**Medicinal plants and medicinal plant material containing saponins.**

The name of these natural compounds is derived from the Latin word “sapo”, which means soap or soap-like. Saponins are mainly glycosides and have a number of characteristic properties, including the following: hemolytic and surface activity and toxicity to cold-blooded animals. According to the nature of the aglycone two kinds of saponins are recognized: steroidal (tetracyclic) and triterpenoid (pentacyclic). Both types have a glycosidal linkage at C3 and have a common biogenetic origin called via mavalonic acid.

The term saponin or saponoside was first proposed by Malone in 1819 for the substance isolated by Shreider in 1811 from soapwort. Saponins are complex glycoside organic compounds.

Saponins as all glycosides consist of two parts: an aglycone or sapogenin and carbohydrate moiety.

According to the number of monosaccharide units (pentoses and hexoses) saponins are divided into monosides, biosides, triosides, tetraosides, pentaosides, and oligosides- number of monose 6 and more. Saponins with two carbohydrate moieties attached to aglycone are called diglycosides.

As the carbohydrate moiety of saponins more often consists of several monosaccharide units, the hydrolysis in certain conditions can proceed stepwise under gradual cleavage of the sugars.  The products obtained by partial hydrolysis are called prosapogenines.

The carbohydrate moiety of saponins includes the following sugars: D-glucose, D-galactose, L-rhamnose, L-arabinose, D-xylose, L-fructose and also D-glucuronic and D-galacturonic acids.

Steroid saponins possess less sugar units than the triterpene saponins. They typically include 1-5 sugar units. Triterpene saponins are rich in sugar units (up to 10 and more).

Saponins with 1-4 monosaccharides are slightly soluble in water, however the solubility of saponins in water increases as the number of monosaccharide units increases.

Carbohydrate moiety of triterpenoid saponins can be attached to aglycone at one or several positions by different bonds, by hydroxyl or carboxyl groups. Monosaccharide units are often attached to hydroxyl group at C3  position of the ring A of carbon skeleton. Carbohydrate chain of some triterpene glycosides is attached to C28 through O-acetylglycosidic bond. Sugar component can be linear or branched.

Steroidal glycosides contain sugar moieties mostly at C-3 position , but furostanol – at C-3 and C-26 positions. The attachment of sugar moieties to other positions is also possible.

Regardless of biological and physical properties saponins are useful to classify according to structural-chemical features. According to chemical nature saponins are divided into two groups, which are sub-divided into several groups.

Steroidal saponins of the spirostan series are natural glycosides, splitting off aglycones during the hydrolysis, containing 27 carbon atoms in molecule and monosaccharide units.

Glycosides of the spirostane series or monodesmosides contain six cycles in aglycone and furostanol – bisdesmosides, in which the ring F of the aglycone is opened are known.

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Spirostanol type Furostanol type

During the hydrolysis of the furostanol glycosides glucose at С-26 is cleaved and the cycle is closed into spiroketal due to the free oxygroup. As a result of hydrolysis the furostanol glycosides can be converted into a spirostanol.

Steroidal sapogenins with five-membered ring F and primary hydroxyl group at С-26, sapogenin with opened ring F are described.

At present there are 35 steroidal sapogenins and about 150 steroidal glycosides.

Steroidal saponins have a genetic connection with sterols, that’s why “squalene” hypothesis is applicable to its biogenesis.

Steroidal saponins are present in the following families of plants: Liliaceae, Dioscoreaceae, Legumes, Ranunculaceae, Scrophulariaceae, Agavoideae and others.

There are 150 steroidal glycosides, 100 of them are spirostanol and 50 – furostanol type.

Triterpene saponins are pentacyclic or tetracyclic terpenoids, in which isoprene structural unit (C5H8) repeats 4 or 5 times.

Pentacyclic triterpene saponins are divided into 4 groups: β-amyrin, α-amyrin, lupeol and fridelin (serin) derivatives.

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β-Amyrin α-Amyrin

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Lupeol Fridelin R = OH

Serin R = OH

Tetracyclic triterpene aglycons are divided into dammarane derivatives (dammarandiol), cycloartane (cycloartenol) and zuphan.

