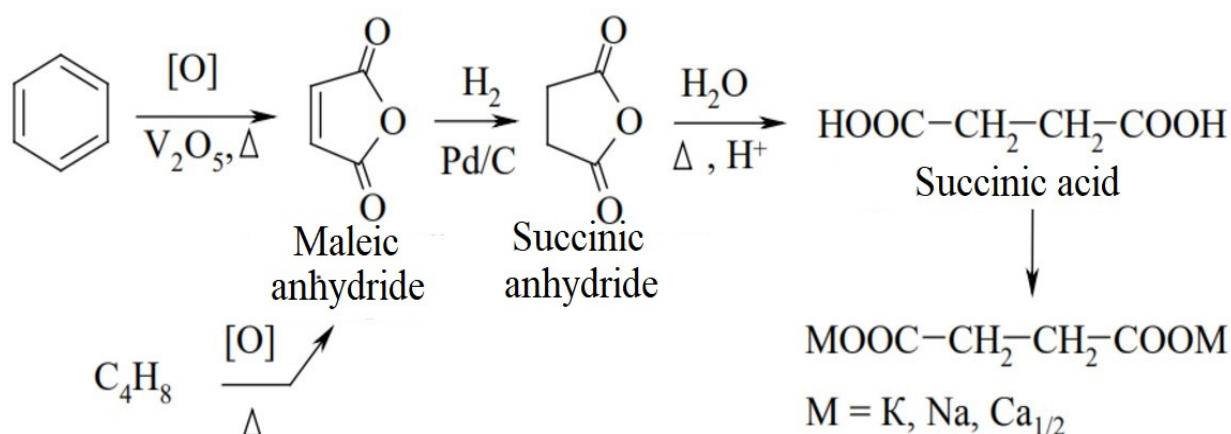


Tartaric acid is a product of winemaking waste processing (wine yeast and wine stone). D-Tartaric acid, as a natural one, is obtained by processing its acidic potassium salt - a waste product of winemaking - with mineral acids. Potassium salt is released in large quantities from juices and wines during their cooling. The sediment of raw tartar, which is deposited on the inner surface of containers, consists of 83 % of potassium salt and 5-6 % of calcium salt of tartaric acid, which is also a valuable raw material for extracting free acid:

It does not irritate the mucous membranes of the gastrointestinal tract and does not undergo metabolic transformations in the human body. The main part (about 80%) is destroyed in the intestine under the action of bacteria. Salts and esters of tartaric acid are called tartrates.

It is used in confectionery and soft drinks (food additive E334).

Succinic acid is a by-product of the production of adipic acid. The method of obtaining succinic acid by benzene oxidation:



The method of its isolation from amber waste is also known. The characteristic chemical properties of dicarboxylic acids form salts and esters, which were named succinates. At a temperature of 235 °C, succinic acid splits off water, turning into succinic anhydride. It is used in the food industry to regulate the pH of food systems (food additive E 363).

Succinic acid is considered not only as a unique energy substrate, but also as a regulator of the function and development of living systems, which formed the basis for the creation of nutritional supplements and preventive products.

It has been established that succinic acid, as a metabolic product, has a powerful protective effect and is a stimulator of the development of immunity to new substances harmful to the body.

Succinic acid is added to beer, juices, and wine to increase stability, accelerate yeast reproduction, and improve their fermentation activity.

Adipic acid is obtained in industry mainly by two-stage oxidation of cyclohexane. Characteristic chemical properties of carboxylic acids, in particular, form salts, most of which are soluble in water. Esterification into mono- and diesters occurs easily. Salts and esters of adipic acid are called adipinates. Food additive (E 355), providing sour taste to products, in particular, soft drinks.

Fumaric acid is found in many plants and fungi and is formed during the fermentation of carbohydrates in the presence of *Aspergillus fumaricus*. The industrial production method is based on the isomerization of maleic acid under the influence of HCl containing bromine. Salts and esters are called fumarates. In the food industry, fumaric acid is used as a substitute for citric acid and tartaric acid (food additive E 297). It is toxic, therefore the daily intake with food is limited to 6 mg per 1 kg of body weight.

Glucono-delta-lactone is a product of enzymatic aerobic oxidation of β ,D-glucose. In aqueous solutions, glucono-delta-lactone hydrolyzes into gluconic acid, which is accompanied by a change in the pH of the solution. It is used as an acidity regulator and leavening agent (food additive E 575) in dessert mixtures and products based on minced meat, for example, in sausages.

Orthophosphate acid and its salts - orthophosphates (potassium, sodium and calcium) are widely distributed in food raw materials and products of its processing.

In high concentrations, phosphates are found in dairy, meat and fish products, in some types of cereals and nuts. Phosphates (food additives E 339-341) are introduced into soft drinks and confectionery. The permissible daily dose, in terms of orthophosphoric acid, corresponds to 5...15 mg per 1 kg of body weight (since an excessive amount of it in the body can cause an imbalance of calcium and phosphorus).

2.4.4. Acids in food systems

The purpose of organic acids in food is determined by their energy value: malic acid – 2.4 kcal / g, citric acid – 2.5 kcal / g, lactic acid – 3.6 kcal / g, as well as active participation in metabolism.

Usually, food acids do not cause an additional load in the body, being oxidized during metabolism at a high speed. The main function of organic acids included in food is related to participation in digestion processes.

They reduce the pH of the environment, contributing to the creation of a certain composition of microflora, take an active part in energy metabolism, stimulate the secretion of juice in the gastrointestinal tract, improve digestion, activate intestinal peristalsis, contributing to the reduction of the risk of developing many gastrointestinal and other diseases, inhibit the development of putrefactive processes in the large intestine. For example, citric acid prevents the formation of carcinogenic nitrosamines in the body, helps reduce the risk of the occurrence and development of oncological pathologies, promotes the absorption of calcium by the body, activates or inhibits the activity of some enzymes. Organic acids have a wide range of biological effects.

Benzene acid and salicylic acid (bark of willow, black and red currant, cranberry, lingonberry) have antiseptic properties.

Derivatives of caffeic acid and other hydroxycinnamic acids, found in plantain and coltsfoot leaves, artichoke shoots, and other plants, have choleretic and anti-inflammatory effects.

Gallic acid is found in tea leaves and other plants, its derivatives (propyl gallate, etc.) have an antiviral effect, and are also used as antioxidants in the food industry.

Tartronic acid, contained in large quantities in cabbage, inhibits the conversion of carbohydrates into fats, thereby preventing obesity and atherosclerosis.

Oxalic acid can be deposited in the form of a calcium salt (calcium oxalate) in the joints or form stones in the urinary tract. Therefore, you should not abuse plants containing a high amount of this organic acid. A lot of oxalic acid is contained not only in sorrel and spinach, but also in unripe gooseberries and nettle leaves.

Questions for discussion and self-examination

- 1. Describe food acids.*
- 2. Properties of food acids.*
- 3. Ways of obtaining food acids.*
- 4. Effect of food acids on food products.*
- 5. Definition of "food acids".*

Topic 2.5. Vitamins

2.5.1. Importance of vitamins in human nutrition

Vitamins are low-molecular organic substances of various chemical structures, which are biological catalysts of chemical reactions taking place in living cells, necessary for normal metabolism and vital activity of the body. Vitamins play a very important role in nutrient absorption processes. Most vitamins enter the human body with food, some of them are synthesized by intestinal microflora and absorbed into the blood.

The following characteristics of vitamins can also be distinguished:

- low molecular weight compounds that are not deposited in the body;
- they are almost not synthesized in the body, but come with food products;
- do not have energy and plastic properties;
- have a biological effect in very small doses;
- act on the body independently or as part of coenzymes, ensuring important metabolic processes.

The first classification of vitamins consisted in empirically marking them with Latin letters according to the corresponding groups. For example, vitamin A (group A), vitamin D (group D). Over time, digital indexes began to be added to vitamins of the same group that occur together in nature, but have different chemical structures and biological effects, for example, vitamin B₁, B₁₂, etc. In addition, the names sometimes indicate the chemical nature of vitamins or their biological action with the prefix anti-, for example, vitamin B₃ – pantothenic acid or antidermatic, vitamin C – ascorbic acid or antiscorvy (antiscorvy). Thus, for many vitamins there is a triple classification: by group, chemical structure and biological action.

Vitamins are divided into water- and fat-soluble:

- water-soluble vitamins: vitamin C, vitamins of group B, PP and vitamin H;
- fat-soluble - vitamins A, D, E and K.

Water-soluble vitamins are metabolized in the body within 24...48 hours, fat-soluble vitamins are stored in fat.

There is also a group of vitamin-like compounds, which include:

- biologically active substances that are synthesized in the body: lipoic acid (vitamin N), orotic acid (vitamin B₁₃), carnitine (vitamin B₁₁);
- biologically active food substances: bioflavonoids (vitamin P), vitamin U, pangamic acid (vitamin B₁₅);
- indispensable nutrients mainly with plastic and lipotropic effects (choline, inositol).

Fat-soluble vitamins (A, D, E, F, K) are involved in the processes of blood coagulation, photoreception. Some vitamins, e.g. vitamin D, have a hormone-like effect, promote calcium absorption, stimulate growth processes, development of the body's immune reactions, increase the body's resistance to infectious diseases.

Vitamins A, D can accumulate in some organs - liver, subcutaneous fat tissue. These vitamins are contained in plant and animal tissues in the form of inactive precursors that are transformed into active forms under the action of enzymes and sunlight.

Water-soluble vitamins (B₁, B₂, B₃, B₅, B₆, C, B₁₂, P, H) are part of enzymes mainly in the form of cofactors and ensure the normal functioning of some organs and systems of the body, regulate metabolism, the functional state of the central nervous system, tissue nutrition, permeability and stability of blood vessels.

According to their physiological effect, vitamins are divided into several groups:

- vitamins that increase the general reactivity of the body (B₁, B₃, PP, A, C);
- antihemorrhagic (S, K);
- anti-anemic (B₁₂, B₆, C);
- anti-infective (C, A).

According to the chemical classification, all vitamins are divided into the following groups:

- vitamins of the aliphatic series (ascorbic acid, pantothenic acid, pangamic acid, methylmethionine sulfonium chloride);
- vitamins of the alicyclic series (retinols, calciferols);
- vitamins of the aromatic series (naphthoquinone derivatives);
- vitamins of the heterocyclic series (tocopherols, bioflavonoids, nicotinic acid and its amide, pyridoxine, thiamine, folic acid, riboflavin, cobalamin).

Vitamins are obtained by chemical (A, C, B₆, B₁) and microbiological (riboflavin, B₁₂) synthesis or isolated from natural sources

There are three levels of the body's supply of vitamins:

- avitaminosis – when vitamins are completely absent;
- hypovitaminosis – a lack of vitamins, sometimes the absence of one or more vitamins;
- hypervitaminosis – their excessive content.

Cases of hypovitaminosis are more common, especially in winter and spring. Avitaminoses are the cause of serious diseases, often with fatal consequences.

The potential toxicity of an excess of fat-soluble and water-soluble vitamins in the body is different:

- fat-soluble vitamins are able to accumulate in the fatty tissue of the body, so their increased amount as a result of excessive consumption of certain products or additional intake of vitamin preparations can lead to the appearance of symptoms of toxic action;
- water-soluble vitamins do not accumulate in the body, so their increased intake leads only to the release of their excess from the body.

However, with a large overdose, water-soluble vitamins can be dangerous for the body. This especially applies to niacin, the excess of which can cause liver damage, and vitamin B₆ – its overdose is accompanied by a violation of the functions of the nervous system.

2.5.2. Water-soluble vitamins

Water-soluble vitamins include vitamins of group B and vitamins C, P, H, as well as vitamin-like water-soluble compounds.

Vitamin B₁ (thiamine, aneurin) - 4-methyl-5-β-hydroxyethyl-N-(2'-methyl-4'-amino-5'-methylpyrimidylthiazole) hydrochloride was discovered by H. Eikman in 1906, and in crystalline was isolated from yeast by A. Windaus only in 1931. The structural formula of vitamin B₁ is shown in Fig. 2.40.

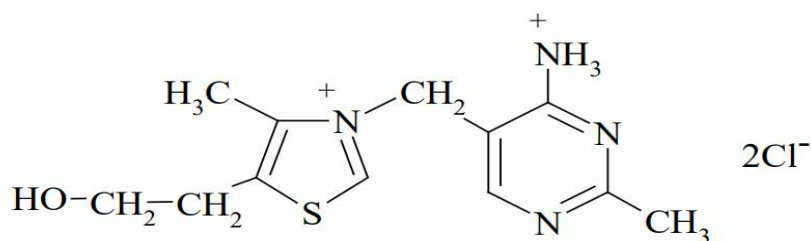


Fig. 2.40. Thiamine chloride

Vitamin B₁ consists of two heterocyclic rings – aminopyridine and thiazole.

Thiamine is well preserved in an acidic environment and withstands heating even at 140°C. In an alkaline or neutral environment, it quickly breaks down and loses its vitamin properties, for example, when baking dough with the addition of soda or ammonium carbonate. Thiamine is destroyed during freezing of products. Thus, 50 % of vitamin B₁ is lost in frozen spinach, 30 % in croutons.

Adding salt to beans or peas during cooking results in the loss of most of the vitamin B₁.

Under the influence of sunlight, vitamin B₁ becomes biologically inactive.

A person's daily need for thiamine is 1...3 mg/day. Thiamine is not synthesized in the body of humans and animals. The body's need for vitamins for children and breastfeeding women is 1...2 mg/day, or rather 1 milligram per 1000 kcal, provided a low-fat diet.

A lot of vitamin B₁ is found in bread made from coarsely ground flour, in the shell of the seeds of bread cereals, in soybeans, beans, peas, and in yeast. Of the products of animal origin, liver, lean pork, brain, and egg yolk are the richest in thiamine (Table 2.14).

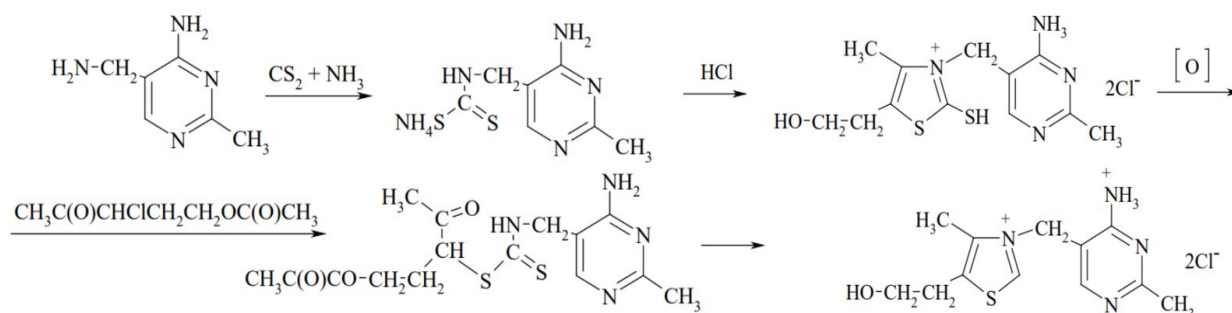
Table 2.14. Vitamin B₁ content in food products

Foodstuff	Content, mg %
Beef liver	0.4
Brain	0.2
Chicken egg	0.3
Cereal plants	0.6
Cabbage	0.22
Carrot	0.15
Dry brewer's yeast	15.6
Wheat sprouts	2.0
Nuts (hazelnuts)	0.4
Bread from coarse flour	0.3

Nowadays, due to the high consumption of sugar, as well as white bread and polished rice, the consumption of this vitamin by the body increases significantly.

Thiamine plays an important role in the normal oxidation of carbohydrates in the body, in the formation of the co-enzyme cocarboxylase, in the absence of which pyruvic acid is not broken down and accumulates in the blood and tissues.

Early symptoms of thiamine deficiency in food are loss of appetite. With a deficiency of this vitamin in the body, a person develops polyneuritis.



Overdose can lead to disruption of coordination of enzyme systems.

To increase the nutritional value of flour and other food products, synthetic thiamine is added to them, which can be obtained according to the following scheme: Vitamin B₁ is widely used in medical practice for the treatment of various diseases. For the prevention of hypo- and vitamin B₁ deficiency, it is used in combination with riboflavin (vitamin B₂) and nicotinic acid, for example, when vitaminizing bakery products. Vitamin B₁ is used to enrich baby food, milk and dairy products, instant cereal products.

It is also broken down under the influence of the enzyme thiaminase, which is contained in raw fish, but is destroyed when it is cooked.

Vitamin B₂ (riboflavin, growth vitamin) – 6,7-dimethyl-9-(1'-Tributyl) isoalloxazine. Riboflavin was first described in 1879 as a yellow pigment of cow's milk. The structure of riboflavin was established and confirmed by synthesis in 1935. at the same time, the groups of P. Carrera and R. Kuhn. Riboflavin has the following structure: the yellow-colored heterocyclic ring of isoalloxazine is connected to the residue of the five-atom ribitol alcohol by an N-glycosidic bond (Fig.2.41). Hence the name – **riboflavin**.

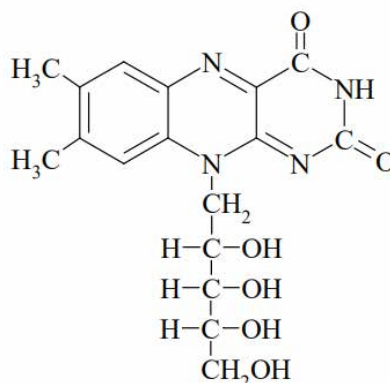


Fig.2.41. Riboflavin

In its biological effect, riboflavin is similar to thiamine, participates in the normalization of various metabolic processes, is necessary for cell respiration (to provide cells with oxygen).

The main source of riboflavin is milk and dairy products, liver, meat, egg yolks, green vegetables, bakery products from coarse flour, legumes, especially brewer's yeast.

Riboflavin is found in nature in a free state, but more often in the form of a derivative phosphorylated by the primary hydroxyl group. The body's daily need for riboflavin is 0.4...1.6 mg for children (depending on age), and 1.5 mg for adults, (Table 2.15).

Table 2.15. Content of vitamin B₂ in food products

Foodstuff	Content, mg %
Liver (beef)	1.5
Chicken egg	0.6
Cow's milk	0.2
Wheat	0.3
Cabbage	0.2

Riboflavin is not easily destroyed at high temperature, so no more than 20 % of it is lost during technological processing of food products.

