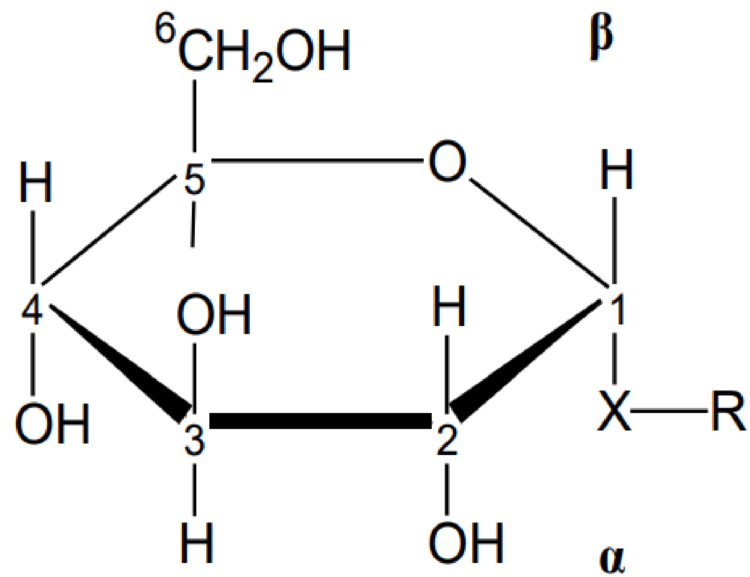
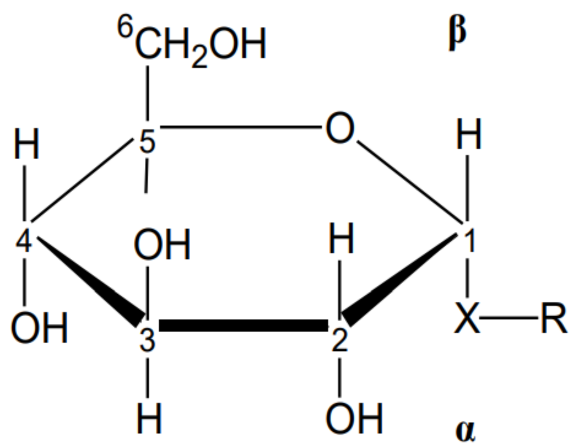
Glycosides. Classification, methods of analysis. Medicinal plants and raw materials containing iridoids.

Glycosides are some of the most common natural substances. They contain fragments of sugars as well as functional derivatives of organic compounds as well as functional derivatives of organic compounds.



The general structural formula of the glycosides.

The carbohydrate part of glycosides is called glycon, and the organic radical that substitutes hydrogen in the glycosidic hydroxyl is called aglycone or genin. The carbohydrate in a glycon is in a cyclic form, and therefore, the OH-group at C1 carbon is a semi-acetal hydroxyl, which readily reacts to form esters. The chemical activity of the ester bond. The chemical activity of the ester bond allows hydrolysis in an acidic environment with the glycoside into 2 components (carbohydrate and aglycon). If oxygen is present in the glycoside in place of the X-atom, the O-glycosides are O-glycosides, If sulphur is S-glycosides, nitrogen is N-glycosides, and carbon is C-glycosides. The most common in nature are O-glycosides.



Monosaccharides are quite often used as carbohydrates, althoughbiose, triose fragments are also found. Therefore, glycosides are sometimes called monosides, biosides, triosides, etc.part of the carbohydrate part, they are sometimes referred to as monosides, biosides, triosides, etc. For-For instance, the biosides are: maltosides (from maltose), lactosides (from lactosides (lactose), etc.

Depending on the position of the glycosidic oxygen, a distinction is made between α and β- forms. α-form, when the group (x - R) is at the bottom, and β-form, when this group is at the top.

A carbohydrate fragment can be in the form of a six-membered ring(pyranose form), or five-membered (furanose form).

However, the main properties of glycosides are due to the nature of the aglycone. Aglycone have a diverse chemical structure from the simplest or to polyfunctional cyclic compounds. The result is the diverse therapeutic actions of the glycosides.