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Cycloartenol

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Dammarane

*Physico-chemical properties.* Triterpene saponins are colourless or yellowish substances without certain melting point (with decomposition). In the derivatives of β-amyrin, α-amyrin and lupeol, if there is one hydroxyl group, it is located at C-3, in fridelin the carbonyl group is located at C-3.

Carboxyl group of the derivatives of β-amyrin and α-amyrin is located at C-28 position (oleanolic and ursolic acid), but it can be connected to other carbon atoms.

Individual sapogenins have different functional groups at the same time, for example in glycerretinic acid OH is located at C-3, O- at C-11 and COOH – at C-30.

Properties of saponins depend on the structure of sapogenins and carbohydrate moieties. Saponins are typically colourless or yellowish amorphous substances without certain melting point. Sapogenins with 4 monosaccharide moieties are crystalline substances with certain melting point. Saponins are obtained in a crystalline form. Saponins possess a high surface activity, which associated with the presence of hydrophilic and hydrophobic groups in one molecule. Adding the ethyl ether or acetone to alcoholic solutions of saponins produces its precipitation, which is used as the purification method. Various groups of triterpene glycosides can be precipitated by different salts of lead and barium hydroxide from aqueous solutions.

Triterpene saponins are neutral or acid compounds. They can be neutral or acid due to the carboxyl group of aglycone or the presence of uronic acid in carbohydrate chain.

Acidity is associated with the presence of carboxyl group in sapogenin or the presence of uronic acids in carbohydrate moiety.

Acidic saponins form soluble salts with mono-valent metals, and insoluble – with di-valent and poly-valent metals.All saponins are unstable towards acid agents, which split the glycosidic bonds. Saponins which are characterized by the presence of O-acylglycosidic bonds, are unstable in alkaline medium. Triterpene glycosides esterified with carboxyl acids, are easily saponified by alkalines.

It should be noted, that most saponins have the ability to form stable complexes with other natural compounds, that’s why their physico-chemical properties are various. Aqueous solutions of steroidal saponins have neutral pH medium. Triterpene glycosides are insoluble in petroleum ether, chlorophorm, acetone, and they are soluble in ethanol and methanol. The solubility of saponins in water increases with increasing number of carbohydrate moieties. Glycosides with 1-4 monosaccharide units are poorly soluble in water. One of the important chemical properties of triterpene saponins is the ability to form complexes with phenols, higher alcohols and sterols. Saponins form complexes with membrane cholesterol, its lipid wall is dissolved, and hemoglobin passess from erytrocyte to blood plasm, makes it bright red and transparent. Sapogenins don’t possess a hemolytic activity.

Extraction of saponins from plant material. Extraction of saponins from plant material includes: obtaining the crude extract, its purification from ballast material (lipids, essential oils, pigments and oth.) and separation of the mixture into individual compounds. For ballast removal, the plant material is preliminary extracted with chloroform. Subsequent operations can be modified depending on the type of plant material and its chemical composition.

Extraction of saponins from plant material includes the following stages: 1) obtaining the extract; 2) obtaining the sum of saponins from the extract and its purification from accompanying substances; 3) separation of saponins into individual glycosides.

Usually, crude extract for isolation of saponins is get out of the plant by processing the row plants materials with the polar solvents; methanol, ethanol or water. Plant material is preliminary treated with petroleum ether or carbon tetrachloride to destoy the saponin complexes with sterols.

Methods of isolation of total saponins from extract depend on their structure. Glycosides with a small number of monosaccharide units (3-4) are usually poorly soluble in water and precipitated by diluting hydroalcoholic solutions with water. Polar saponins are poorly soluble in methanol and ethanol and precipitate on cooling or during long standing of alcohol solutions, or when alcohol is added to aqueous or hydroalcoholic solutions. Acidic saponins are soluble in water solutions of alkalines and precipitated in the acidic solution. Triterpene saponins are precipitated from water solutions with ethyl ether, acetone, chloroform (some of them with butyl and isoamyl alcohols). Accompanying lowpolar impurities are extracted from water solutions with ethyl ether, chloroform, carbon tetrachloride but triterpene glycosi des – butyl or isoamyl alcohol. Obtaining saponin fractions are purified by reprecipitation. The method based on the ability of saponins to form water or hydroalcoholic insoluble salts with hydroxide barium or lead acetate and complexes with cholesterol, tannins, proteins for detection of saponins from accompanying substances. Obtained salts are decomposed by sulfuric acid, cholesterinic complexes – extraction of cholesterol by benzene, ether or pyridine, tannin complexes – water suspension of oxide zinc, protein complexes are decomposed by organic solvents. These methods give a pure total saponins. Saponins forming colloidal solutions are purified, which give true solutions (monosaccharides, mineral substances), by dialysis and electrolysis. Good results of purification of saponin fractions from plant pigments and reduced sugars are obtained by gelfiltration with sephadexes U-25, U-50, A-25.