Deficiency of vitamin B₂ in humans leads to stunted growth (in children), decreased appetite, weight loss, weakness, redness, itching and inflammation of the eyes, increased sensitivity to light, impaired vision due to vascularization of the cornea, anemia, focal hair loss (alopecia) is observed, seborrheic scaly dermatitis near the nose, around the mouth and on the body as a whole, itching and inflammation of the skin of the external genitalia, depression and degradation of the face.

In medical practice, vitamin B₂ is used for conjunctivitis, corneal ulcers and cataracts, for various skin diseases (dermatoses, neurodermatitis, seborrhea), for carbon monoxide poisoning, toxicosis, liver damage, and exhausting muscle work.

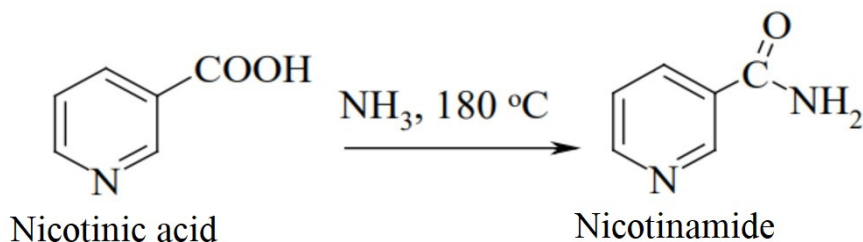
In the food industry, riboflavin is used to enrich some food products with vitamin B₂ (bread) or as a food dye (E 101) – needle crystals of yellow-orange color.

In the human body, riboflavin can be synthesized by intestinal microflora. It does not accumulate in the body, so it is necessary to regularly consume products rich in this vitamin. Riboflavin tolerates heat well, is resistant to an acidic environment (preserved during canning). Under the influence of light, it turns into an inactive form and loses its vitamin properties.

With the participation of riboflavin, vitamins K, PP, B₆ are transformed into their most active forms in the human body.

Niacin (vitamins B₅, PP) exists in two forms – nicotinic acid (vitamin B₅) and nicotinamide (vitamin PP).

The discovery of niacin is related to the study of the skin disease – pellagra. In animal products, niacin is found in the form of nicotinamide, and in vegetable products – in the form of nicotinic acid.



Niacin (nicotinic acid, nicotinamide) participates in the synthesis of fatty acids, helps the digestive system work, and participates in the conversion of proteins, fats, and carbohydrates into energy.

It also keeps the skin and nervous system in good condition. Nicotinic acid, especially its amide, exhibits the properties of an antipelargic vitamin. Among other vitamins, nicotinic acid is the most resistant to external factors. It is not easily destroyed during cooking (15...20 %), tolerates autoclaving well, is not subject to the destructive influence of sunlight, air, and alkaline solutions. Such properties of nicotinic acid ensure its preservation in food products during technological processing.

Unlike other vitamins, niacin can be synthesized in the human body from an irreplaceable amino acid - tryptophan, which is abundant in proteins of animal origin, but practically absent in plant proteins (60 mg of tryptophan is required to produce 1 mg of nicotinamide).

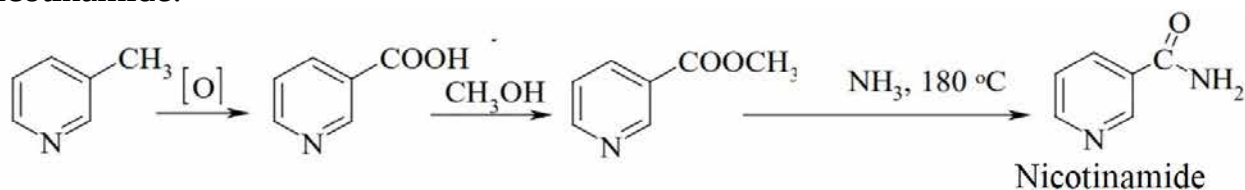
An adult's daily need for this vitamin is 15...25 mg/day, newborns – 3...8 mg/day, teenage children – 10...15 mg/day.

A large amount of vitamin PP is found in rice and wheat bran, liver, and yeast (Table 2.16).

Table 2.16. Vitamin PP content in food products

Foodstuff	Content, mg %
Liver	1.5
Fish	0.6
Milk	0.2
Wheat	0.3
Potato	0.2
Carrot	0.05
Yeast extract	58
Chicken meat	8
Beef chop	6
Soybeans	2
Raisins	0.6
Wholemeal flour bread	4

The industry uses several synthetic methods of obtaining nicotinic acid and nicotinamide:



Niacin, which comes with food, is transported with the blood to the liver and other tissues, where it penetrates into the cells. Moreover, nicotinic acid enters the cells faster than nicotinamide. A healthy person does not experience a deficiency of niacin in food products, because the provitamin of niacin is tryptophan, which in the human body is converted into nicotinamide adenine dinucleotide (NAD) through a number of intermediate stages (Fig.2.42).

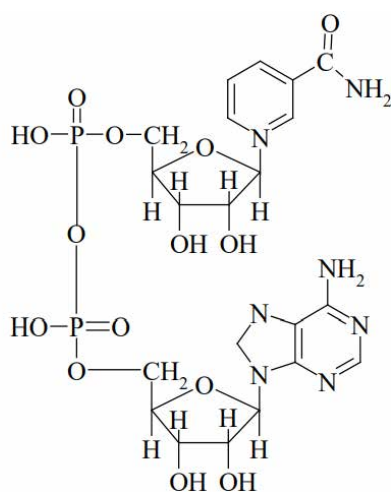
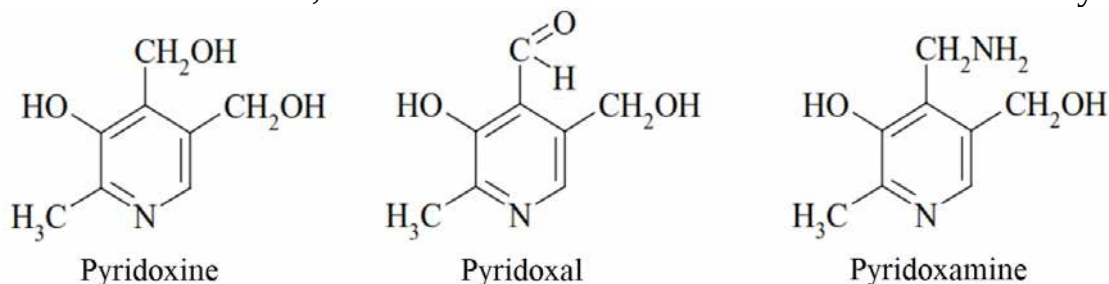


Fig. 2.42. NAD and NADPH

Vitamin PP is used to vitaminize bakery products. Technological processing does not lead to significant losses of niacin. However, during cooking of meat or vegetables, up to 25 % of it can pass into water.

Vitamin B₆ (pyridoxine, pyridoxal, pyridoxamine) was first isolated from polished rice in 1932, and its structure was established and confirmed by synthesis in 1939.

It exists in three forms, which are transformed into one another in the body.



Phosphorylated derivatives of pyridoxine are coenzymes of enzymes that play an important role in the transformation of amino acids. The daily requirement of an

adult for this vitamin is 3...4 mg/day. The largest amount of vitamin B₆ is found in liver, eggs, yeast, carrots, milk, and fruit (Table 2.17).

Table 2.17. Vitamin B6 content in some food products

Foodstuff	Content, mg %
Chicken egg	0.12
Cow's milk	1.5
Liver	0.64
Carrot	0.53
Oat	3.3
Wheat	3.3
Baker's yeast	2.0
Mackerel	1.03
Nuts (hazelnuts)	0.59
Soybeans	0.38
Potato	0.33
Bananas	0.29

Vitamin B₃ (pantothenic acid) was first isolated by R. Williamson in 1933, and in 1940 the chemical structure was deciphered and its synthesis was carried out.

According to the chemical structure, pantothenic acid is a derivative of β-alanine or a dimer of β-alanine and 2,4-dihydroxy-3,3-dimethylbutanoic acid, connected by an amide bond:

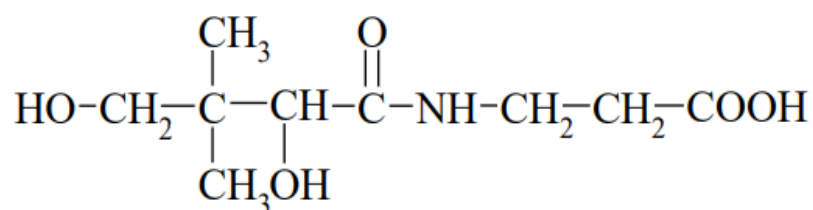


Fig.2.43. Vitamin B₅ (pantothenic acid)

Due to the presence of a chiral center, it has optical properties ($[\alpha]_{25}^D = +37.5^\circ$ in water). At the same time, only the dextrorotatory D-isomer exhibits biological activity, and the racemate has 50% vitamin activity.

The daily requirement of an adult is 3...5 mg/day. The main food sources of pantothenic acid for humans are baker's yeast, liver, walnuts, fish, egg yolk, and green parts of plants.

In addition, pantothenic acid is synthesized by intestinal microflora (Table 2.18).

Deficiency of pantothenic acid (vitaminosis) leads to weight loss, skin damage, baldness, impaired gastrointestinal tract functions.

Technological processing does not lead to a significant destruction of pantothenic acid, but approximately 30 % of it can pass into water during cooking. It is sensitive to the action of acids and alkalis.

Table 2.18. Pantothenic acid content in food products

Foodstuff	Content, mg %
Baker's yeast	11
Chicken egg	1.3
Liver	5.0
Fish	2.03
Potato	1.2
Wheat (sprout)	2.0
Chicken meat	1.2
Oat	1.2
Soybeans	0.8
Nuts	2.0

Vitamin H (biotin) was isolated from egg white and obtained in a crystalline state in 1936 by R. Kegl. In 1939-1940, a series of works by P. Giorgi was published, dedicated to the food factor necessary for protection against the toxic effect of raw egg white, as well as against dermatitis.

Its structure was identified in 1942 by A. Du Vigneault, who obtained this vitamin in a crystalline state. At the same time, it turned out that biotin is identical to vitamin H.

According to its chemical structure, biotin is a heterocyclic compound. Its molecule consists of imidazole and thiophene cycles, and the side chain is represented by a residue of valerian acid (Fig.2.44).

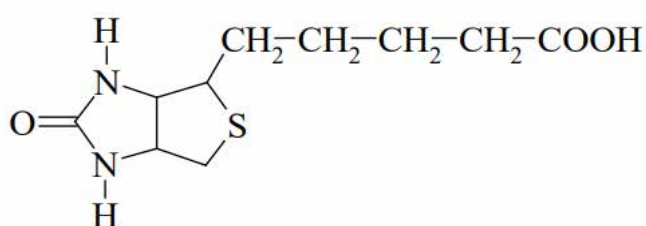


Fig. 2.44. Biotin

In products of animal origin, biotin is bound to proteins, in plants it is in a free state.

Free biotin with chicken egg glycoprotein forms an insoluble complex that does not break down in the gastrointestinal tract. Therefore, when consuming raw eggs, biotin is not absorbed, although it is contained in the food product.

The daily requirement of an adult for this vitamin is approximately 250 µg/day. Moreover, part of it comes with food, and part is synthesized by the intestinal microflora.

The main food sources of biotin are baker's yeast, beef liver, soybeans, milk, green peas, egg yolk, green onions, etc.

Biotin is called anti-seborrheic because it prevents the development of a specific disorder of the sebaceous glands of the skin (Table 2.19).

Table 2.19. Biotin content in food products

Foodstuff	Content, mg %
Baker's yeast	200
Beef liver	200
Chicken eggs (yolk)	30
Milk	40
Soybeans	60
Green peas	35
Mushrooms	16
Onion (green)	28
Colored cabbage	17
Bread from coarse flour	6

Biotin is part of multivitamin preparations. In the process of technological processing of food, biotin is practically not destroyed. It is used as a stimulant for growing baker's yeast.

Vitamin B₉ (folic acid, folacin, anti-anemic vitamin) - according to its chemical structure, it is a derivative of pteridine (1,3,5,8-tetrazanaphthalene, the molecule of which can be imagined as a combination of pyrimidine and pyrazine cycles. The pteridine residue is part of folic acid in the form of 2 -amino 4-oxopteridine in lactam form (Fig.2.45).

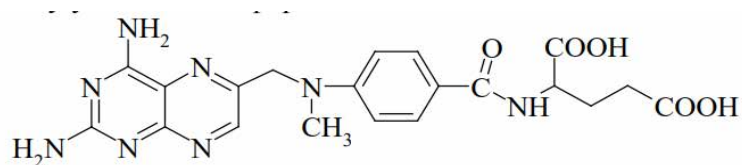


Fig. 2.45. Folic (pteroylmoglutamic) acid

Folic acid is optically active due to the asymmetric carbon atom $[\alpha]_{20}^D = +16^\circ$. The daily need for vitamin B₉ for an adult is 0.5...1.0 mg/day.

The body's need for this vitamin is met through dietary intake and synthesis by intestinal microorganisms. The main dietary sources of folic acid include yeast, soybeans, wheat germ, peas, beans, spinach, lettuce, cabbage, black currants, and others.

For the first time, folic acid was isolated in 1938 from liver extract. Synthetically, folic acid can be obtained by condensation of 2,4,5-triamino-6-oxypyrimidine, 2,3-dibromopropionic aldehyde and paminobenzoyl-L-(+)-glutamic acid (Table 2.20).

Table 2.20. Folacin content in food products

Foodstuff	Content, mg %
Yeast	400
Bean	150
Parsley	116
Green onion	100
Blackberry	150
Cheese	33
Bananas	33
Orange	31
Soybeans	370
Wheat sprouts	331
Pea	180
Spinach	150
Nuts	48

Vitamin B₉ plays an important role in the synthesis of purine and pyrimidine nucleotides, and therefore, nucleic acids and protein.

Antivitamin of folic acid is aminopterin. It differs from folic acid in that the OH group in position 4 is replaced by an NN group.

Aminopterin and other less toxic derivatives of folic acid have the opposite effect: they inhibit the biosynthesis of nucleic acids, proteins, cell reproduction, including tumor cells.

Folic acid deficiency can lead to inhibition of DNA biosynthesis, proteins and reproduction of hematopoietic cells with a short life span (erythrocytes, platelets) – this is very dangerous for the fetus in pregnant women.

Folic acid is destroyed during heat treatment and exposure to light. During pasteurization of milk, 75 % of folic acid is lost. It is easily destroyed in vegetables during their technological processing (up to 90 %). However, it is more stable in meat products and eggs, so during the technological processing of meat, its losses are insignificant.

Vitamin B₁₂ (cyanocobalamin, anti-anemic vitamin). For the first time, this vitamin was obtained in crystalline form in 1948 by E. Ricketts and E. Smith, and in 1961-1971, organic chemist R.B. Woodward synthesized vitamin B₁₂.

Its dark red crystals are well soluble in water and do not dissolve in organic solvents. B₁₂ is sensitive to light – under the influence of light, cyanocobalamin turns into oxycobalamin.

Cobalamin is the only vitamin that contains the metal cobalt ion (Co²⁺). The chemical structure of vitamin B₁₂ is very complex.

Vitamin B₁₂ is not synthesized by plants or animals. It is synthesized only by some types of microorganisms (Fig. 2.46).

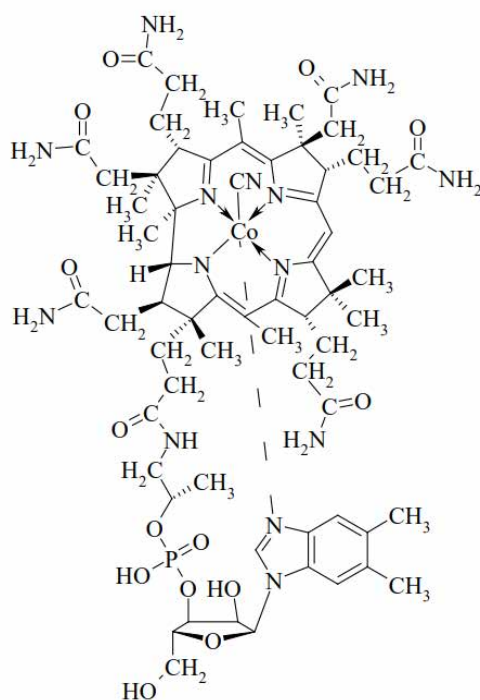


Fig. 2.26. Vitamin B₁₂

Vitamin B₁₂ participates in hematopoiesis, regulates carbohydrate and fat metabolism in the body. The daily requirement of adults is 2...4 µg.

The increased need for vitamin is observed in pregnant and lactating women, in the elderly and patients with AIDS, in vegetarians and those who abuse alcohol, smoking.

Vitamin B₁₂ is the only water-soluble vitamin that accumulates in the body (accumulates in the liver, kidneys, lungs, spleen).

The main food sources of the vitamin are mainly products of animal origin: liver, kidneys, heart, beef, poultry, fish and seafood, eggs, milk and dairy products. Plant sources include seaweed, soy and soy products, yeast, and hops (Table 2.21).

Table 2.21. Vitamin B12 content in some food products

Foodstuff	Content, mg %
Pork liver	26
Pork kidneys	15
Fish	2.0
Mutton	2
Chicken egg	1.1
Pork	2
Beef	2
Mackerel	6
Cheese	1.1
Cow's milk	0.4

With a deficiency of vitamin B₁₂, anemia develops, functional disorders of the central nervous system (irritability, sleep disturbances, depression) and even irreversible disorders (paralysis) occur.

Vitamin B₁₂ is relatively stable at high temperatures and when exposed to light. When cooking food under normal conditions, its losses are minimal.

Vitamin B₁₂ is destroyed by prolonged exposure to light rays, in acidic and alkaline environments.

Vitamin C (L-ascorbic acid) is structurally an internal cyclic ether (γ-lactone) of 2-keto-L-gulonic acid), (Fig.2.47).

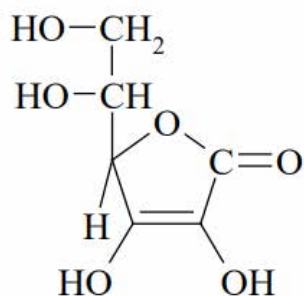
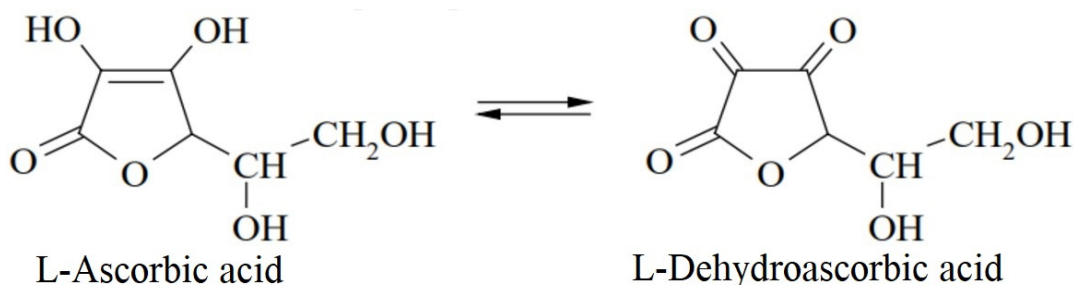


Fig.2.47. Ascorbic acid

Ascorbic acid has two asymmetric carbon atoms (C*) and is an optically active compound, forming four optical isomers and two racemates.

The most active stereoisomer is L-ascorbic acid. One of the main properties of ascorbic acid is its ability to reverse redox transformations.



The discovery of vitamin C is associated with the treatment of scurvy, a disease caused by a lack of fresh vegetables in the diet.

For the first time, ascorbic acid was isolated in a crystalline state by M. Bezsonov (1922) from cabbage juice, and its chemical structure was established by R. Herbert, E. Horst, and G. Eller (1933) thanks to its synthesis from L-xylose.

The daily requirement of vitamin C for an adult is 80...100 mg.

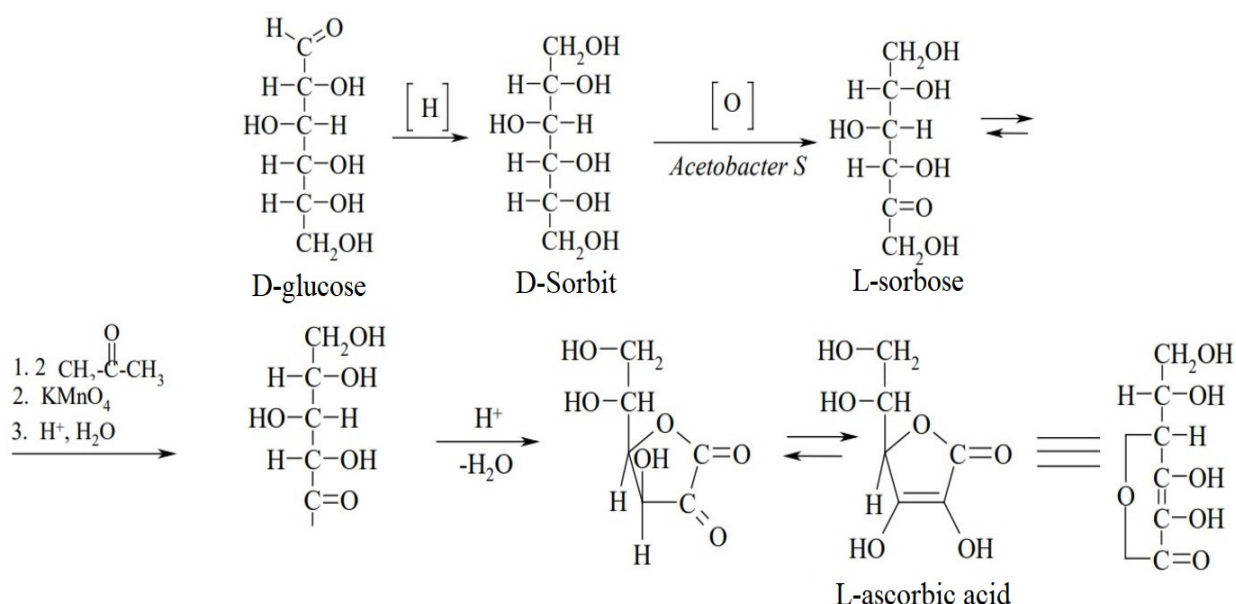
The main natural source of vitamin C is fresh vegetables and fruits. Especially rich in this vitamin are the fruits of rose hips, black currants, red pepper, parsley leaves, citrus fruits - lemons, oranges, grapefruits.

However, the most important sources of vitamin C are potatoes and cabbage. A lot of ascorbic acid is found in tomatoes, fresh cabbage, and strawberries. Cereals, meat, eggs, milk are poor in vitamin C (Table 2.22).

Table 2.22. Vitamin C content in some food products

Foodstuff	Content, mg %
Rosehip fruits	2000 – 4500
Walnut	max 3000
Black currant	100 – 400
Red pepper	100 – 400
Dill	135
Strawberries	60
Citrine	55
Liver and spleen	20 – 50
Tangerines	25 – 45
Cabbage	30 – 40
Young potatoes	20 – 40
Tomatoes	20 – 40
Apples	5 – 40
The onion is green	16.5 – 33
Grape	0.4 – 12
Onion (turnip)	2 – 10
Cow's milk	0.7 – 2.6
Meat	0.9

In industry, L-ascorbic acid is obtained from D-glucose:



Isolation of L-ascorbic acid in the form of its concentrates from plant raw materials is practiced to a lesser extent. Ascorbic acid protects the body from scurvy, participates in oxidation-reduction processes, protein and carbohydrate metabolism, increases resistance to infectious and other diseases, promotes the removal of

cholesterol from the body, which prevents lipid metabolism disorders (prevents the development of atherosclerosis).

Deficiency of vitamin C causes a decrease in gastric secretion, a violation of its acid-forming and motor functions, the development of pathological processes in the organs of the gastrointestinal tract (formation of erosions on the mucous membrane of the stomach). It has been proven that vitamin C prevents the formation of nitrosamines in the body – substances that have a strong carcinogenic effect.

Ascorbic acid is an antidote for aniline or carbon monoxide poisoning. Vitamin C is used individually or as part of various multivitamin preparations. Facilitates the absorption of trace element iron in the intestine. Vitamin C is the least stable of all vitamins. It is easily destroyed by contact with air oxygen, prolonged heating, in contact with iron or copper. Due to instability, the content of vitamin C in vegetables and fruits quickly decreases during their storage. During the storage of potatoes, the vitamin C content decreases by 50...65% on average until spring. With proper storage of whole heads of fresh cabbage, vitamin C is stored in it without significant losses for 4-5 months.

Sauerkraut with brine is rich in vitamin C, without brine and dry it contains almost no vitamin C. Brine contains up to 40% of vitamin C. Sauerkraut washed in running water loses 60% of vitamin C.

In the process of technological processing of vegetables, the loss of vitamin C exists:

- in cabbage soups, borschts 60-80 %;
- in pureed soups, 80 % or more;
- in mashed potatoes 70-90 %.

Especially a lot of vitamin C is lost when cooking vegetable dishes. During the cooking of vegetable dishes in cast iron cauldrons, 50...70 % of vitamin C is destroyed, in autoclaves – 25...30 %. In an acidic environment, vitamin C is well preserved, in an alkaline environment it is inactivated.

Starch, flour, various cereals, sucrose, salt, proteins have a stabilizing effect on this vitamin. The presence of starch and common salt inhibits the oxidation of ascorbic acid by copper and iron salts.

In order to preserve vitamin C as much as possible in ready-made dishes, the following rules must be strictly followed:

- waste should be minimal (according to the season);
- cleaned and chopped vegetables should be immediately subjected to heat treatment;
- vegetables must be placed in boiling water or broth, which are pre-salted;
- the dishes should be filled to the top (the contact of vitamin C with air decreases);
- ready-made vegetable dishes should be consumed immediately;
- overcooking and secondary heating of food is not allowed.

Vitamin C is used to enrich juices, water-soluble drinks, breakfast cereals, milk, as a bakery improver, to preserve the color of meat products along with nitrates and nitrites.

Ascorbic acid is an antidote for aniline or carbon monoxide poisoning.

2.5.3. Fat-soluble vitamins

Vitamin A became the first of the discovered vitamins, so its compound was designated by the letter A in accordance with the alphabetical nomenclature.

For the first time, vitamin A was isolated from carrots, so the name of the group of vitamins A - carotenoids – came from the English carrot.

It exists in two forms:

- directly vitamin A (retinol);
- provitamin A (carotene) is a substance that is converted into vitamin A in the human body.

According to the chemical structure, vitamin A is a cyclic unsaturated alcohol, which consists of a cyclohexene fragment of β -ionone and two isoprene units (the active form of the vitamin is found only in animal products – liver, fish oil, butter, etc.), Fig. 2.48.

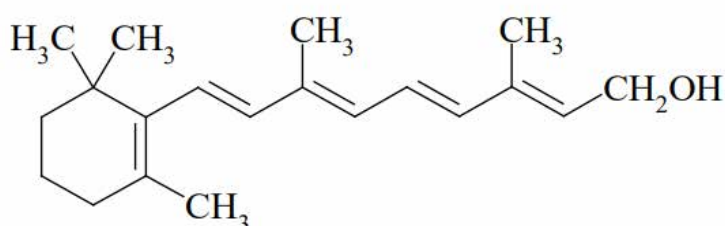


Fig. 2.48. Vitamin A

β -Carotene is a dimer of retinol (an inactive provitamin that enters the body from plant sources and is converted into active vitamin A when necessary due to the enzymatic cleavage of mainly β -carotene), Fig. 2.49.

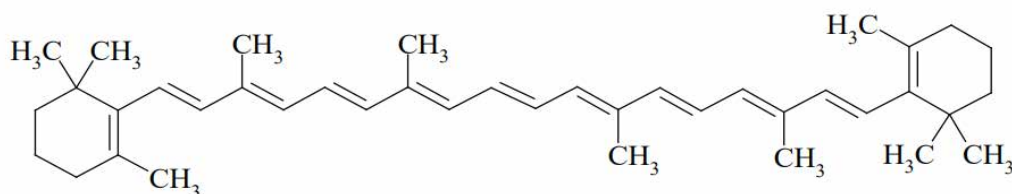


Fig. 2.49. β -Carotene

Plant foods contain carotenoids - provitamin A (alpha- and beta-carotene, lutein, lycopene, zeaxanthin, etc.). About 500 carotenoids are known in total.

The most famous carotenoid is beta-carotene (in the liver it is converted into vitamin A as a result of oxidation).

The daily need for vitamin A depends on biological activity, so it is converted to pure retinal in international units (IU). 1 IU = 0.3 μ g retinal.

The daily requirement of an adult is 1.5 μ g of vitamin A, Table 2.23.

Vitamins of group A exist in the form of optical isomers, but only compounds with trans-configuration show physiological activity, cis-isomers do not show such activity.

The biological role of vitamin A is that it participates in redox processes, in the regulation of protein synthesis, plays an important role in the formation of bones and teeth, as well as fat deposits, and slows down aging.

Table 2.23. Vitamin A content in some products of plant and animal origin

Foodstuff	Content, mg %
Spinach	37
Carrot	11
Tomato	7.2
Cabbage	5-7
Melon	2.1-6.2
Red pepper	1.75
Liver	254
Chicken egg	10
Butter	7.5
Cow's milk	1
Cheese	3.25
Fish Oil	19

Like β -carotene, it is a powerful antioxidant.

Deficiency of vitamin A is manifested in impaired vision (so-called "chicken" or "night" blindness), dry skin. Most often, vitamin A deficiency is observed in infants, because the liver of newborns does not have a reserve of vitamin A.

In addition, they do not synthesize this vitamin from carotene due to the absence of the carotenase enzyme. Lack of vitamin A also leads to growth retardation. With hypervitaminosis (in connection with vitamin overdose), mineral metabolism is disturbed, the process of bone demineralization is observed.

Vitamin A and carotene are well preserved during heat treatment. Carotene dissolves in fats when vegetables are sautéed and is better absorbed by the body. Sunlight, air oxygen and acids have a harmful effect on vitamin A. It is stable when heated without access of oxygen and even at 120-130 °C it does not lose its chemical and biological properties. Due to this, it is well preserved during canning. In general, up to 30% of vitamin A is destroyed during technological processing.

Vitamin D comes in several forms. They are called calciferols and they are presented mainly in the form of two substances: ergocalciferol (vitamin D₂) and cholecalciferol (vitamin D₃), Fig.2.50.

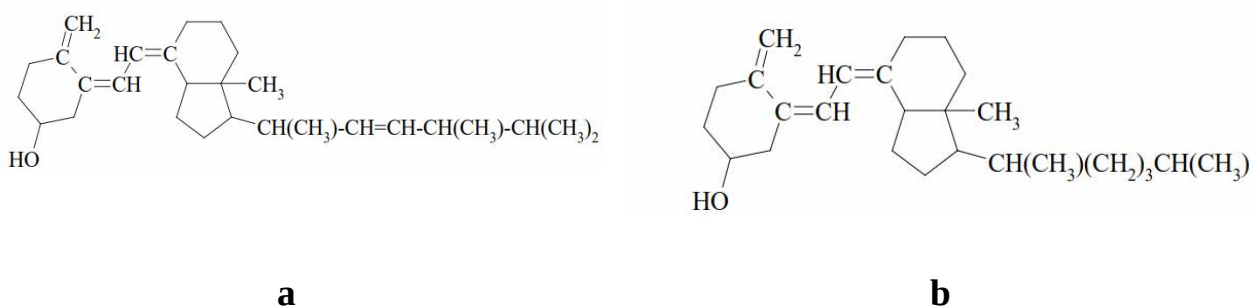
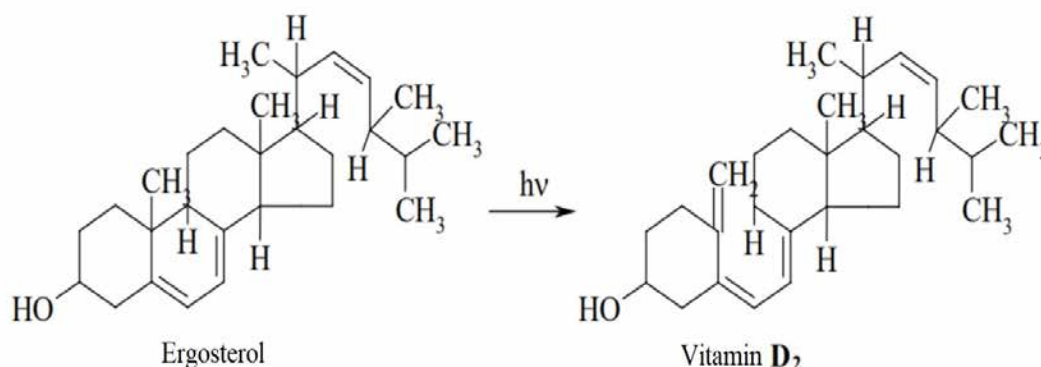
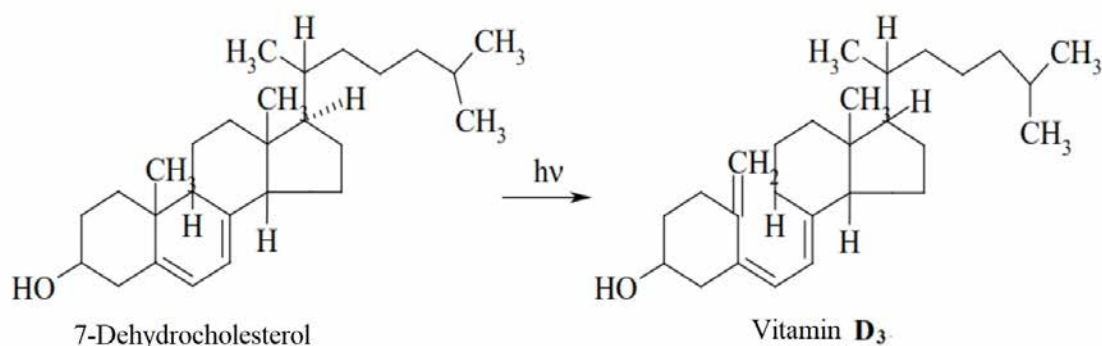


Fig. 2.50. Vitamin D₂ (ergocalciferol) (a) and vitamin D₃ (cholecalciferol) (b)

Ergocalciferol is considered a vitamin of plant origin, and cholecalciferol is of animal origin. For vitamin D₂, ergosterol isolated from yeast is a provitamin:



For vitamin D₃ contained in the skin, 7-dehydrocholesterol is a provitamin:



Back in the 17th century, the disease rickets was known, which was cured by certain foods, including fish oil. Later, scientists discovered the influence of sunlight on this disease.

In 1924, it was established that some anti-rickets factors are activated in food under the action of ultraviolet radiation. Mixtures of these substances were identified as sterols. In 1932, after irradiating ergosterol from yeast, A. Windaus obtained a substance that has an anti-rickets effect and is called ergocalciferol or vitamin D₂. In 1936, a drug called vitamin D₃ was isolated from fish oil, and its precursor is not ergosterol, but cholesterol.

The main function of vitamin D is to ensure normal growth and development of bones, prevention of rickets in children, prevention of osteoporosis in adults. Also, vitamin D is necessary for the functioning of the thyroid gland and normal blood clotting. It is effective in the prevention and treatment of oncological diseases, strengthens the work of the immune system. The daily requirement for this vitamin for adults is 2.5 mcg (100 IU).

Sources of vitamin D:

- vegetable products (whole grain cereals, alfalfa, lettuce, chestnuts, horsetail, nettle, parsley, mushrooms, yeast);
- animal products (milk and dairy products, butter, eggs, fish oil, caviar, liver of fish and animals);

– synthesis in the body (formed in the body under the influence of UV radiation), Table 2.24.

Table 2.24. Vitamin D content in food products

Foodstuff	Content, mg %
Mackerel liver	1400
Flounder liver	80
Cod liver	3.0
Beef liver	0.025
Chicken egg	0.05
Butter	0.03

The industrial production of vitamin D₂ consists in the photoisomerization of ergostyrene, which is obtained from yeast or mycelium of mushrooms (waste from the production of penicillin with a sterol content of 0.5 %). Vitamin D is not destroyed during technological processing, but it is very sensitive to light, the action of oxygen, and metal ions.

Vitamin E (α -tocopherol) was discovered as an antisterile factor. Tocopherols are a group of vitamins that can prevent the development of infertility in animals and support the function of reproduction (from the Greek. Tokos – offspring, phero – carrier), Fig. 2.51.