Chromatographic methods for purification of total saponins have been widely used. Glycosides containing free carboxyl groups can be separated from accompanying substances, including mineral impurities, by the ion-exchange chromatography.

The fraction of saponins is a mixture of glycosides with similar structure and properties. Only in recent years the separation has become possible due to the chromatographic methods. Aluminium oxide, silicagel, activated carbon, polyamide are used as a adsorbent for isolation and separation of saponins by column chromatography

In contrast to other classes of natural compounds (carbohydrates, aminoacids and oth.) there are no universal elution systems for saponins. The most suitable systems for neutral saponins: n-butyl alcohol-ethanol –water; n-butyl alcohol – acetic acid – water ( in various ratio, upper layer); chloroform – methanol – water (65:35:10).

Same reagents which give characteristic colours with saponins, can be used for the treatment of chromatogram. For detection of steroidal saponins the chromatogram is sprayed with 1% alcohol solution of SbCl3, then after drying with 20% solution of H2S04 and acetic anhydride. Yellow spots are formed.

For detection of steroidal glycosides in plant material the alcohol extraction is obtained and silicagel thin-layer chromatography on silica plates is carried out in system of solvents: chloroform –methanol–water (65:30:10). Chromatographic plate (silicagel plate) is sprayed with Sannie reagent (5% alcohol solution of vaniline) and heated at 1100C for 10 min, it is treated with 50% solution of sulfuric acid and dried. As a result the steroid glycosides appear as yellow spots. Furostanol glycosides appear as pink spots after spraying with Ehrlich’s reagent (1 g of p-dimethylaminobenzaldehide in 98 ml of ethanol and 2 ml of concentrated HCL).

For detection of triterpene saponins the 20% solution of sulfuric acid is used. Purple spots are appeared after spraying the chromatogram with this solution and heated in the desiccator at 120o C for 15 min. Saturated chloroform solution of SbCl3 with SbCl5 traces are also used. Triterpene saponins produce pink-violet colour.

During the clarification of the structure of saponins, as other glycosides, the structure of the aglycone and carbohydrate and the position and attachment of the carbohydrate moiety to the aglycone are determined.

In addition to the traditional methods (elementary analysis, determination of molecular weight) UV-, IR- , proton NMR are widely used for the establishment of saponin structure.

During the study of triterpenes IR-spectroscopy is used for detection and characterization of double bonds, hydroxyl groups, O-acyl groups, carbonyl, carboxyl, heminal and angular -methyl groups. Tetracyclic triterpenes are distinguished from pentacyclic, and also alpha-amyrin destinguishedfrom betta-amyrin by the characteristic absorption bands at 1245-1392 sm.

Affiliations of saponins to steroid compounds can be made on the basis of IR-spectroscopy. The presence of absorption bands at 853 (866), 900 (900), 922 (922), 987 (982) sm-1 (spiroketal group normal and iso –series) allows to attribute the saponins to the steroid series.

Nowadays mass spectrometry and proton NMR have been widely used to identify the structure of pentacyclic triterpenes.

The establishment of the structure of carbohydrate component of triterpene and steroid saponins is carried out by the structural chemistry of oligosaccharides and polysaccharides. It includes: 1) qualitative and quantative determination of monosaccharides; 2) establishment of the sequence of monosaccharide units in carbohydrate chain; 3) determination of position of glycosidic bonds in monosaccharide units; 4) determination of oxide cycles dimensions of monosaccharides; 5) establishment of configuration of glycosidic centres. Extraction with aqueous methanol, ethanol or isopropanol is the most widely used method of isolation of triterpenoid glycosiedes at present. The material is preliminary degreased with petroleum, diethyl ether, hexane, methylen chloride, tetrachloromethane or chloroform. The importance of this operation is associated with the removal of fat-like substances from plant material (particularly sterols, with which the most triterpenoid glycosides are able to form the complex compounds insoluble in hydroalcoholic solutions).