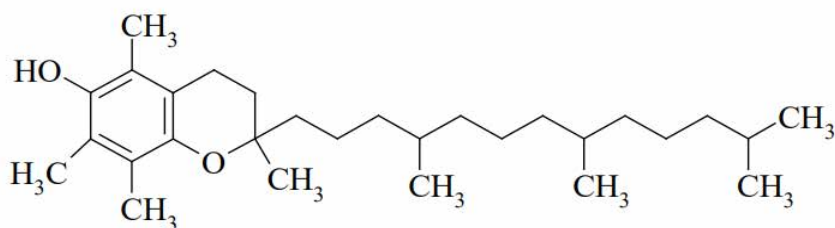
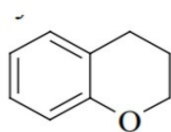


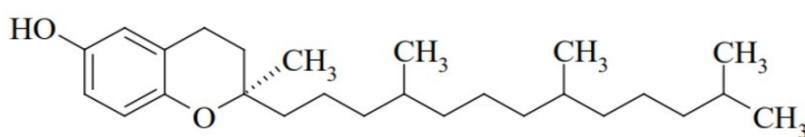
Fig. 2.51. α -Tocopherol

For the first time, the influence of the vitamin activity of a substance from lettuce leaves on the ability of some animals to regenerate offspring was noticed by G. Evans and A. Bisho, who in 1922 discovered a fat-soluble vitamin, which they called tocopherol (literally "promoting childbirth" because it ensures the functioning of the reproductive organs in both women and men). Later, he got the name vitamin E. In 1936, they managed to isolate two substances with the properties of vitamin E from wheat germ oil, which were named α - and β -tocopherols.

According to their chemical structure, tocopherols can be considered as methyl derivatives of tocol.



Chroman

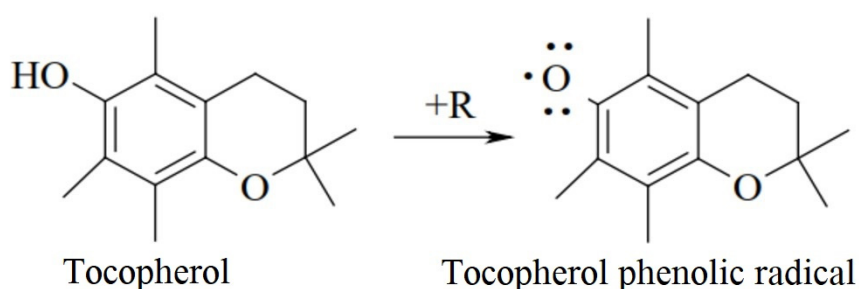


Tokol

All natural tocopherols exhibiting biological activity are derivatives of the aromatic compound tocol and differ from each other only in the number and location of methyl groups and some features of the side chain.

Different tocopherols are denoted by the Greek letters α -, β -, γ -, δ -, ϵ -, η -, ξ -tocopherols. α -tocopherol has the greatest biological activity.

The main biological role of vitamins E is in their antioxidant effect, especially in case of peroxidic oxidation of cell membrane lipids, more precisely the unsaturated higher carboxylic acids that are part of them. At the same time, tocopherols are able to bind active intermediate radicals in oxidation processes due to the transfer of a radical chain to a tocopherol molecule with the formation of stable phenoxyl radicals:



The biochemical functions of vitamin E are also to ensure the functioning of the heart muscle; it is also effective in the treatment of diabetes and asthma, prevents the formation of blood clots, cleaning veins, arteries, capillaries from blood clots.

The daily requirement of an adult for vitamin E is 10 mg/day.

Vitamins of group E are found in vegetable oils (sunflower, soybean, peanut, corn), lettuce, cabbage, cereal seeds, to a lesser extent in meat, butter, egg yolk, Table 2.25.

Table 2.25. Vitamin E content in food products

Foodstuff	Content, mg %
Soybean oil	1150
Cottonseed oil	830 – 1100
Sunflower oil	510
Peanut oil	340
Coarse bran	3
Wheat grains	158
Small seeds	32
Grade I wheat flour	15

Traditionally, the main food source of vitamin E is vegetable oils, however, only fresh, cold-pressed oils.

Vitamin E should be used in combination with vitamins A and C (butter, cream, sour milk, as well as with vegetables – potatoes, cabbage, lettuce, carrots, green parts of plants). Several methods of synthesis of group E vitamins have also been developed.

With vitamin E deficiency, muscular dystrophy and infertility are observed. However, vitamin deficiency is practically not found in humans, the daily requirement is easily met with normal nutrition. It is necessary to remember that in the first two years of life (the period of increased growth) and in the time preceding puberty (12...14 years), the child needs an additional amount of vitamin E. Vitamin E is relatively stable when heated, it is destroyed under the influence of UV rays and light.

Vitamin K is a large group of coagulation vitamins, or antihemorrhagic vitamins (phyloquinone, menaquinones). Vitamin K (from the English "coagulation" - coagulation) was discovered in 1929 by the Danish biochemist H. Dam as an antihemorrhagic factor in chickens.

Hemorrhage is a disease that is associated with a violation of the integrity of the walls of blood vessels and subcutaneous and intramuscular bleeding caused by a low blood clotting rate. Its plant variety is K₁ (phyloquinone), isolated from alfalfa in the laboratory of P. Carrera in 1939. A group of vitamins K₂ (menaquinones) was isolated and characterized from fish meal, which differ only in the length of the side chain and are classified by the number of isoprenoid residues or by the number carbon atoms in the chain.

To top it off, Doyza synthesized artificial vitamin K₃ – medion. Vitamin K is mainly represented by two compounds - vitamins K₁ (phyloquinone) and K₂ (farnoquinone or menaquinone), Fig. 2.52.

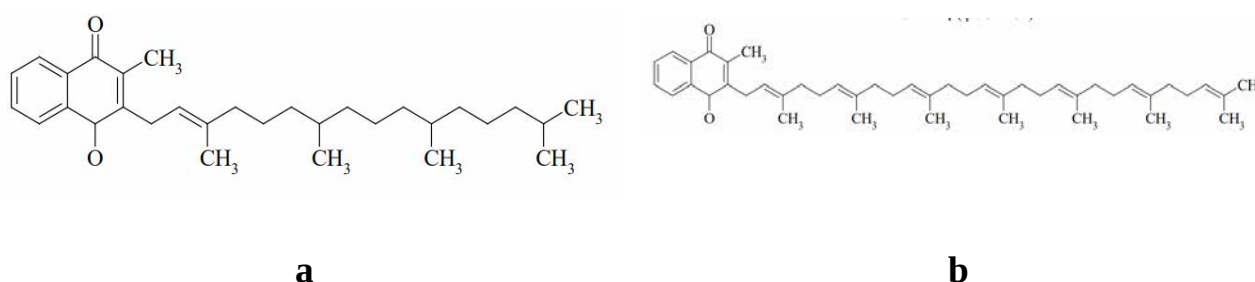


Fig. 2.52. Vitamin K₁ (phyloquinone) (a) and vitamin K₂ (menaquinones) (b)

The activity of vitamin K decreases under the conditions of exposure to radiation and X-rays, freezing, taking aspirin.

Vitamins K₁ and K₂ are necessary for a person to normalize or accelerate the process of blood clotting. Vitamin K is also used in diseases of the gastrointestinal tract, before major surgical interventions to reduce blood loss, in case of severe radiation sickness.

The daily norm of vitamin K consumption for adults is 0.1 mg.

Green parts of plants are especially rich in vitamin K. It is also found in soybean oil, liver, walnuts, and cabbage (white, blue). In addition, it is synthesized in sufficient quantity by bacteria of the small intestine (microflora of the stomach). Therefore, vitamin K deficiency occurs only in newborns; in adults, the deficiency can be caused either by the neutralization of gastric microorganisms by sulfonamide drugs or by antibiotics, Table 2.26.

Table 2.26. Vitamin K content in food products

Foodstuff	Content, mg %
Soybean oil	542
Soybeans (fresh)	189
White cabbage (fresh)	148
Egg yolk	147
Carrot	3.2
Spinach	4.4
Pork liver	0.8
Tomatoes	0.6

Vitamin K is resistant to elevated temperatures, is destroyed under the influence of light and in an alkaline environment.

Vitamin N (lipoic acid) was discovered in 1951 as a factor in the growth of yeast, as a factor in the growth of lactic acid bacteria, a number of other microorganisms, and is found in many plant and animal organisms.

It is a light yellow crystalline powder, sparingly soluble in water and much better in lower alcohols, benzene. Alkali metal salts of lipoic acid dissolve well in water. By chemical structure, lipoic acid or 5-(1,2-di-thiolan-3-yl) pentanoic acid is a cyclic disulfide, Fig.2.53.

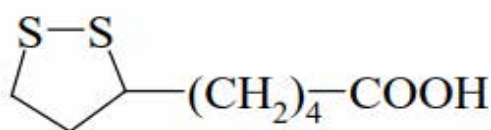


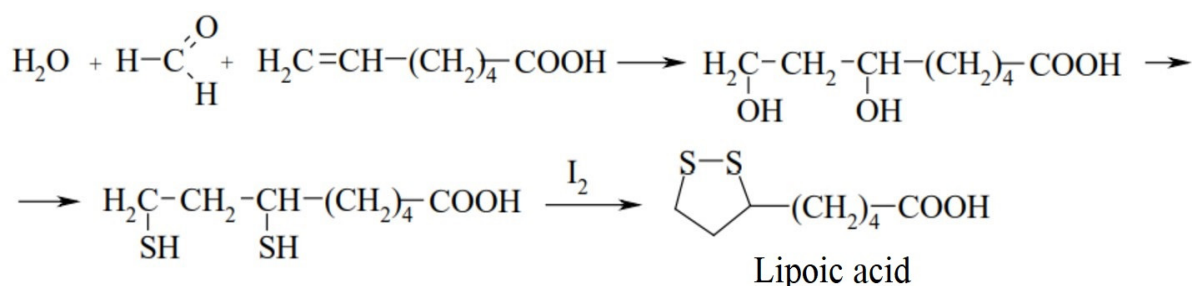
Fig.2.53. Lipoic acid

Due to the ability to change from the sulfide form (oxidized state) to the sulfhydryl form (reduced state), lipoic acid participates in redox reactions, as well as in the processes of transferring hydrogen atoms and acyl groups.

In addition, lipoic acid exhibits antioxidant properties, participates in the regulation of carbohydrate, lipid and cholesterol metabolism, detoxification in various poisonings, etc. In terms of biochemical action, it is similar to group B vitamins.

(+)-Lipoic acid is quite common in plants, animals, and microorganisms. It is found in the body mainly in the liver, heart, and kidneys. Therefore, it is obtained from the liver of cattle by hydrolysis with dilute sulfuric acid, subsequent extraction with an organic solvent and final purification on aluminum oxide.

The method of synthesis of lipoic acid developed by E. Braude and R. Linsted in 1956 consists in the condensation of 6-heptenoic acid with formaldehyde in an acidic environment according to the reaction of H. Prins.



For humans, the daily need for lipoic acid is 1...2 mg. This amount is formed by the intestinal microflora.

Lipoic acid is used in medicine to normalize lipid metabolism, treat some liver diseases (cirrhosis, Botkin's disease), diabetes, atherosclerosis, and some poisonings.

2.5.4. Characteristics of vitamin compounds and antivitamin

Vitamin-like compounds are a variety of chemical compounds that exhibit the properties of vitamins, and which are partially synthesized in the body and sometimes become part of tissues. These are biologically active substances, the deficiency of which does not lead to clearly expressed disorders, and which are closer to essential nutrients in terms of their functions. They can be divided into several groups (Table 2.27).

Table 2.27. Vitamin-like compounds

Compound	Technological function
Choline; inositol (myo-inositol, meso-inositol)	Indispensable food substances with a plastic function
Lipoic acid; orotic acid; carnitine	Biologically active substances synthesized in the human body
Bioflavonoids; methylmethionine sulfonium (vitamin U); pangamic acid (vitamin B ₁₅)	Pharmacologically active food substances
Para-aminobenzoic acid	Growth factors of microorganisms

Bioflavonoids (P) are vitamin-like substances, anti-scurvy, capillary-strengthening factor:

- strengthens blood vessels, protects against hemorrhages;
- provides tissue respiration;
- contributes to the accumulation of vitamin C;
- lowers blood pressure;
- promotes bile secretion.

There is a lot of substance P in tea (especially green), as well as in rose hips, lemons, persimmons, black currants and mountain ash, grapes, plums, capsicum and buckwheat groats.

Methylmethionine sulfonium (vitamin U) – a substance that promotes the healing of stomach and duodenal ulcers, was first discovered in cabbage juice by Chiney in 1948...1950.

In the future, the antihistaminic and antisclerotic effect of vitamin U was established, it also has a lipotropic effect.

Methylmethionine sulfonium (vitamin U) is a vitamin-like substance, an anti-ulcer factor:

- stimulates regeneration processes of the mucous membrane of the gastrointestinal tract;
- has an analgesic effect.

It is used for peptic ulcer disease of the stomach and duodenum, chronic gastritis. It has a positive effect on the function of the stomach, intestines, liver, gall bladder, as it helps to reduce secretion. Vitamin U is destroyed during heat treatment the more the longer it is. The need for vitamin U has not been established.

Contained in many vegetables: asparagus, white cabbage, parsley, onions, lettuce, pepper, carrots, tomatoes

Pangamic acid (vitamin B₁₅) is a vitamin-like substance, lipotropic, antisclerotic, antitoxic factor:

- a participant in the biosynthesis of choline;
- prevents fatty degeneration of the liver;
- stimulates the exchange of lipids and proteins;
- improves tissue respiration;
- strengthens regenerative processes in the liver;
- increases the amount of creatine in the myocardium.

Pangamic acid is part of rice bran, yeast, blood, and liver

Choline is a vitamin-like substance that takes part in the main metabolic processes, primarily in fat metabolism.

Choline is necessary for the biosynthesis of lecithin, prevents fatty degeneration of the liver, that is, it belongs to lipotropic substances. From choline, a mediator of the nervous system is formed – acetylcholine, which is necessary for the transmission of nerve impulses.

Thus, choline is a lipotropic, antisclerotic factor:

- regulates the metabolism of fats and proteins;
- structural element of lecithin and acetylcholine;
- prevents fatty degeneration of the liver;
- affects hematopoiesis.

Sources of choline are: liver, kidneys, cheese, unrefined vegetable oils, legumes, cheese, some vegetables – cabbage, spinach, etc.

Lack of choline often accompanies protein deficiency, causes fatty degeneration of the liver, which leads to the death of part of the cells and the development of cirrhosis.

Choline deficiency can also lead to an increase in cholesterol in the body, hypertension and diabetes

Inositol is a vitamin-like substance, lipotropic and antisclerotic factor:

- normalizes the metabolism of fats and cholesterol, reduces its level in the blood;
- normalizes the state of the nervous system;
- stimulates the motor function of the digestive tract.

Inositol, together with para-aminobenzoic and pantothenic acid, is considered the "vitamin of youth". Like choline, it helps maintain a healthy liver, lowers cholesterol in the blood, and prevents the fragility of blood vessel walls.

Especially active lipotropic effect of inositol is manifested in the presence of vitamin E.

Inositol is found in meat, heart, eggs, grain products, green peas, citrus fruits, and cabbage.

Lipoic acid is a vitamin-like substance, lipotropic, antisclerotic factor and growth factor:

- a participant in oxidation processes;
- performs coenzyme functions;
- regulates lipid metabolism, lowers the level of cholesterol in the blood;
- has growth properties;
- promotes the removal of toxic substances;
- vitamin C antioxidant.

Lipoic acid is widely distributed in nature, but mainly in bound form. Food sources include meat and offal, dairy products, and baker's yeast.

Lack of lipoic acid has not been detected in humans.

Carnitine is a vitamin-like substance that is necessary for normal muscle function and maintaining an optimal physiological state.

Carnitine is necessary for the transfer of fatty acids to the mitochondria, where energy is released from them.

Carnitine:

- strengthens protein metabolism, promotes fatty acid oxidation;
- transports fatty acids with long chains into mitochondria;
- regulates the concentration of ammonia in the blood.

Due to a lack of carnitine, unused fatty acids accumulate in the cytoplasm and an energy deficit occurs, which is most noticeable for the heart muscle and skeletal muscles.

Carnitine is not synthesized in the human body, and the need for it is provided by food.

The main sources of carnitine in the human body are meat and meat products.

Vitamin B₁₃ (orotic acid) has a stimulating effect on protein metabolism (on protein synthesis) and growth processes, and has a beneficial effect on the functional state of the liver.

The main food products containing vitamin B₁₃ are yeast, liver, milk and dairy products.

The lack of orotic acid leads to a violation of protein metabolism, methionine synthesis, folacin metabolism and transformations of pantothenic acid.

The role of orotic acid in metabolism determined the areas of its use in medicine.

Thus, it is used in the treatment of hematological diseases, hepatitis and gout.

The ability of orotic acid to stimulate protein synthesis is used in feeding premature babies.

Para-aminobenzoic acid (PAA) takes part in the synthesis of folic acid. It protects against intoxication with preparations of trivalent and pentavalent Arsenic and Stybium, as well as against poisoning with boric acid, bismuth, and mercury.

Para-aminobenzoic acid is quite widespread in nature.

The daily need for PAA has not been established. According to some data, it is 2...4 mg.

With a balanced diet, this need is completely satisfied due to the natural content of PAA in the food products of the diet.

Manifestations of vitamin deficiency and PAA toxicity have not been established.

Antivitamins are substances that reduce the activity of vitamins or completely inactivate them.

Antivitamins are divided into two groups:

1. Similar in structure and competing with vitamins for enzyme systems, although they cannot perform the functions of vitamins:

- deoxypyridoxine antivitamin of pyridoxine (B₆);
- pyrithiamine - thiamine (B₁);
- glucoascorbic acid – ascorbic acid (C);
- niacin - niacin (PP).

2. Substances capable of modifying, binding or destroying vitamins, reducing their biological activity:

- avidin antivitamin of biotin (H);
- ascorbate oxidase, ascorbinase;
- ascorbic acid (C);
- thiaminase (freshwater fish);
- thiamine (B₁).

The effect of antivitamins is affected by:

- degree and duration of structure violation;
- modes of technological processing (temperature, duration);
- the presence of inhibitors of anti-vitamin action (bioflavonoids, organic acids).

Most anti-vitamins lose their anti-alimentary effect due to heat treatment. Yes, 2...3 minutes of boiling inactivates ascorbatoxidase.

Bioflavonoids, organic acids inhibit the action of ascorbate oxidase (tomatoes, lemons, oranges, apples, plums, currants).

The anti-alimentary effect of ascorbate oxidase is influenced by the degree of disruption of the fetal structure (the destruction of ascorbic acid is accelerated).

2.5.5. Stability of vitamins before destruction

A significant number of vitamins are rather unstable compounds and are easily destroyed under the influence of light, air oxygen, high temperature, environment (acidic, alkaline, neutral), as a result of contact with metals, technological processing.

The influence of these factors on the stability of vitamins is presented in Table 2.28. (qualitative characteristics that only roughly describe the stability of vitamins).

Table 2.28. Influence of factors on the stability of vitamins

Vitamin	Neutral environment	Acidic environment	Alkaline environment	Air oxygen	Action of light	Heating	Maximum losses during technological processing, %
A	+	—	+	—	—	—	40
C	—	+	—	—	—	—	100
H	+	+	+	+	+	+	60
B ₁₂	+	+	+	—	—	+	10
D	+	+	—	—	—	—	40
B ₉	—	—	—	—	—	—	100
K	+	—	—	+	—	+	5
B ₃	+	+	+	+	+	+	75
B ₅	+	—	—	+	+	—	50
B ₆	+	+	+	+	—	—	40
B ₂	+	+	—	+	—	—	75
B ₁	—	+	—	—	+	—	80
E	+	+	+	—	—	—	55

+ – stable (no significant destruction),

– unstable (significant destruction is observed).

Questions for discussion and self-examination

1. Name the water-soluble vitamins.
2. What is hypovitaminosis A?
3. What are the functions of vitamin E in the body?
4. Name the functions of vitamin C.
5. Which enzymes include vitamins B₁ and B₂?
6. How is hypovitaminosis B₁₂ and folic acid manifested?
7. Which enzymes are part of vitamin PP? What are its functions in the body?
8. Differences of vitamin-like powders from vitamins.

Topic 2.6. Mineral substances

2.6.1. The role of minerals in the human body

In a rational diet, minerals are just as indispensable as proteins, lipids, carbohydrates and vitamins.

Due to the lack or excess of mineral substances in the human body, specific disorders occur, which lead to various serious diseases. Mineral substances perform a plastic function in the processes of human life and in the construction of bone tissue. Mineral substances make up a relatively large part of the human body (about 3 kg of ash).

In bones, they are present in the form of crystals, in soft tissues – in the form of a true or colloidal solution in combination mainly with proteins. Mineral substances enter the human body with food and water. The content of minerals in certain food products is given in the Table 2.29.

The concentration of mineral substances in the body is not the same. If the content of some chemical elements in human tissues is measured in grams, then the concentration of most other elements in body tissues is 1:100,000 and below. Chemical elements, the content of which is calculated in grams in the human body, are called **macroelements**, and elements found in very small concentrations are called **microelements**.

By concentration in the body, minerals are classified into:

- macroelements;
- minor elements;
- trace elements;
- ultramicroelements.

Macroelements – the content of which is calculated in grams in the human body and is more than 10 g/per kg of body weight (Table 14.2), include the following elements:

- alkali metals: Sodium (Na) and Potassium (K);
- alkaline earth metals: Magnesium (Mg) and Calcium (Ca);
- non-metals: Chlorine (Cl), Phosphorus (P) and Sulfur (S).

Table 2.29. The content of mineral substances in certain food products

Foodstuff	Macroelements, mg/100g							Microelements, µg / 100 g							
	K	Ca	Mg	Na	S	P	Cl	Fe	I	Co	Mn	Cu	F	Cr	Zn
Bread															
rye	245	35	47	610	52	158	980	3900	5,6	–	1610	220	35	2,7	1210
wheat	129	23	33	506	59	84	837	1860	–	1,8	825	134	–	2,2	735
Dairy products															
cow's milk	146	120	14	50	29	90	110	67	9	0,8	6	12	20	2	400
sour milk cheese	112	150	23	41	–	216	–	461	–	–	8	74	–	–	394

Meat															
pork	316	8	27	64,8	220	170	48	1940	6,6	8	28,5	96	69	13,5	2070
beef	355	10,2	22	73	230	188	59	2900	7,2	7	35	182	63	8,2	3240
mutton	329	9,8	25,1	101	165	168	83,6	2090	2,7	6	35	238	120	8,7	2820
Fish															
carp	265	35	25	55	180	210	55	800	5	35	150	130	25	55	2080
cod	340	25	30	100	200	210	165	650	135	30	80	150	700	55	1020
Vegetables															
cabbage	185	48	16	13	37	31	37	600	3	3	170	75	10	5	400
potato	568	10	23	28	32	58	58	900	5	5	170	140	30	10	360
carrot	200	51	38	21	6	55	63	700	5	2	200	80	55	3	400
Fruits															
plum	214	20	9	18	6	20	1	500	4	1	110	87	2	4	100
apples	278	16	9	26	5	11	2	2200	2	1	47	110	8	4	150

Minor elements – the content of which is calculated in grams in the human body and is less than 10 g/per kg of body weight - is an intermediate group between macro- and microelements, including d-metals Ferrum (Fe) and Zinc (Zn).

Microelements – the content of which is calculated in the human body in milligrams per kg of human body weight and is more than 1 mg/kg of human body weight; important trace elements are:

- d-metals: Cobalt (Co), Chromium (Cr), copper (Cu), Manganese (Mn), Molybdenum (Mo), Nickel (Ni), and sometimes Zinc (Zn);
- metal Aluminum (Al);
- non-metals: Iodine (I) and Selenium (Se).

Ultramicroelements – contained in an amount of less than 1 µg/kg (less than 0.0001% by weight); possible ultramicroelements in the human body are:

- metalloids Boron (B) and Silicon (Si);
- non-metals: Fluorine (F), Arsenic (As);
- d-metals: Vanadium (V), Table 2.30.

Table 2.30. The content of minerals in the body of an adult
(body weight 70 kg)

Element	Contents
Calcium (Ca)	1000...1500 g
Phosphorus (P)	420...840 g
Potassium (K)	140...180 g
Sulfur (S)	about 140 g
Chlorine (Cl)	70...110 g
Sodium (Na)	70...100 g
Magnesium (Mg)	25...40 g
Ferrum (Fe)	3...5 g
Zinc (Zn)	1.4...3 g

Fluorine (F)	0.8...2.5 g
Cuprum (Cu)	100...180 mg
Manganese (Mn)	10...20 mg
Cobalt (Co)	1...1.5 mg
Chromium (Cr)	5 mg
Molybdenum (Mo)	5...10 mg

2.6.2. The role of individual macronutrients in the human body and their content in food products

Macroelements are chemical elements present in the body in high concentrations exceeding 2...10 %.

The content of macroelements in the body is quite constant, but even relatively large deviations from the norm are compatible with the vital activity of the body. Macroelements, as a rule, are included in the composition of organic compounds in the body.

Calcium (Ca). Calcium is the main structural component of bones and teeth; it is part of cell nuclei, fluids contained in cells and tissues, is necessary for blood clotting.

Calcium forms compounds with proteins, phospholipids, organic acids; participates in the regulation of the permeability of cell membranes, the processes of transmission of nerve impulses, the molecular mechanism of muscle contractions, controls the activity of a number of enzymes. Thus, calcium performs not only plastic functions, but also affects a large number of biochemical and physiological processes in the body.

Calcium belongs to poorly absorbed elements. Calcium compounds that enter the human body with food are practically insoluble in water.

The alkaline environment of the small intestine promotes the formation of poorly soluble calcium compounds, and only the action of bile acids ensures its absorption.

The assimilation of calcium by tissues depends not only on the content in products, but also on its ratio with other components of food, primarily with fats, magnesium, phosphorus, and proteins.

If there is an excess of fats, there is competition for bile acids and a significant part of calcium is excreted from the body through the large intestine.

The absorption of calcium is adversely affected by an excess of manganese - experts recommend that the ratio of these elements should be 1:0.5.

If the amount of phosphorus exceeds the level of calcium in food by more than 2 times, then soluble salts are formed, which are removed by blood from bone tissue. Calcium gets into the walls of blood vessels, making them brittle, and into kidney tissue, which can contribute to kidney stone disease.

For the adult population, the recommended ratio of calcium and phosphorus in food is 1:1.5.

Phytin and oxalic acid, contained in a number of plant products, have a negative effect on calcium absorption. These compounds form insoluble salts with calcium. The daily need for calcium for an adult is 800 mg, and for children and adolescents – 1000 mg and more.

With insufficient calcium intake or impaired absorption of it in the body (with vitamin D deficiency), a state of calcium deficiency develops.

Increased removal of it from bones and teeth is observed. In adults, osteoporosis develops – demineralization of bone tissue, in children, the formation of the skeleton is disturbed, and rickets develops.

In the composition of food products, calcium is in the form of compounds that are poorly soluble or completely insoluble in water. Only the action of bile acids on them, which is accompanied by the formation of complex compounds, allows calcium to be transferred to an assimilable state. As a result of entering the human body with food, approximately 10...40% of calcium is absorbed.

The balance of calcium, phosphorus, and magnesium is best studied in diets. The optimal ratio of calcium and magnesium in products is 1:0.6.

In bread, meat and potatoes, the ratio of calcium to magnesium is on average 1:2, in milk – 1:0.1, in cheese – 1:0.15, cod – 1:0.6, in many vegetables and fruits – 1:4,5.

The optimal ratio for calcium absorption to phosphorus should be 1:1.5 for adults (according to some data 1:1), for children – 1.25:1, for infants – 1.5:1.

The best sources of calcium are milk and dairy products (cream, milk, sour milk cheese). It is somewhat less in garden greens (green onions, parsley, spinach), vegetables (beans, beans), nuts, and fish. The highest content of calcium in sesame - only 75 g of this product provides the daily need for 1100...1200 mg of calcium for women and men, respectively.

100 g of sunflower seeds contains about a third of the norm of this macroelement. Among the leaders in calcium content among dairy products are dry milk and hard cheeses with a fat content of 45-50 % (Table 2.31).

Table 2.31. Calcium content in certain food products

Foodstuff	Content, mg %
Sesame	1474
Sunflower seeds	367
"Dutch" cheese	1000
Parsley	245
Hazelnut	188
Chicken egg yolk	136
Buckwheat groats	20
Low-fat kefir	126
Parmesan	1184
Skimmed milk powder	1155
Milk chocolate	352

Dill	223
Almond	273
Bo-tree fruits	144
Dried apricots	160
Yogurt	122

Magnesium (Mg). Magnesium is necessary for the activity of a number of key enzymes that ensure the body's metabolism. Magnesium is involved in:

- maintenance of normal function of the nervous system and heart muscle;
- has a vasodilating effect; stimulates the separation of bile;
- increases the motor activity of the intestines, which in turn contributes to the removal of waste products from the body (including cholesterol).

The absorption of magnesium is hindered by the presence of phytin and excess fats and calcium in food. The daily need for magnesium is not precisely determined, but it is believed that a dose of 200...300 mg/day prevents the manifestation of a deficiency of this macroelement (it is assumed that about 30 % of magnesium is absorbed).

In case of magnesium deficiency, the assimilation of food is disturbed, growth is delayed, calcium is deposited in the walls of blood vessels, and a number of other pathological phenomena develop.

In humans, magnesium deficiency due to the nature of nutrition is extremely unlikely.

Magnesium is contained in significant quantities mostly in food products of plant origin (Table 2.32). A large amount of it is contained in wheat bran, various cereals (40...200 mg/100 g of product), legumes, uricus, dried apricots, prunes. In dairy products, meat, fish, pasta products, most vegetables and fruits do not contain a large amount of magnesium (20...40 mg/100 g).

Table 2.32. Magnesium content in certain food products

Foodstuff	Content, mg %
Wheat bran	490
Sprouted wheat	336
Almond	270
Cashew nuts	267
Brewer's yeast	231
Buckwheat	229
Hazelnut	184
Peanut	175
Millet	162
Grains of wheat	160
Pecan nuts	142
Walnuts	131
Rye grains	115

Tofu	111
Dried coconuts	90
Soybeans	88
Dried apricots	62
Garlic	36
Raisins	35
Green peas	35
Potato	34
Crabs	34
Bananas	33
Batata	31
Blackberry	30
Beet	25
Broccoli	24
Cauliflower	24
Carrot	23
Celery	22
Beef	21
Chickens	19
Tomatoes	14
White cabbage	13

Potassium (K). About 90 % of potassium is inside the cells. Together with other salts, it performs the following functions:

- osmotic pressure;
- participates in the transmission of nerve impulses, regulation of water-salt exchange; promotes the removal of water, and therefore, waste products from the body;
- supports the acid-alkaline balance of the body's internal environment;
- participates in the regulation of the activity of the heart and other organs;
- necessary for the functioning of a number of enzymes.

Potassium is well absorbed from the intestines, and its excess quickly leaves the body with urine. The daily need for potassium for an adult is 2000...4000 mg.

Symptoms of potassium deficiency in the body are impaired function of the neuromuscular and cardiovascular systems, drowsiness, a decrease in blood pressure, and heart rhythm disturbances.

Most of the potassium enters the body with plant products. Baked potatoes are one of the most significant sources and contain approximately 900 mg per serving (Table 2.33).

Table 2.33. Potassium content in selected food products

Foodstuff	Content, mg %
Dried apricots	1717
Pea	870
Spinach	774
Walnuts	664
Bean	1100
Mushrooms	440...460
Cabbage	185...375
Potato	570
Peaches	363
Beet	288
Carrot	234
Ground ginger	1343
Turmeric	2625
Radish	255
Apples	278
Grape	255
Dairy products	145
Chicken egg	140
Wheat flour	122
Cheese is fatty	112
Almond	748
Tomato	290

Sodium (Na). Sodium is contained in all tissues and biological fluids of the body. He participates in:

- in maintaining osmotic pressure in tissue fluids and blood;
- in the transmission of nerve impulses;
- regulation of acid-alkaline balance, water-salt exchange; increases the activity of digestive enzymes.

Sodium metabolism has been comprehensively studied due to its physiological properties and importance for the body. This nutrient is easily absorbed from the intestines. Sodium ions cause tissue colloids to swell, which causes water retention in the body and prevents its release.

Sodium balance is controlled by a complex interdependent system that includes the nervous and hormonal systems. An increase in plasma sodium concentration stimulates osmoreceptors in the center of the hypothalamus, regardless of the amount of liquid, which leads to a feeling of thirst.

Usually, sodium salts are not highly toxic, since fully developed kidneys effectively remove sodium from the body.

Mostly, sodium ions enter the body due to table salt – NaCl.

In case of excessive consumption of sodium chloride, the removal of water-soluble end products of metabolism through the kidneys, skin and other organs worsens.

Retention of water in the body complicates the activity of the cardiovascular system, contributes to an increase in blood pressure.

Sodium is naturally present in all foods. The method of obtaining food products largely determines the final content of sodium in it.

For example, frozen green peas contain much more sodium than fresh. Fresh vegetables and fruits contain it in the range from 10 mg/kg to 1 g/kg, in contrast to cereals and sour-milk and hard cheese, which can contain sodium in the amount of 10...20 g/kg.

The removal of sodium chloride from the body, and therefore the need for it, is affected by the amount of potassium salts produced by the body.

Phosphorus (P). Phosphorus is part of all body tissues, especially muscles and brain.

This element participates in:

- in all processes of vital activity of the organism: synthesis and splitting of substances in cells;
- regulation of metabolism; is part of nucleic acids and a number of enzymes.

In body tissues and food, phosphorus is contained in the form of phosphoric acid and its organic compounds (phosphates). Its main mass is in bone tissue in the form of calcium phosphate, other phosphorus is part of soft tissues and fluids.

Phosphoric acid is involved in the creation of molecules of many enzymes, nucleic acids, etc. The content of organic phosphorus compounds in the blood varies widely. But the amount of inorganic phosphorus is approximately constant.

The content of inorganic phosphorus increases during the consumption of dairy products, as well as during a number of kidney diseases, with fractures in the healing stage, diabetes, etc.

The concentration of inorganic phosphorus decreases in blood serum with increased thyroid function and a number of other diseases.

With a long-term deficiency of phosphorus in the diet, the body uses its own phosphorus from bone tissue. This leads to demineralization of bones and disruption of their structure – thinning. With phosphorus deficiency in the body, mental and physical activity decreases, loss of appetite, apathy is observed. The daily requirement of phosphorus for adults is 1200 mg. It increases during heavy physical or mental stress and certain diseases.

A significant amount of phosphorus is contained in products of animal origin, especially in liver, caviar, as well as in cereals and legumes. Its content in these products ranges from 100 to 500 mg per 100 g of product. Cereals (oats, pearl barley) are a rich source of phosphorus, they contain 300...350 mg of phosphorus/100 g. However, phosphorus compounds from plant products are absorbed worse than when consuming products of animal origin (Table 2.34).

Table 2.34. Phosphorus content in food products

Foodstuff	Content, mg %
Pumpkin (seeds)	1233
Poppy (seed)	900
Groats	320...350
The fish is fresh	~ 250
Beef	~ 180
Condensed cow's milk	235
Cheese is hard	500...600
Cheese	192
Egg yolk	524
Walnuts	560
Bean	~ 480
Pea	~ 330
Milk	90...180
Cream cheese	430...760
Oil	13-18
Kefir, sour cream	85...150

Sulfur (S). Sulfur is one of the most common elements found in living organisms and the biosphere. It is part of a wide variety of natural and synthetic compounds, having oxidation states from 2(–) to 6(+), along with inorganic forms.

These are volatile products of anaerobic decomposition of organic substances, thiophene and its derivatives, which are part of coal and oil, carbon compounds (thiocyanates, carbon (IV) oxide, methanethiol) formed in nature and technological cycles, thiols, amino acid mercaptans, antibiotics and xenobiotics, dyes, etc.

The total content of sulfur in the body of an adult is 140 g. Blood plasma contains 2.7 g of sulfur. Some authors indicate that plasma contains 1527 µg/ml of sulfur, and whole blood – 1784 µg/ml.

Sulfur enters the human body mostly in the form of amino acids: cysteine and methionine in the amount of 8.5 mg/day.

The intestine has limited permeability for elemental sulfur. Getting into the body in this way, it is poorly absorbed and difficult to excrete, as it forms mucopolysaccharide in the gastrointestinal tract - chondroitin of sulfuric acid, which has a long elimination period.

Sulfur penetrates better through the skin, where it turns into sulfides and sulfates, which then enter the blood and are excreted by the kidneys. Sulfur plays an important role in the body's inflammatory reactions, which is expressed in the slowing down of all three stages of this process due to the suppression of inflammatory mediators and the reduction of lipid peroxidation. At the same time, organosulfur compounds stimulate reparative regeneration processes.

Excessive concentrations of sulfur-containing compounds can cause ischemic disease, circulatory disorders, diseases of all parts of the respiratory system, and also affect reproductive function.