*Qualitative reactions.* For detection of saponins in plant material are used the reactions, which are divided into three groups:

- reactions based on physical properties of saponins (foam-forming and determination of chemical nature of saponins).

- reactions based on chemical properties of saponins (colour and precipitation reactions).

- reactions based on biological properties of saponins (hemolysis test).

The foam-forming reaction is belonged to the first group, it is characteristic test. Because other substances with foam-forming ability are not present in plants.

The second group includes precipitation and colour reactions. The concentrated sulfuric acid, aldehydes and concentrated sulfuric acid with metal traces (table) are used in most colour reactions as a reagent. Most triterpene and steroidal saponins are precipitated with cholesterol solution, bromine water, barium hydroxide and magnesium, salts of mercury, copper, zinc, lead.

Triterpenoid saponins precipitate with lead subacetate, steroidal saponins with lead acetate basic solution.

Triterpene saponins are detected with acetic anhydride in the presence of sulfuric acid. The substance is dissolved in chloroform, 10 drops of acetic anhydride and 2-3 drops of concentrated sulfuric acid are added. The low layer turns into orange.

The Liebermann-Burchard test, chlorosulfuric acid and antimony trichloride are used for the detection of saponins. Chlorosulfuric acid turns the oleanolic acid into different shades of brown coloration, but betulinic acid- into light blue coloration. Phosphoric and sulfuric acid alone or their mixture with vanilin and anisaldehyde are used for the detection of saponins.

 Reaction with sulfuric acid is used for quantitative determination.

The presence of saponins in plant material is detected by thin layer chromatography. The chromatogram is sprayed with a 20% solution of sulfuric acid, then heated at 1100 C for 10 min in desiccator.

UV-spectroscopy is used for the detection of saponins. Saponins adsorb UV light in the range of 240-260 nm. Saponins are optically active.

Reaction with cholesterol gives a possibility to determine the steroidal nature of glycosides (5 ml of 1% saponin solution mix with 1,5 ml of 0,3% alcohol solution of cholesterol, 1,5 ml of water is added and the white precipitation is formed). The reactions of saponins are carried out in the presence of formaldehyde with sulfuric acid. 5-7 drops of formaldehyde solution with sulfuric acid is added to the saponin solution in methanol; the blue-violet colour is formed, which rapidly turns into brown or greenish-brown.

Table. Colour reactions of sapogenins

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| Reagent | Colour |
| Concentrated H2SO4 | yellow→red-violet |
| Liebermann-Burchard test(acetic anhydride, conc. H2SO4, chloroform) | boundary layer: ring red →violet→ emerald-green |
| formaldehyde, conc. H2SO4 | yellow →crimson |
| Lafon’s reagent (conc. H2SO4, Cu2+ salts,  > t0C) | blue-green |
| Salkowski’s test (conc. H2SO4, chloroform) | low layer gives an orange colour |
| Solutions of Sb (III), Sb (V) chlorides in chloroform | red→violet |
| Sannie (vanilin, conc. H2SO4, , > t0C) | triterpenoid saponins: →red;  steroidal saponins →yellow |
| Ehrlich reagent(p-dimethylaminobenzaldehyde, conc. HCl) | furostanol →pink |
| Chlorsulfuric acid | β-amyrin →brown, violet;  betulinic acid→blue |

*Quantitative determination of saponins.* The methods based on the biological and physical properties of saponins, i.e. the determination of haemolytic, fish toxicity and foam index are used for the quantitative determination of saponins in plant material. The chemical methods are also used. The common chemical methods for quantitative determination of saponins in medicinal plant material are not present. Gravimetric, titrimetric and photometric methods are often used. Colorimetric and spectrophotomertirc methods of analysis are more often used for the quantitative determination of saponins (steroidal saponins and its preparations). Triterpenoid saponins are determined by potentiometric titration. Aglycones are titrated with sodium hydroxide after the hydrolysis in solution of methanol - benzene (indicator – glass electrode, reference electrode – calomel). Escin is determined by the method of potentiometric back -titration.