The value of this element in nutrition is determined, first of all, by the fact that it is part of proteins in the form of sulfur-containing amino acids (methionine and cysteine), and is also a component of some hormones and vitamins.

As a component of sulfur-containing amino acids, sulfur participates in the processes of protein metabolism, and the need for it increases sharply during pregnancy and body growth, which are accompanied by the active inclusion of proteins in the tissues that are formed, as well as during inflammatory processes. Sulfur-containing amino acids, especially in combination with vitamins C and E, have a strong antioxidant effect.

Along with zinc and silicon, sulfur determines the functional state of hair and skin. The sulfur content is usually proportional to the protein content of food products, so it is higher in animal products than in plant products.

The need for sulfur (400...600 mg/day) is met by the usual daily diet.

Chlorine (Cl). Chlorine is a macroelement that is a component of the human body. In the body, it is mainly in an ionized state due to the dissociation of salts of sodium, potassium, calcium, magnesium, etc.

The main depot of the trace element is the skin, which concentrates up to 30...60% of the introduced chlorine. In addition, this element is contained in bone tissue, blood and extracellular fluid.

It enters the body mostly together with sodium in the form of table salt. Chlorine, together with sodium, participates in maintaining the water-electrolyte balance in the body, and is also part of hydrochloric acid, the main component of gastric juice.

In addition, chlorine:

- participates in the formation of blood plasma;
- activates a number of enzymes;
- helps to remove toxins from the body, improving liver function;
- helps digestion;
- participates in the formation of special substances that contribute to the breakdown of fats;
- ensures that carbon dioxide leaves the body in a timely manner;
- deals with the state of red blood cells (erythrocytes).

The daily need for chlorine is approximately 5000 mg. The natural content of chlorine in food products varies slightly between 2...160 mg/100 g of product.

Chlorine-rich products of animal origin, cereals and beans, a smaller amount of the substance is found in fruits and vegetables. A person's need for chlorine is mostly met by table salt (up to 90%).

Chlorine in the form of metal chlorides is contained in almost all animal and plant organisms. Bread, meat and dairy products are especially rich in chlorine.

2.6.3. The role of individual trace elements in the human body and their content in food products

Ferrum (Fe). Ferrum is an element widely distributed in nature, previously it was classified as a macroelement due to its relatively high content in the body (4.2 g in the body of an average person). But if you remove hemoglobin iron, which is 75...80% of its total amount, then the concentration of iron in the tissues will be equal to or even less than the concentration of such a typical trace element as zinc.

It has been established that 20...25% of iron is reserve, from 5 to 10% is included in monoglobin, about 1 % is contained in respiratory enzymes.

This element is necessary for the biosynthesis of compounds that ensure respiration and hematopoiesis; it participates in immunobiological and redox reactions; is part of the cytoplasm, cell nuclei and a number of enzymes.

Iron-containing biomolecules perform four main functions:

- 1) electron transport;
- 2) transport and deposition of oxygen;
- 3) participation in the formation of active centers of redox enzymes;
- 4) iron transport and storage.

The assimilation of ferrum is facilitated by ascorbic acid, which forms chelate complexes with it. Another component of the diet that improves iron absorption is the 'animal protein factor', it is believed to occur due to the formation of complexes of iron with amino acids (primarily with free or peptide-bound cysteine). These complex compounds are easily absorbed by the body.

Simple carbohydrates - lactose, fructose, sorbitol, as well as such amino acids as histidine and lysine – improve the assimilation of iron. Assimilation of iron is prevented by oxalic acid and phytin. Iron absorption is inhibited by soy protein, phosphates, and fiber. Such drinks as coffee, tea, polyphenolic compounds make it difficult to absorb iron due to strong binding of iron. Vitamin B₁₂ is necessary for the assimilation of this nutrient. Ascorbic acid also contributes to the assimilation of iron, since iron is absorbed in the form of a divalent ion. Deficiency of iron in the body can lead to the development of anemia, gas exchange, cellular respiration, i.e. fundamental life-sustaining processes, are disrupted.

An adult's need for iron (14 mg/day) is completely satisfied by a normal diet. But when eating bread made from finely ground flour, which contains insufficient amounts of iron, iron deficiency is often observed.

The content of ferrum in some food products is given in the Table 2.35.

Table 2.35. Iron content in certain food products

Foodstuff	Content, mg %
Brewer's yeast	17.3
Wheat bran	14.1
Pumpkin seeds	11.2
Zucchini seeds	11.2
Sprouted wheat	9.4

Beef liver	8.8
Sunflower seeds	7.1
Buckwheat	8.3
Parsley	6.2
Seafood	6.1
Raisins	3.5
Bilberry	7.0
Dates	3.0
Pork	2.9
Pecan nuts	2.4
Eggs	2.3
Beef	3.1
Lungs	10.0
Mutton	1.9
Treacle	19.5
Green peas	1.9
Chicken heart	6.2
Salmon	1.5
Broccoli	1.1
Currant	1.1
Cauliflower	1.1
Sesame	11.5
Red cabbage	0.8
Chocolate	2.3
Mushrooms	0.8
Bananas	0.8
Beet	0.7

Copper (Cu). Copper is one of the most important irreplaceable trace elements necessary for human life. The body of an adult contains 1.57...3.14 mmol of cuprum, and half of this amount falls on muscles and bones, 10 % on liver tissue.

Food intake of copper should be 2...5 mg (0.031...0.079 μ mol) per day, and daily consumption of less than 2 mg is dangerous due to the possibility of copper deficiency conditions.

The main processes of copper absorption take place in the stomach and small intestine, the mucous membrane of which contains metallothionein, which forms complex compounds with copper. The key role in the exchange of copper is played by the liver and its main structural elements - hepatocytes.

Copper participates in biochemical processes as a component of proteins that carry electrons and carry out oxidation reactions of organic substrates with molecular oxygen. Copper owes this role to its special property as a transition metal. Having two valence states, depending on the nature and location of the ligands, it allows copper-containing proteins to cover a wide range of redox potentials, as well as to bind oxygen and carbon (IV) oxide back.

Copper is a necessary element in human metabolism, playing a role in the formation of red blood cells, the release of tissue iron, and the development of the skeleton, central nervous system, and connective tissue.

Usually, copper is combined with proteins: hemocuprene in erythrocytes and ceruloplasmin in blood plasma, in which copper is an integral part of their structure; metallothionein is a protein responsible for copper accumulation.

A number of copper-containing enzymes were isolated and studied, in particular, cytochrome oxidase, ascorbic acid oxidase, and uricase. Copper has a pronounced anti-inflammatory effect, softens the manifestation of autoimmune diseases, such as rheumatoid arthritis.

In addition, copper is necessary for the formation of unsaturated fatty acids. The daily requirement for this element is about 2 mg. Food products such as liver, egg yolk, and green vegetables are sources of copper (Table 2.36).

Iodine (I). Iodine performs its biological function as a component of thyroid hormones, which to some extent is explained by its high affinity to tyrosine.

Iodine deficiency in humans is a serious problem, despite hypiodosis prevention programs that are carried out at the state level in various countries.

Iodine is a real biomicroelement. In the body of an adult, it is contained in the amount of 20...30 mg, including about 10 mg in the thyroid gland.

A person's daily need for iodine is 50...60 µg, which most researchers consider to be insufficient, since the optimal activity of the whole organism requires significantly larger amounts of iodine, at least 300 µg.

In food and water, iodine is present in the form of iodides, which are absorbed throughout the digestive tract.

Sea products are the richest in iodine. Thus, in sea fish, the iodine content is about 50 µg/100 g, in cod liver up to 800, in sea cabbage, depending on the type and time of collection, from 50 to 70,000 µg/100 g of product. But it should be taken into account that during long-term storage and heat treatment of food products, a significant part of iodine (from 20 to 60%) is lost.

Table 2.36. Copper content in food products

Foodstuff	Content, mg %
Brewer's yeast	3.2
Pollock liver	10.0
Wheat bran	1.4
Beef liver	3.8
Pork liver	3.7-7.5
Sesame	4.1

Rosehip fruits	1.8
Mushrooms	0.9
Squids	1.5
Raisins	0.36
Strawberries	0.13
Potato	0.14
Cabbage	0.075
Apples	0.110
Cod liver	12.5
Chocolate	1.2
Cocoa powder	3.9
Mutton	0.24
Cucumbers	0.1
Spinach	0.12
Sunflower seeds	1.8
Peanut	1.14
Pea	0.75
Apricot	0.14
Tomatoes	0.12
Corn	0.29
Carrot	0.08
Onion	0.085

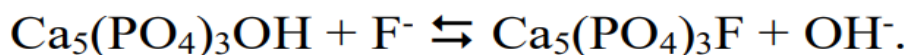
According to the WHO, iodine deficiency leads to mental retardation, which can be prevented by mass iodine prophylaxis (biologically active supplements, food products rich in iodine or enriched with it). For this, iodine is introduced into drinking water and table salt. The most effective way to prevent deficiency states and optimize the body's supply of iodine is to use iodized salt with an iodide content of 25...55 µg/g.

Fluorine. The basis of the biological role of fluorine is its ability to effectively replace the hydroxyl ion not only in the apatite of bone tissue, but also in non-mineralized tissues. In addition, it is believed that the substitution process can also occur in the active centers of enzymes.

The fluoride ion can replace the hydroxide ion better than any other ion because they have almost the same ionic radii, the same charge, and a degree of hydration equal to two. Fluorine is added to apatite either during the formation of the primary crystal or by replacing the hydroxide ion in the transformed mineral.

So, for example, the mineral base of dental tissues - dentin - consists of hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$ and fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

The fluoride ion easily replaces the hydroxyl ion in hydroxyl apatite, forming a protective enamel layer of harder fluorapatite:



The main source of fluoride for humans is drinking water. Recently, more and more attention has been paid to the control of fluoride content in drinking water.

Fluoride, which a person uses with water, is almost completely absorbed.

The use of fluoridated water in food processing enterprises can often double the level of fluoride content in finished products.

Chromium (Cr). Chromium has an important biological role, the main manifestations of which are its interaction with insulin in the processes of carbohydrate metabolism, participation in the structure and function of nucleic acids and the thyroid gland.

Chromium is absorbed mainly in the small intestine. Normally, the assimilation of this element does not exceed 0.4...0.7 % of the administered dose, while for patients with diabetes, this indicator is 3 times higher. Absorption of chromium depends on chelating agents. Thus, oxalic acid increases, and phytic acid significantly decreases the assimilation of this element. Ligands that increase the absorption capacity of chromium prevent its precipitation in the form of basic salts in the near-neutral environment of the intestinal tract.

Chromium absorption is also affected by iron and zinc. With a deficiency of these trace elements, the absorption capacity of chromium increases.

It is believed that chromium is necessary for glucose and lipid metabolism and for the utilization of amino acids by some body systems. It is also important for the prevention of mild forms of diabetes and atherosclerosis in humans. Chromium is absorbed both from the gastrointestinal tract and from the respiratory tract. The amounts absorbed are different for each of these systems and depend on the form of chromium. Trivalent chromium is an essential form of the element for humans, hexavalent chromium is toxic. Chromium is distributed throughout the tissues of the human body in varying but usually low concentrations.

Today, it is considered the norm to consume about 150 mg of chromium per day.

Inorganic chromium is poorly absorbed, much easier - in organic compounds, that is, in the form in which it is in living organisms.

Foods vary greatly in chromium levels, ranging from 20 to 550 µg/kg. Rich sources of chromium are brewer's yeast, liver (10...80 µg/100 g). In smaller quantities, this element is found in unpeeled potatoes, beef, fresh vegetables, bread made from coarsely ground flour, cheese. Particularly poor in chromium are highly refined foods such as refined sugar, fine wheat flour and bread baked from it.

Manganese (Mn). Normally, the body of an adult weighing 70 kg contains 10...20 mg of manganese.

Manganese is required as a cofactor in a number of enzyme systems; it contributes to the correct functioning of flavoproteins, in the synthesis of sulfonated mucopolysaccharides, cholesterol, hemoglobin, and in a large number of other metabolic processes. The main ways of absorption of manganese are the respiratory and gastrointestinal tracts. Due to the low solubility of manganese in gastric juice, only 3...4 % of the administered amount of the substance is absorbed from the gastrointestinal tract. The absorption of manganese is closely related to the absorption of iron.

The need for manganese is 0.2...0.3 mg per 1 kg of human weight per day. The content of manganese in food products is sufficient to meet the body's needs for this trace element.

Its content in products of vegetable origin ranges from 8 to 50 mg/kg, in products of animal origin it is much less - 0.1...2 mg/kg.

The most manganese is found in cranberries and tea, not much less in chestnuts, cocoa, vegetables, fruits (100...200 µg/100 g).

Nickel (Ni). Recently, the biological effect of nickel has been intensively studied in connection with global environmental pollution, annually 15,000 tons of nickel are released into the atmosphere and soil of the planet.

A significant part of soluble nickel compounds is absorbed by both photosynthetic organisms of the world's oceans and marine animals.

Eating products of animal and vegetable origin leads to increased entry of this trace element into the human body. Another source of nickel penetration into the body is local man-made geochemical anomalies, which are formed around enterprises that process nickel. Absorption of nickel, even with its increased content in the diet, ranges from 1 to 10%, requires energy and is carried out by a common transport system with iron. Experiments on laboratory animals have proven that, in conditions of iron deficiency, the assimilation of nickel occurs much more.

When considering the vital necessity of nickel for humans, it is necessary, as in the case of cobalt, to consider two main aspects - its indirect effect on the body through microorganisms and exogenous enzymes of the digestive tract and its direct participation in metabolism.

The microflora of the gastrointestinal tract contains a number of enzymes that contain nickel. These enzymes are involved in the digestion of food and can significantly affect the physiological state of a person.

At this time, its role as a coenzyme in the processes of iron metabolism has been established. As a cofactor of an unidentified iron-binding bioligand or involved in the enzymatic conversion of Fe^{3+} to Fe^{2+} , nickel promotes iron absorption in the gastrointestinal tract. At the same time, an increase in the intake of iron in the body is accompanied by an increase in the need for dietary nickel.

The biological effect of nickel on the body is also explained by the fact that it participates in the structural organization and functioning of the main cellular components - DNA, RNA and protein. Along with this, there is an opinion that nickel is involved in the hormonal regulation of the body.

In addition, nickel promotes the assimilation of copper, another essential element for hematopoiesis. During experimental studies of nickel preparations, a significant acceleration of the regeneration of erythrocytes and an increase in the amount of hemoglobin were shown. The importance of nickel in food or extracted from natural products is emphasized by the fact that synthetic compounds of this element belong to carcinogenic substances.

Nickel is present in most foods, but in concentrations below (and usually much below) 1 mg/kg. Little is known about the chemical form of nickel in foods, although it may partially form complexes with phytic acid.

The intake of nickel with food, according to the available data, varies from 200 to 900 µg/day. It was determined that the nickel content in wines and beer is 100 and 50 µg/l, respectively.

Zinc (Zn). It is known that up to 85% of the total amount of this element is absorbed from food that is not rich in zinc, and only 10...30% from ordinary food.

Zinc as a coenzyme participates in a wide range of protein biosynthesis reactions (more than 70) and nucleic acid metabolism (including DNA replication and transcription processes), which ensure, first of all, the growth and sexual maturity of the organism. At the same time, zinc, together with manganese, are specific trace elements that affect the state of sexual function, namely the activity of some sex hormones, spermatogenesis, the development of male gonads and secondary sexual characteristics.

Zinc, together with sulfur, participates in the processes of growth and regeneration of skin and hair. Along with manganese and copper, zinc largely ensures the perception of smells and tastes. Zinc, as an irreplaceable component, is part of the insulin molecule, and its level is found to be reduced in patients with diabetes.

It is very important that this trace element is a coenzyme of alcohol dehydrogenase, which ensures the metabolism of ethyl alcohol. At the same time, the level of absorption of zinc in chronic alcoholism is sharply reduced. It is also necessary to take into account the participation of zinc in porphyrin metabolism, which is closely related to hematopoietic processes. In addition, zinc (along with vitamin C) is necessary for the activation of folic acid from the bound form, after which folacin can penetrate into cells and be included in hematopoietic processes.

Another important relationship between zinc and vitamins is traced to vitamin A.

First, zinc as a coenzyme promotes the release of vitamin A from the intrahepatic depot.

Secondly, zinc is necessary for the transformation of retinol into retinal, which is involved in the formation of the visual pigment of the retina.

Thus, the so-called "chicken blindness" (i.e., impaired night vision) can develop not only in the absence of vitamin A, but also zinc.

Zinc together with vitamin B₆ ensures the metabolism of unsaturated fatty acids and the synthesis of prostaglandins.

Zinc is very important for the processes of digestion and assimilation of nutrients. Thus, zinc ensures the synthesis of the most important digestive enzymes in the pancreas, and also participates in the formation of transport particles, in the composition of which food fats can be absorbed into the blood.

Along with B vitamins, zinc is an important regulator of nervous system functions. In case of zinc deficiency, emotional disorders, emotional instability, irritability can occur, and in very severe cases, cerebellar dysfunction.

Finally, more and more data are accumulating in favor of the participation of zinc in the processes of maturation of lymphocytes and reactions of cellular immunity. The primary importance of this trace element for body functions is emphasized by the fact that zinc is one of several minerals for which separate and quite specific deficiency syndromes have been described.

In the case of zinc deficiency, the so-called enteropathic dermatitis develops. This disease is especially characteristic of certain national groups that use unleavened bread as their main food.

This bread contains large amounts of phytic acid salts, which are usually broken down by yeast phytase. Phytase binds dietary zinc to insoluble compounds.

The content of zinc in food products usually ranges from 150 to 25,000 µg%. But in liver, meat and legumes it reaches 3000...5000 µg%. The daily need for zinc is completely satisfied by the usual diet. The average daily intake of zinc with only drinking water is about 400 µg, Table 2.37.

Selenium (Se). In the 70s, 19 cents. properties of selenium were comprehensively studied and it turned out that this element is necessary for the activation of one of the key enzymes of the body's antioxidant system - glutathione peroxidase.

This enzyme prevents the activation of peroxidation of membrane lipids – a process that causes a violation of the structural and functional integrity of cell membranes, contributes to an increase in permeability and a decrease in the resistance of cellular structures to damage.

Selenium can be absorbed through the digestive tract, skin and lungs. The absorption of soluble forms of selenium in the digestive tract is 8...100%.