The quantitative determination of saponins by haemolytic method is based on the following: haemolytic action is directly proportional to the number of substance in solution.

Haemolytic index (HI) is the least concentration of infusion (1:10), which totally cause hemolysis of the erytrocytes, calculated per unit of test substance. HI for some types of plant material are: glycyrrhiza root – 250-300; ginseng root – less than 100; chestnut semen – 6000 (escin 9500-12500); ivy leaves – 1000 -1500; soapwort root -2600-3900; senega root -2500-4500; sapsaparilla root -3500-4200; soapberry root – 35000-4500.

Each solution must have its standard – solutions of pure saponins because various saponins at the same concentration have different haemolytic index.

However the positive result of haemolytic test is not a proof of the presence of saponin. Because other plant substances also cause hemolysis (some essential oils, acids, alcohols). In plants saponins also can be present as a complex with sterols and do not exhibit hemolytic activity before the destruction of complex.

The methods for the determination of saponins based on the high toxicity of these compounds for cold-blood animals (fish, polliwog, worm, toad) don’t have advantages in comparison to the hemolytic index and retain its main disadvantages – low reliability, the inability to classify strictly the substances into saponins.

Qualitative analysis of saponins

5,0 g of crushed material is placed in a 100 ml conical flask, 50 ml of 50% alcohol is added, the contents of flask are heated in a boiling water bath under reflux for 15 min. The extraction is cooled and filtered. 20 ml of the filtered solution is evaporated in a water bath to 10 ml for alcohol removal.  Aqueous extraction is used for carrying out the foam-forming reaction, some precipitation reaction and the determination of the chemical nature of saponins, hydroalcoholic extraction - for other qualitative reactions and chromatographic analysis.

Foam-forming test

1. 2-3 ml of aqueous extraction is vigorously shaken for 1 min. Copious and stable foam is formed.

Precipitation reactions

2. Add 3-4 drops of bromine water to 1 ml of aqueous extract in test tube. The precipitation is observed.

3. Add 3-4 drops of 10% lead acetate solution to 1 ml of aqueous extract. The precipitation is observed.

4. Add 1 ml of 1% alcohol solution of cholesterol to 1 ml of hydroalcoholic extract. The precipitation is observed.

Colour reactions.

5. Lafon’s reaction. Add a drop of 10% copper sulphate solution, 1 ml of concentrated sulfuric acid to 2 ml of hydroalcoholic extract in a test tube and carefully heat. The bluish-green colour is produced.

6. Salkowski’s reaction.  Add 1 ml of chloroform and 5-6 drops of concentrated sulfuric acid to 2 ml of hydroalcoholic extract in a test tube. The organic layer acquires an orange colour.

7. Reaction with antimony pentachloride. Add 0,5 ml of saturated antimony pentachloride solution in a chloroform to 1 ml of hydroalcoholic extract in a test tube. The red colour is produced turning into violet.

8. Sanje’s reaction. Add 1 ml of 0,5% vanillin alcohol solution, 3-4 drops of concentrated sulfuric acid to 2 ml of hydroalcoholic extract in a test tube and heat in water bath at 600C. The red or yellow colour is developed.

The determination of chemical nature of saponins.

Take 2 volumetric tubes having same diameter with ground stoppers. 5 ml of hydrochloric acid 0.1 mol / l is poured into one of the volumetric tube, 5 ml of sodium hydroxide solution 0.1 mol / l – into other tube. 0,5 ml of aqueous extract are added to each tube and shaken at the same intensity for 1 min. The presence of triterpene saponins - the foam height in both tubes will be approximately the same. Steroidal saponins forms more foam in a test tube with alkaline.

*The detection of saponins by chromatographic method.* Paper and thin layer chromatography are commonly used for identification of saponins. The following strongly acid reagents are used as developing reagents: saturated solution of antimony (III and V) chlorides in chloroform, 25% alcohol solution of phosphor-tungstic acid, sulfuric acid and etc. Sulfuric acid typically reacts with sapogenin part. However, if the carbohydrate chain is larger, the relative proportion of genin is less and consequently, the sensitivity of the reaction is also less. Sheep blood solution in phosphate-buffer is used as developing reagent for erythrocytes hemolysis.

The detection of saponins by TLC.

2,0 g of crushed material is placed into a 25 ml flask, 10 ml of 70% alcohol is poured and heated in a boiling water bath under reflux for 15 min. The extract is filtered and evaporated two times. Then 25-40 mkl is applied on start line of silicagel-coated plate. Standard solution of saponins are applied in parallel (for example, escin). The plate for separation of saponins is placed into chamber with solvent system: chlorofrom –methanol –water (65:50:10). When the front of the solvent system pass the distance of 10-11 cm, the plate is removed from the chamber, dried in a fume hood, and the chromatogram is visualized in visible and UV light. Then the plate is sprayed with 5% sulfuric acid solution in ethanol and 1% alcohol solution of vanillin. The chromatogram is dried in the desiccator at 110 ° C for 5-10 min. Mark the colour of standard samples and extract spots.

Determination of foam number in a sample of saponin- contianing medicinal plant material.

According to the foam number, the saponin- containing medicinal plant material are divided into three groups: more 5000 –high foam number; 2000-5000 – middle foam number; less 2000 – low foam number. The sample of investigated plant material is dried to constant weight in the desiccator at 600C. Then it is grind into powder and passed through a sieve No.355. 1% infusion is prepared from 1 g of powder according to the rules of SPh XI (art. “Infusions and decoctions”, p.147). 10 ml of infusions is filled into a measuring cylinder with a ground stopper. From the mark of 10 ml it should have a free length of 7-8 cm to the edge of the cylinder. Cylinder with infusion is vigorously shaken for 15 seconds. Minimum infusion concentration which gives a foam, not disappeared during 1 min, is determined.

For example. 1% of investigated solution is diluted 30 times (2 ml of primary infusion and 58 ml of water). Total dilution is 100 х 30 = = 3000. Therefore, the foam number is 3000.

Determination of hemolytic index of plant material containing saponins.

Haemolytic index (HI) is the least concentration of infusion, which totally cause hemolysis of the erytrocytes, by 1g of test substance.

1—2 g of coarsely powdered plant material (weight of samples depends on the hemolytic activity) is weighed on a scale and placed in an Erlenmeyer flask, 0.9 g of sodium chloride and 100 ml of boiling water are added. The flask with content is weighed on a balance accurate to 0,01 g, it is infused in a boiling water bath during 15 min. Then the water is added to a primary weight and filtered. The experiment is carried out in 9 test tubes. A pipette with a 0.01 ml division is measured in the first tube with 0.9 ml of the investigated infusion, in the next appropriate 0.8, 0.7; 0.6; 0.5; 0.4; 0.3; 0.2; 0.1 ml. After the content of each test tube are adjusted with an isotonic solution to 1 ml. 1 ml of red blood cells suspension is added to each test tube and shaken. The test tubes is observed for hemolysis in 24 hours. If the hemolysis was occurred in the last test tube, then part of the main infusion is diluted with isotonic solution exactly 10 times and a new series of dilutions is prepared from it.

The content of test tubes are investigated in 24 hours. In test tubes with the maximum dilution, a colorless solution with red cells dot (mass) at the bottom is usually observed (no hemolysis has occured). Then there are test tubes containing a red-colored solution, but with a precipitation at the bottom (partial hemolysis). In a test tube with bright red colored solution without precipitation on the bottom, indicates that a complete hemolysis of erythrocytes has occurred.

Hemolytic index is calculated according to the formula:

Where, a – initial concentration of solution, %;

b – volume of the primary solution in a test tube, the contents cause complete hemolysis, ml.

Since the blood of different animals gives various results, this blood is studied on a standard solution and the correction factor is determined. 0,02% solution of pure saponin in isotonic medium is used as a standard. The dilution series of standard solution is carried out and the factor F is calculated the following day. The unit is an ability to cause the complete hemolysis with dilution of pure saponins 1:25 000.

Factor F is calculated by dividing 25 000 by the actual concentration.

Example. The complete hemolysis is occurred in a test tube, containing 0,5 ml of primary solution.

The factor is determined simultaneously with the hemolytic index and the result is multiplied by a factor.