It has been proven that organic compounds of selenium are absorbed better than inorganic ones. The cardiovascular system especially suffers from selenium deficiency. This manifests itself in the form of progressive atherosclerosis and weakness of the heart muscle, and under conditions of chronic selenium deficiency, almost incurable cardiomyopathy can develop.

Table 2.37. Table of zinc content in food products

Foodstuff	Content, mg %
Fresh oysters	148.7
Ginger root	6.8
Steak	5.6
Mutton	5.3
Pecan nuts	4.5
Pea	4.2
Beef liver	3.9
Egg yolk	3.5
Grains of wheat	3.2
Grains of rye	3.2
Oat	3.2
Peanut	3.2
Almond	3.1
Walnuts	3.0
Sardines	2.9
Chicken meat	2.6
Buckwheat	2.5

Green peas	1.6
Shrimps	1.5
Turnip	1.2
Parsley	0.9
Potato	0.9
Garlic	0.6
Carrot	0.5
Whole grain bread	0.5
Cow's milk	0.4
Pork	0.4
Corn	0.4
Grape juice	0.3
Olive oil	0.3
Cauliflower	0.3
Spinach	0.2
White cabbage	0.2
Lentil	0.2

In addition, it has been proven that selenium is a necessary coenzyme of iodine peroxidase, the main enzyme for the synthesis of thyroid hormones, that is, selenium deficiency can significantly increase the manifestations of iodine deficiency, and the prescription of iodine-only drugs can be ineffective.

Recently, at the level of modern research, one of the important observations of ancient Chinese medicine has been confirmed, which indicates that adequate supply of selenium to the body slows down the aging process and leads to longevity.

It has been established that vitamin E and selenium act on different links of the same process and are strictly complementary to each other, that is, their antioxidant activity under the conditions of joint use increases sharply. The synergism of both antioxidants is particularly interesting in the context of anticancer activity. Thus, it was shown that the appointment of selenium preparations simultaneously with vitamin E significantly enhanced the anti-carcinogenic effect in relation to experimental tumors. In this regard, it is interesting to note that plant seeds, along with vitamin E, also contain significant amounts of selenium. The intake of selenium with food depends on the conditions and nature of consumption and the level of selenium content in food products.

Vegetables and fruits are a "poor" source of selenium, in contrast to grains, grain products, meat (especially offal), seafood, which contain significant amounts of selenium, usually much higher than 0.2 mg/kg on a raw weight basis.

Molybdenum (Mo). Molybdenum is the only element of the second series of transition elements whose biological function is currently understood.

Molybdenum is well absorbed both from food and from most of its inorganic compounds. The total amount of molybdenum in the body of an adult is approximately 7 mg. The content of molybdenum in the blood is about 0.5 µg per 100 ml.

Higher concentrations of this element were found in people living in regions where the soil is most rich in compounds of this metal. Thus, in some areas of Armenia, frequent cases of gout disease were noted in residents who eat, for the most part, local products, in which extremely high concentrations of molybdenum were found. Its content in the diet of residents of this area is 10–15 mg. In other areas, where cases of gout were less common, people received only 1–2 mg of molybdenum per day with food.

Molybdenum is a component of a number of enzymes, such as xanthine oxidase, aldehyde oxidase, sulfate oxidase. It is known that molybdenum inhibits the development of tooth decay. The daily need for molybdenum is 2 µg per 1 kg of body weight.

Various types of vegetables (for example, legumes) and internal organs of animals are the richest in molybdenum.

Cobalt. All data accumulated to date indicate that the main biological function of cobalt in the body is its presence in the vitamin B₁₂ molecule. Some authors believe that cobalt deficiency is a deficiency of vitamin B₁₂.

Cobalt is better absorbed by the human body than other trace elements. The maximum concentration of cobalt in tissues is approximately 100 µg/kg. The total content of cobalt in the body of an adult is 5 mg.

A person receives with food 5.63...7.94 µg of cobalt, of which 73...97 % is absorbed per day.

The average daily requirement for cobalt is 60 µg per 1 kg of body weight.

It is believed that a person needs cobalt only in the form of cyanocobalamin (vitamin B₁₂). The intake of cobalt with drinking water can reach up to 10 µg per day. 90% of the total amount of cobalt consumed by humans comes from plant products. In cow's milk, the level of this trace element is low and ranges from 0.4 to 1.1 µg/l.

The liver and kidneys of animals usually contain 0.15...0.25% of dry matter.

The ability to absorb cobalt and iron increases significantly with a deficiency of the latter.

2.6.4. The influence of technological processing on the mineral composition of food products

Mineral substances, unlike vitamins and amino acids, cannot be decomposed under the influence of heat treatment, light, oxidants, extreme pH values or other factors that affect organic nutrients. Essentially, minerals are indestructible. However, they can be removed from foods by leaching or physical separation.

During the processing of food raw materials, as a rule, there is a decrease in the content of mineral substances (except for the addition of table salt). In products of plant origin, they are lost with waste. Thus, the content of a number of macro- and especially microelements in the production of groats and flour after grain processing decreases, since there is more of these components in the removed shells and germs than in the whole grain.

For example, on average, wheat grain and rye contain about 1.7 % of ash elements, while flour, depending on the variety, contains from 0.5 (in the highest grade) to 1.5 % (in the first and second). A comparative analysis of the mineral

composition in wheat flour of the highest grade and in flour from whole grain is given in Table 2.38.

Table 2.38. Content of micro- and macroelements in wheat, mg/100 g

Element	Wheat	
	Whole grain	Highly purified
Ca	41	16
P	372	87
Fe	3.3	0,8
K	370	95
Mg	60	16
Zn	3.50	0.07
Cu	1.00	0.32
Mo	0.14	0.02
Mn	3.2	0.83
Cr	0.014	0.002

When cleaning vegetables and potatoes, 10 to 30 % of minerals are lost. If they are subjected to thermal processing, depending on the technology, another 8 to 48 % is lost (Table 2.39)

Table 2.39. Effect of heat treatment on the content of mineral substances in individual food raw materials

Food raw materials	Losses of mineral substances after heat treatment, % (calculated as ash)		
	boiling	steaming	frying, baking
Whole peeled potato	19–38	8–19	insignificant
Beet root	26–42	13–21	
Carrot root	18–48	9–24	

Meat, fish products and poultry mainly lose macronutrients such as calcium and phosphorus during the separation of the flesh from the bones.

During thermal processing (boiling, frying, stewing), meat loses from 5 to 50% of mineral substances. However, if the processing is carried out in the presence of bones containing a lot of calcium, it is possible to increase the calcium content in technologically processed meat products by up to 20%.

A certain amount of microelements can pass into the final product in the technological process due to insufficient quality equipment. Thus, during the production of bread, the iron content can increase by 30 % as a result of the contact of the dough with the equipment. This process is undesirable, since toxic elements contained in the form of impurities in the metal can pass into the product along with iron. During the storage of canned goods in cans that do not meet the sanitary and hygienic requirements or under the conditions of violation of the protective varnish layer, such highly toxic elements as lead, cadmium, and tin can enter the product.

It should be taken into account that a number of metals, such as iron and copper, even in small concentrations, can cause unwanted oxidation of products. Their catalytic oxidizing abilities are particularly evident in relation to fats and fat-containing products.

So, for example, at concentrations of iron above 1.5 mg/kg and copper 0.4 mg/kg during long-term storage of butter and margarines, these metals cause rancidity of products. During the storage of beverages in the presence of iron above 5 mg/l and copper 1 mg/l, under certain conditions, clouding of beverages can often be observed.

Questions for discussion and self-examination

1. *What chemical elements are called macroelements? Name them.*
2. *What chemical elements are called trace elements?*
3. *Name the essential trace elements.*
4. *Name conditionally toxic and toxic elements.*
5. *What are the functions of calcium in the body?*
6. *What are the norms of calcium consumption for adults and children?*
7. *What is the biological role of phosphates in the body?*
8. *What is the role of magnesium in the body?*

Topic 2.7. Enzymes and enzyme preparations

2.7.1. Characteristics and classification of enzymes

Enzymes are biological protein catalysts that significantly increase the rate of chemical reactions without the formation of byproducts. Enzymes got their name from the Latin word fermentum – leaven. Enzymes are produced only in the cells of animals, plants and microorganisms.

The composition of some enzymes may include a non-protein component, which is bound to the enzyme and takes part in catalytic reactions. As a rule, the coenzyme binds to the protein component of the enzyme – the apoenzyme, and together with it forms a catalytically active holoenzyme complex.

Features of enzymes are as follows:

- 1) great power of catalytic action (increase the rate of reactions by 10⁸...10²⁰ times);
- 2) specificity of action, i.e. they catalyze clearly specific reactions; main types of specificity:
 - absolute specificity – the enzyme catalyzes the transformation of only one substrate (enzymes with broad substrate specificity, such as lipases, esterases, phosphatases are also known);
 - group specificity – the enzyme acts on a group of related substrates that have certain structural features; for example, on a certain type of bond: α -amylase hydrolyzes polymers of α -1,4-linked glucose;

– specificity in relation to certain types of reactions – such enzymes show the least specificity, they act regardless of which groups are present near the bond to which the enzyme's action is directed;

– stereochemical specificity – the enzyme catalyzes the conversion of only one stereochemical form of the substrate (converts only the L- or only the D-form of the substrate);

3) lability, that is, they change their activity under the influence of pH, temperature, the presence of activators and inhibitors, etc (Fig. 2.54).

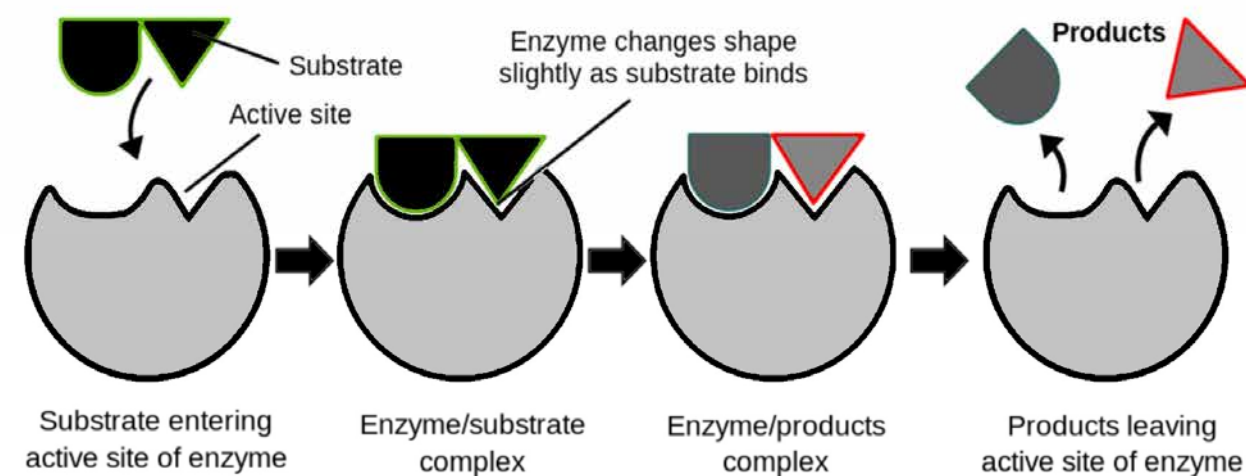
The biological role of enzymes is significant, as they take an active part in most transformations occurring in organisms:

- processes of digestion and absorption;
- reactions of synthesis and decay of substances;
- ensure the passage of biochemical reactions.

Action of enzymes. The enzymatic reaction consists of two stages:

1) an enzyme-substrate complex is formed, which requires a significantly lower activation energy (compared to the course of the reaction without an enzyme);

2) this complex breaks down into reaction products and a free enzyme that can interact with a new substrate molecule. The enzymatic reaction can be represented by



the following scheme:

Fig. 2.54. Scheme of the interaction of an enzyme and a substrate

About 3,000 enzymes are already known. According to the classification of the International Commission on Enzymes, all enzymes are divided into separate classes (Fig. 2.55), according to the reactions they catalyze:

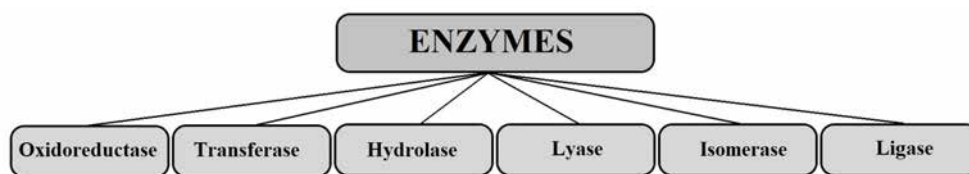


Fig. 2.55. Classification of enzymes according to their origin

Given that enzymes are protein substances, pH and temperature play a major role in the manifestation of their activity. It should be remembered that when the pH of the medium changes, the charge of the protein changes, sometimes causing a significant change in the conformation of the polypeptide chain. The effect of temperature on the activity of enzymes manifests itself to the same extent as on all chemical reactions, i.e. a temperature increase of 10°C increases the reaction rate by 2-3 times (Van Hoff's rule).

2.7.2 Hydrolases. The mechanism of their action and the importance of food technologies

Class 3 hydrolases catalyze the splitting of complex compounds into simpler ones with the addition of water. Hydrolases are divided into 11 subclasses (Fig. 2.56).

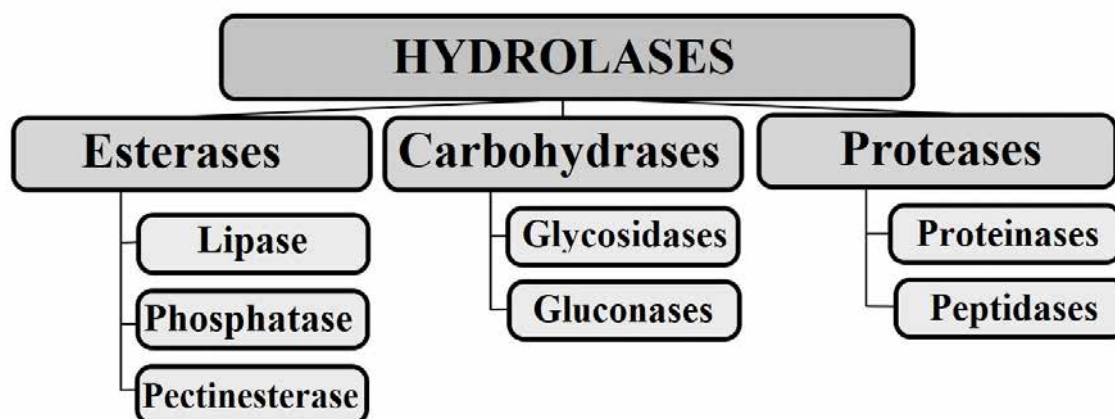
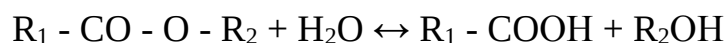


Fig 2. 56. Classification of hydrolases

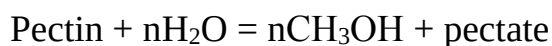
Subclass 3.1. Esterases. They split the ester bond.



Can catalyze fission and synthesis reactions. Lipases, pectinesterases, and phosphatases are particularly important among the enzymes in this class.

Lipases catalyze the breakdown of fats. They have an important role in milk – lipase contributes to the formation of aromatic substances; wheat lipase leads to bitterness of flour; in cereals – to increase acidity and decrease quality.

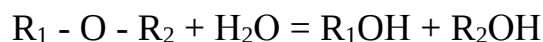
Pectinesterase catalyzes the reaction of cleavage of methanol from pectin:



A highly active enzyme contained in tomatoes, oranges, alfalfa, mold mushrooms. Phosphatases hydrolyze esters of phosphoric acid (nucleotides, phosphatides). The sources of these enzymes are milk, potatoes, and yeast.

Phosphatases lead to a deterioration in the quality of pasta made with eggs.

Subclass 3.2. Carbohydrases. They catalyze the hydrolysis of carbohydrates according to the equation:



There are glycosidases that catalyze the cleavage of oligosaccharides (up to 10 monomeric units) and glycosides, and gluconases that act on substrates with a high degree of polymerization.

Proteases. Enzymes that act on peptide bonds and perform hydrolytic cleavage of proteins and peptides. They hydrolyze proteins and polypeptides according to the equation:



Due to the fact that these enzymes catalyze the cleavage of a peptide bond, they are called peptide hydrolases.

Proteases are divided into proteinases and peptidases (Fig. 2.57).

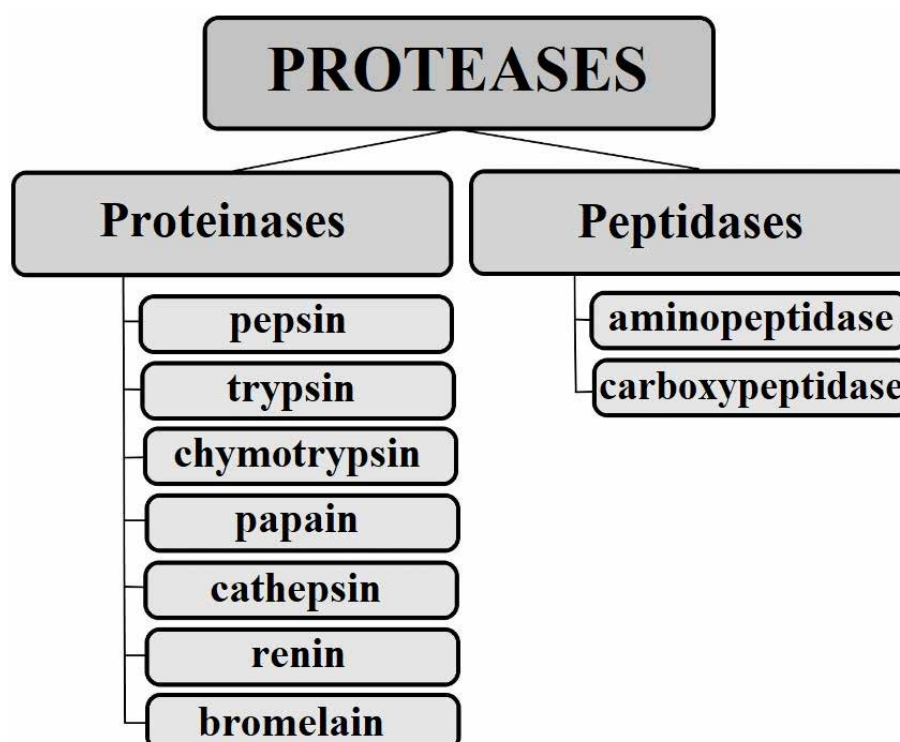


Fig. 2.57. Classification of proteases

he first perform hydrolysis of proteins, the second - polypeptides and dipeptides.