Note. Hemolytic index of some species of medicinal plant material composes; chestnut semen – 6000 (including escin -9500-12500), licorice root – 250-300, ginseng root - <100; ivy leaves – 1000-1500, soapwort root – 2600-3900, senega root -2500-4500.

*Biological activity*. Saponins stimulate and tone up CNS and regulate water-salt exchange. Adaptogen, expectorant, diuretic, neuroleptic, sedative, anti-inflammatory, antiviral activity is characteristic for medicinal plant material and drugs, containing saponins. All saponin preparations are orally administered to avoid hemolysis. Emulsifying properties of saponins are used to stabilize emulsions, suspensions and other dispersed dosage forms. Toxicity of saponins to cold-blooded animals is due to the impaired gill function. This property is used in fishing. In the food industry saponins are used in the manufacture of confectionery products, and effervescent beverages.

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Spirostan type (monodesmosides)

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C

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Furostanol type (bisdesmosides)

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Tigogenin

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Yuccagenin

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β-amyrin

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α-amyrin

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Lupeol

R

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Friedelin R = OH

Serine R = OH

HO

O

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2

5

Friedelin

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Serine

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1

7

2

1

2

0

2

2

2

3

2

4

2

6

2

5

2

7

Cycloartenol

2

1

2

2

2

0

2

4

2

3

1

5

1

6

2

6

2

5

1

7

2

7

1

1

1

2

1

3

1

4

8

9

7

6

3

0

1

8

1

9

9

2

2

8

5

1

0

3

4

1

2

Dammaran

O

H

C

O

O

H

2

9

3

0

Ursolic acid

O

H

O

H

O

H

O

H

O

H

O

H

Mesoinosit

O

-

nose

i

b

a

r

a

-

rhamnose

C

O

O

-

glucose-glucose-rhamnose

C

H

2

O

C- hederosaponin

O

C

O

O

H

3

O

O

C

O

O

H

O

H

O

O

C

O

O

H

O

H

O

H

O

H

O

H

1

2

Glycyrrhizic acid

O

1

R

O

O

O

R

2

R1 = R2 = H – Liquiritigenin

R1 – H, R2 = Glc – Liquiritin

R1=glucose; R2=H - Neoliquiritin

O

H

O

O

OH

Liquiritigenin

O

H

O

O

O - Glc

Liquiritin

glucose– O

O

O

OH

Neoliquiritin

O

1

R

O

O

H

O

R

2

R1 = R2 = H – Isoltquiritigenin

R1 – H, R2 = Glc – Isoliquiritin

R1=H; R2=rhamnose – Rhamnoisoliquiritin

O

H

O

O

H

OH

Isoltquiritigenin

O

H

O

O

H

O - Glc

Isoliquiritin

O

H

O

O

H

O - rhamnose

Rhamnoisoliquiritin

O

H

O

O

O

C

H

3

Formononetin

O

O

H

O

O

H

c

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G

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A

Licuraside

C

O

H

C

H

3

C

H

3

C

O

O

H

3

H

C

C

H

3

C

3

H

3

1

1

1

2

1

8

3

0

O

H

O

O

H

O

H

C

O

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H

O

O

C

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H

4

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H

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2

Glyciram

R

1

C

H

2

O

H

R

2

R

3

C

H

2

O

H

R

4

Longispiogenol:

R = R1 = R3 = R4 = H; R2 = OH

AR1- barrigenol:

R = R1 = R2 = OH; R3 = R4 = H

R1- barrigenol:

R = R1 = R2 = R3 = OH; R4 = H

Camelliagenin E:

R = R1 = R2 = OH; R3 = H; R4 = CHO

O

H

O

H

O

H

O

3

6

1

9

1

8

1

2

2

6

2

7

Panaxatriol

2

7

O

H

O

H

O

3

6

1

9

1

8

1

2

2

6

Panaxadiol

2

1

9

2

0

2

1

2

2

2

3

2

4

2

5

2

6

2

7

2

8

2

9

20S- Protopanaxadiol:R1 = H; R2 = OH

20S- Protopanaxatriol:: R1 = R2 = OH

O

1

R

C

O

O

R

2

R1, R2 = H oleanolic acid

Araloside A – R1 = glucuronic acid (4 → 1) arabinose

R2 = glucose

Araloside B – R1 = glucuronic acid (4 → 1) arabinose

(3 → 1) arabinose

R2 = glucose

C

O

O

O

O

O

H

O

A

r

C

O

O

H

O

r

A

O

O

H

O

H

H

O

H

2

C

O

H

2

9

2

8

2

7

2

6

2

5

2

4

3

2

3

3

0

Araloside B

C

O

O

O

O

O

H

O

G

a

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C

O

O

H

O

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X

O

O

H

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H

H

O

H

2

C

O

H

2

9

2

8

2

7

2

6

2

5

2

4

3

2

3

3

0

Araloside C

C

O

O

O

O

O

H

O

H

C

O

O

H

O

r

A

O

O

H

O

H

H

O

H

2

C

O

H

2

9

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8

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7

2

6

2

5

2

4

3

2

3

Araloside A

O

O

H

O

O

H

O

H

O

Fructose

O

A

r

a

b

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o

s

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Equisetrin

Biological action of steroidal saponins.

Inhibition of the vital activity of some lower organisms is characteristic for saponins. Particularly saponin glycosides have a powerful effect toward fungi. Spirostanol glycosides and some steroidal alkaloids are the most active. Antifungal activity of saponin glycosides are used in agriculture. Spirostan glycosides have antitumor activity. Steroidal saponins have antisclerotic effect. They reduce the amount of cholesterol in blood. Steroidal saponins are also used as a starting material for the synthesis of steroidal hormones.

Biological action of triterpenoid saponins.

Most triterpnoid saponins have a hemolytic action. When saponins enter the blood, they have a very strong toxic effect, causing hemolysis and paralysis of the central nervous system (primarily the respiratory center). The resorptive action is not presented by saponins when taking them orally. Saponins increase the secretion of bronchial glands, thinning mucus, reduce its viscosity, that’s why they are used to treat bronchitis, and also dry cough. Some triterpenoid saponins have hormone-like, stimulating and adaptogenic activity. Saponins and dust of saponin-containing materials cause irritation of the mucous membrane of the eyes, nose, throat and pharynx. They have a burning bitter taste, irritate the mucous membrane of the stomach and intestine, causing reflex initiation of th vomiting centre.

Compounds with adaptogenic and stimulating action include a unique group of triterpene saponins from plants of Araliaceae family (ginseng, oplopanax, aralia, eleutherococcus). All these compounds do not belong to the sterols and have similar biological activity. Several kinds of activity are characteristic for all this chemically quite various group of glycosides,:

1. Increasing nonspecific resistance to a wide range of unfavorable, including extreme effects: hypoxia, stress, climate change, a variety of toxic agents, infections, etc. The phenomenon is based, apparently, on the optimization of energy (improving the transmembrane glucose transport, including lipids in the energy metabolism, enhancing gluconeogenesis from metabolic slags), adaptive synthesis of RNA and enzyme, enhance the functions of protective systems at the right time. The action of glycosides is realized, first of all, at the cellular level, and also through the central nervous and endocrine systems. Increased resistance is observed after taking appropriate medications.

2. Increasing the physical and cognitive performance of the body can be clearly seen by repeated intake of these kinds of drugs and repeated load of the body. As a result, the volume and quality of work gradually increase, and fatigue decreases. The ability of plant adaptogens to increase workability is advantageously different from that of stimulants such as phenamine. Due to the optimization of energy metabolism and increasing its efficiency, plant adaptogens make biochemical processes more economical.  They potentiate insulin action, improve the intake of glucose into the cells by activation of hexokinase reaction. They increase gluconeogenesis from metabolic waste and increase the utilization rate in energy metabolism.

3. Improvement of endocrine gland functions is one of the pharmacodynamic properties of plant adaptogens, which is associated with increased adaptation and performance. Under the influence of glycosides, the involution of the adrenal glands and the hyperglycemic effect of glucocorticoids are weakened (the opposite effect of corticosteroids on insulin). The actions of the ginseng and eleutherococcus preparations are better studied in mild diabetes.

4. Stimulation of immunity (along with an increase in nonspecific resistance to infections) has a great practical interest in the treatment of infectious diseases, as well as in the manifestation of other hypoimmune and dissymune states. The influence of glycosides on individual units of the immune system has been little studied.