Proteinases: pepsin, trypsin, chymotrypsin, papain, cathepsin, renin, bromelain, etc.

Pepsin hydrolyzes bonds formed by aromatic amino acids - tyrosine, phenylalanine. It is a digestive enzyme. In industry, it is used to precipitate casein in the manufacture of cheeses, sometimes replacing rennin, in brewing - to stabilize beer, as a medical drug.

Renin is similar in specificity to pepsin. It is used in the production of cheese.

Trypsin and chymotrypsin. The first hydrolyzes bonds formed by arginine and lysine, the second – by aromatic amino acids.

Papain, bromelain, ficin are plant proteinases that hydrolyze peptide bonds formed with the participation of leucine and glycine.

Peptidases: aminopeptidases (or N-terminal) and carboxypeptidases (C-terminal). Dipeptidases split dipeptides into free amino acids.

2.7.3. Oxidoreductases. Mechanism of their action and role in food technology

As the name suggests, enzymes belonging to the class of oxidoreductases catalyze redox reactions. The oxidizing substrate is considered as a hydrogen or electron donor. Oxidoreductases are divided into 17 subclasses (Fig. 2.58).

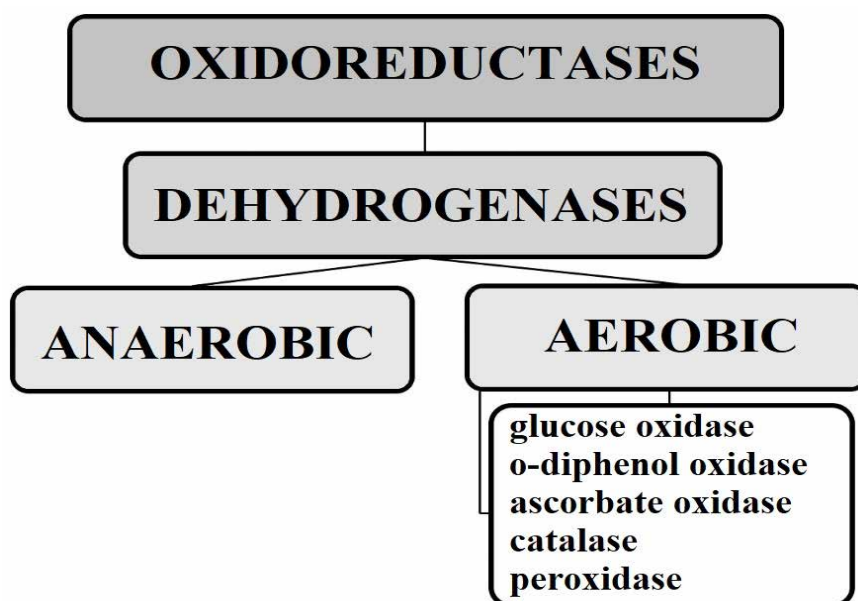
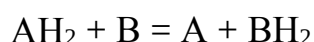
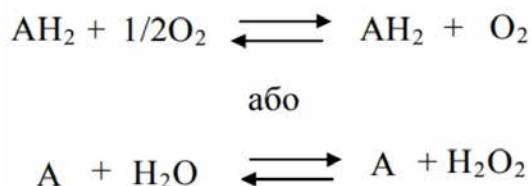


Fig. 2.58. Classes of oxidoreductases

The leading place in the class of considered enzymes is occupied by **dehydrogenases**, which carry out the dehydrogenation reaction:



According to the mechanism of hydrogen transfer to the acceptor, dehydrogenases are divided into aerobic and anaerobic. Aerobic dehydrogenases are able to transfer hydrogen to the air oxygen substrate (with the formation of water and hydrogen peroxide):



Among the representatives of aerobic dehydrogenases:

Glucose oxidase transfers H₂O from glucose to O₂ with the formation of H₂O₂. This enzyme is used to remove O₂ from products whose color or aroma deteriorates as a result of oxidation processes (beer, drinks, juices, fatty products). Synthetic films impregnated with glucose oxidase, glucose and buffer are used for packing fat-containing products. Removal of small amounts of glucose is desirable to prevent the reaction of melanoid formation when obtaining egg and milk powder.

o-Diphenoloxidase – (trivial names tyrosinase, catecholase, phenolase, polyphenoloxidase), the enzyme catalyzes the oxidation of mono-, di- and triphenols. During the oxidation of monophenol, the enzyme acts bifunctionally:

First, O₂ binds to an aromatic ring to form o-diphenol, and then H₂ is removed from diphenol and transferred to oxygen to form water.

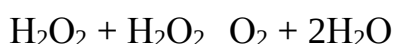
Diphenols are oxidized without combining with the oxidation of monophenols. Dark products (phlobaphens, melanins) arise as a result of the action of an enzyme during a purely chemical condensation reaction of two formed quinones.

The enzyme is found in potatoes, fruits, and plant leaves. In some cases, the action of o-diphenoloxidase leads to the appearance of the desired color and aroma of food products, for example, during tea fermentation. At the same time, slowing down or preventing the browning of plant materials, fruits, vegetables, and juices is of great interest. Enzyme inhibitors are used for these purposes. Substances complexing with o-quinones, for example, meta- and tetraborates, are used. Ascorbic acid contributes to the reduction of o-quinones, but high concentrations are required. Most often, when processing plant material to prevent browning, sodium sulfite and sulfur dioxide are used as reducing agents.

In some cases, it should be taken into account that the enzyme is thermolabile, so heat treatment allows to exclude the effect of this enzyme.

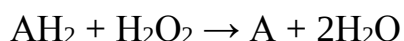
Ascorbate oxidase catalyzes the oxidation of ascorbic acid. This enzyme is found in many plants and is responsible for the destruction of vitamin C. There are natural inhibitors of this enzyme: oxalic, citric, tartaric acids, pectins, flavonoids, some proteins.

Catalase **dehydrogenates** a hydrogen peroxide molecule:



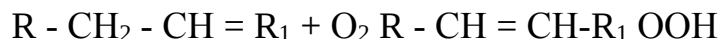
The hydrogen taken from the substrate is transferred to the second molecule of hydrogen peroxide. Catalase preparations from the liver or microorganisms are used for pasteurization and sterilization of milk.

Peroxidase catalyzes the reaction:



During tea fermentation, peroxidase, along with phenoloxidases, contributes to the formation of colored and aromatic components.

Lipoxygenase catalyzes the reaction: unsaturated fatty acid + O₂ = unsaturated fatty acid peroxide



This enzyme is found in wheat, oilseeds, legumes, its content is especially high in soy flour. The action of the enzyme must be limited, as its activity leads to rancidity of fats in products, destruction of carotene. Tocopherol is an inhibitor of this enzyme. At the same time, the oxidation of wheat flour fats during dough kneading leads to strengthening of gluten.

2.7.4. Characteristics of enzyme preparations

Enzyme preparations are compositions of enzymes with different functional properties or individual enzymes.

In food technology, enzyme preparations are used for the purpose of intensifying biochemical processes, obtaining new products, and accelerating technological processes.

Enzyme preparations are mainly obtained by microbiological synthesis by cultivating producer microorganisms: fungi, bacteria, yeast. Depending on the type of producers, enzyme preparations differ in the mechanism of action on the substrate, final products, optimal conditions for their maximum activity.

Thus, the bacterial enzyme preparation amylosubtilin has better thermal stability compared to fungal amylorizin.

A number of factors affect the activity of enzymes, namely:

- substrate concentration and availability;
- enzyme concentration;
- reaction temperature;
- pH of the medium;
- duration of fermentation;
- the presence of activators or inhibitors in the environment.

Enzyme preparations with different activity are most widely used in the food industry (Fig. 2.59).

Amylolytic enzyme preparations. The main enzyme contained in amylolytic enzyme preparations is amylase.

Under the action of amylase, starch is hydrolyzed with the formation of sugars and dextrans, which contributes to the intensification of alcoholic and lactic acid fermentation, activation of melanoid formation at elevated temperatures.

The main producers of these enzymes are fungi *Aspergillus oryzae* and bacteria *Bacillus Subtilis*. The predominant enzyme in amylolytic enzyme preparations is alpha-amylase.

Amylolytic enzyme preparations are used in bakery, winemaking, brewing, canning production, as well as for the purpose of converting glucose into fructose (glucoisomerase).

In bakery production, amylolytic enzyme preparations are used in the case of processing flour with low sugar and gas-forming capacity; in order to intensify fermentation processes; to improve the volume of products, crust color, smell and taste; extending the shelf life.

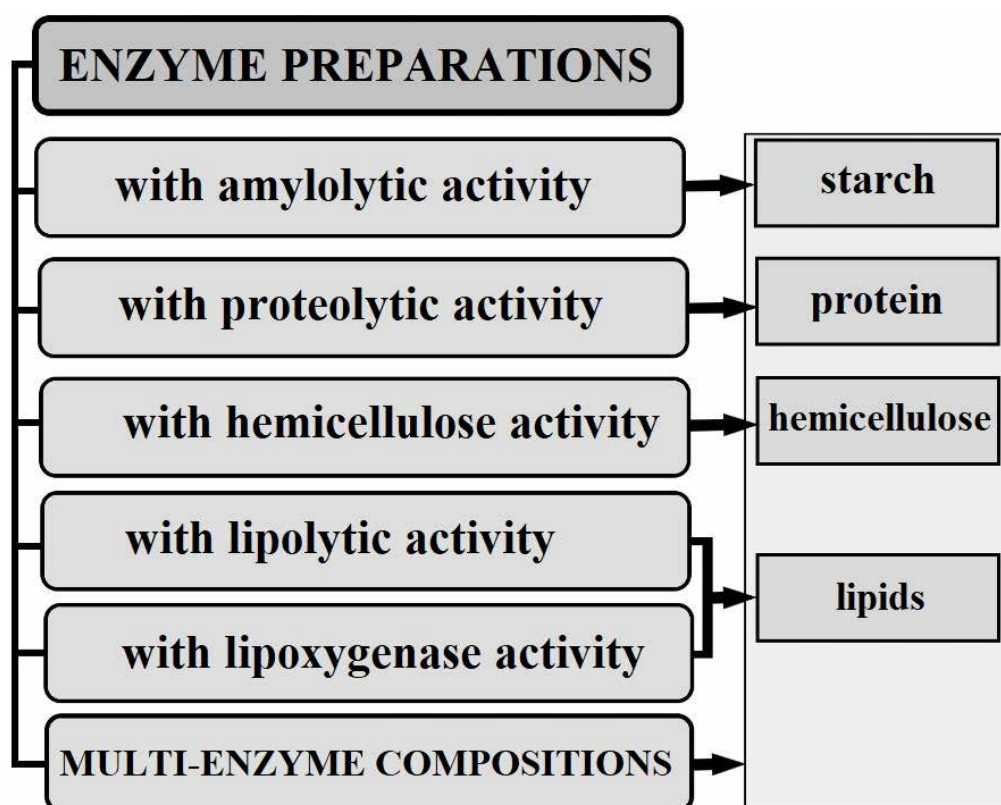


Fig. 2.59. Classification of enzyme preparations

Enzyme preparations used in bread baking are listed in Table. 2.40.

Table 2.40. Characteristics of amylolytic enzyme preparations

Preparation	Producer	The enzymes it contains	Optimal operating conditions	Dosage. g/100 kg of flour
Amilorizine P1Ox	Mold mushroom <i>Aspergillus oryzae</i>	α -amylase, protease	pH = 4.5-5.4 t = 40-45 °C	1.5-2.5
Amylsubtilin	Bacteria <i>Bacillus Subtilis</i>	A-amylase, protease P-gluconase	pH = 5.6. t = 50-65 °C	0.06-0,10
Glucoamylase purified	Mold mushroom <i>Aspergillus awamori</i>	Glucoamylase	pH = 3.0-5.5 t = 55-60 °C	0.0003-0.001
Fyngamil BG	Mold mushroom <i>Aspergillus oryzae</i>	Purified α -amylase	pH = 4.5-5.0 t = 53-55 °C	0.2-1.0

Fyngamil Super	Mold mushroom <i>Aspergillus oryzae</i>	α -amylase	pH = 5,0-6,0 t = 53-55 °C	5,0-15.0
AMG	Mold mushroom <i>Aspergillus niger</i>	Glucoamylase	pH = 3.0-5.0 t = 55-70 °C	3,0-30.0
Producent	Bacteria <i>Bacillus Subtilis</i>	Maltogenic α -amylase	pH = 4.8-6.0 t = 54-76 °C	50.0-60.0

Amylolytic enzyme preparations are used to accelerate the ripening of herrings (Amilorizin P10x), to sweeten jams in the production of beer, to clarify juices, and in the production of alcohol.

Proteolytic enzyme preparations – proteases. Proteases catalyze the hydrolytic cleavage of proteins along peptide bonds with the formation of peptones, polypeptides, peptides and amino acids. They are able to weaken or destroy the structure of the protein molecule, depending on the depth of its hydrolysis. This makes it possible to obtain the desired technological effect in the production of food products.

Thus, in bakery production, in the case of processing flour with excessively strong or short-cut gluten, the use of proteolytic enzymes leads to its weakening, increasing elasticity, which helps to increase the volume and improve the dimensional stability of the products.

The products of proteolytic hydrolysis are used by the microorganisms of dough systems for nutrition, which helps to increase the intensity of alcoholic fermentation.

In addition, peptides and amino acids participate in the reaction of melanoid formation. In the confectionery industry, they are used in the production of galettes, crackers, and long-drinking cookies to give the dough the rheological properties necessary for its processing, rolling, and shaping.

The characteristics of individual enzyme preparations, which are used in the manufacture of flour products, are given in the Table. 2.41.

Table 2.41 Characteristics of enzyme preparations of proteolytic action

Preparation	Producer	The enzymes it contains	Optimal operating conditions	Dosage. g/100 kg of flour
Protosubtilin P10x	Bacteria <i>Bacillus Subtilis</i>	Protease	pH = 7.0-7.5 t = 50 °C	0.002-0.01
Protorizin P10x	Mold mushroom <i>Aspergillus oryzae</i>	Protease	pH = 5.0-7.0 t = 45-50 °C	0.002-0.01
Neutrasa 5.0 BG	A selective strain of bacteria <i>Bacillus Subtilis</i>	Protease	pH = 5.5-7.5 t = 45-55 °C	0.1-0.2

At that time, the enzyme preparation Neutrasa 5.0 BG was widely recognized in the case of processing flour with short-cut gluten. Protosubtilin P10x is used in the production of salted herrings, beer, and Protorizin P10x is used as a softener for semi-finished products from coarse-fiber meats, in the production of alcohol, etc.

Lipolytic enzyme preparations. These enzyme preparations catalyze the hydrolysis of triacylglycerols with the formation of fatty acids and glycerol.

Intermediate products of hydrolysis of mono- and diglycerides are surface-active substances. They are used in various branches of the food industry. Yes, the lipase enzyme preparation (E1104) is used to regulate the appropriate taste and aroma of fat-containing products. Liopan 50 VH – to improve the structural and mechanical properties of the dough. This drug is a purified 1,3 specific lipase produced by a strain of *Aspergillus oryzae*. It contributes to increasing the volume and porosity of bakery products, improving dimensional stability. It works in a wide pH range – 5.0-8.0, its dosage is 0.5-5.0 g/100 kg of flour.

Cellulites and other enzyme preparations. Enzyme preparations that have hemicellulase activity catalyze the splitting of high-molecular carbohydrates - cellulose, hemicellulose, pentosans. pectins with the formation of low molecular weight compounds. These are cellulases, hemicellulases, pentosanases, pectinases. Yes, an enzyme preparation

Cytoselin PX is used in brewing, Cytoselin P10x in winemaking, Pectofetidia P10x - in the production of wine and juices. Cellulolytic preparations are used in bakery production to improve the structural and mechanical properties of the dough and increase its water-absorbing capacity. Enzyme preparations such as cytoroselin P10x, Pentopan BG, Pentopan Mono BG are well-known in baking (Table 2.42).

Table 2.42. Enzyme preparations with hemicellulase activity

Preparation	Producer	The enzymes it contains	Optimal operating conditions	Dosage. g/100 kg of flour
Cytrosemin P10x	<i>Triothecium rozeum</i>	Hemicellulose, cellulase, pentosanase	pH = 7.0-7.5 t = 50 °C	10.0-100,0
PentopanMono BG	Genetically modified strain <i>Aspergillus oryzae</i>	Pentosanase	pH = 4.0-6.0 t = 40-75 °C	0,6-1.0
Pentopan BG		Hemicellulose, pentosanase	pH = 4.0-6.0 t = 40-75 °C	2.0-29.0

Enzyme preparation Pentopan Mono has pentosanase activity, activity, hydrolyzes soluble and insoluble pentosans of flour, and preparation Pentopan BG, in addition to pentosanase, also contains hemicellulose.

These preparations condition the modification of fractions of non-starch polysaccharides of the powder, improve the flexibility of the gluten network. As a result of their action, the water-absorbing capacity of flour increases, the structural and mechanical properties of the dough improve, and the volume of bread increases. Some enzyme preparations are effective oxidizers, they channel redox transformations of food components.

Glucosidase is used as an enzyme and antioxidant in the production of water-based soft drinks and fruit juices. In baking, it is advisable to use it in a mixture with catalase in a 1:1 ratio.

In the confectionery and non-alcoholic industry, the enzyme preparation **Invertase** is used for the inversion of sucrose. It acts as an enzyme and stabilizer. So, in the production of fudge candies, it is used to prevent the crystallization of sucrose and preserve the structure.

The enzyme preparation **Catalase** is used in the production of invert syrup. It is convenient to dose enzyme preparations in the form of solutions in water at a temperature of 25-30 °C at a hydromodule of 1:10 or 1:20. The solution of enzyme preparations can be stored at a temperature of 5 °C for 24 hours.

Enzyme preparations are inactivated during the baking process. To achieve the complex effect of enzyme preparations on the components of the food system, it is effective to use multi-enzyme compositions. They include enzymes with different functional properties, while a synergistic effect of their action is observed.

The advantage of multi-enzyme compositions is a complex effect on the components of the food system, which has a positive effect on the course of product manufacturing processes and their quality.

Questions for discussion and self-examination

- 1. The role of enzymes in food technology.*
- 2. Classification of enzymes.*
- 3. Enzymes of plant and animal products.*
- 4. Classification of enzyme preparations.*
- 5. Use of enzyme preparations in food production.*

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