The structure of the glycosides allows easy transport of the aglycone to different. The structure of the glycosides allows the aglycon to be easily transported to different regions of the body, where, following the hydrolysis of the glycoside, the aglycon most often. The free form of the aglycoside has a pharmacological effect.

Therefore, glycosides are most commonly classified according to their aglycone structure.
The glycosides are therefore divided into the following groups:

1. Bitter glycosides (bitter). In this case, the aglycosides are monoterpenes (iridoids).
2. Cardiac glycosides. Here the aglycon are derivatives of1,2 - cyclopentanoperhydrophenanthrene. These derivatives are most common lyare most often steroids.
3. Saponins. In this case the aglycon is a triterpene or steroids of a different structure from the previous one.
4. Glycosides, which contain phenolic compounds or phenolglycosides. These have phenols of different nature.

In their **physical properties**, glycosides are mostly crystalline substances, well soluble in water, are crystalline substances, well soluble in water, but poorly in organic solvents, especially in non-polar solvents.
Glycosides are precipitated with lead acetate solution, barite water [Ba(OH)2] , tannin solution. Almost all glycosides are optically active. Saponins, which contain several sugar residues, usually crystallise poorly.
Glycosides are synthesised in plant tissues and are hydrolysed by enzymes belonging to the group of hydrolases. The most common are glycosidases. The structure of the enzyme depends on the glycan structure. There are glucosidases, fructosidases, etc.
In this regard, when storing raw materials, it should be remembered that glycosidases. Therefore it has to be kept in mind that glycosides are the labile part, and as a result the drying out of the raw material will cause an increase in the enzyme activity.

When a plant dies off and when living cells are damaged or destroyed. The enzymatic breakdown of the glycosides is rapid, especially If freshly harvested plants are stacked in piles, this leads to self-heating and creates optimum temperature conditions for enzymatic breakdown. Therefore, the raw material should be spread out for drying immediately after harvesting, and plants with particularly unstable glycosides should be dried quickly.

Slow drying can lead to a stepwise disintegration of the cardiac glycosides, for example, when the primary (native) glycosides begin to split off monosaccharide molecules are split off, so that the "secondary" glycosides tend to have less pharmacological effect. The sugars provide better solubility and therefore easier resorption of the glycosides.

What has been said about drying also applies in full measure to the storage of glycosidic medicinal raw materials.

When storing glycosidic raw materials, as already it has already been noted, it is necessary to pay special attention to the dryness of the storages. The storage area and prevent the raw material from drying out.

Glycosides are widespread in the plant world and can be found in all parts of plants. They are soluble in the cell sap. Usually there are several different glycosides in plants.

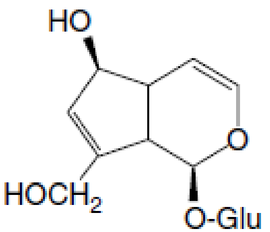
However, despite the abundance of glycosides in nature, only a small proportion have medicinal significance. The study of the chemical structure of glycosides has been slow due to their glycosides, due to their easy degradability and the difficulty of obtaining them in pure form, as well as to their diversity.

The first pure glycoside amygdalin was obtained by German pharmacists Liebich and Wehler in the first half of the nineteenth century. They were the first to establish the concept of glycosides. At the end of the nineteenth century, a monograph on glycosides was first compiled by the Russian master pharmacist E.A. Shatsky.
At the beginning of the twentieth century, a monograph by Dutchman Van Rijn appeared and soon a third monograph by soon followed by a third monograph by the Russian Master of Pharmacy, F.A. Kurroth (1915).
In the study of the sugars component of the glycosides the most famous is the work of the German chemist Emil Fischer (XXc). The nature of the aglycon continues to be studied by chemists of all countries.

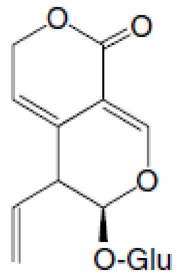
Iridoids

The iridoids are cyclopentan-[*c]-pyran monoterpenoids and constitute* a group of which the number of known members is constantly increasing.

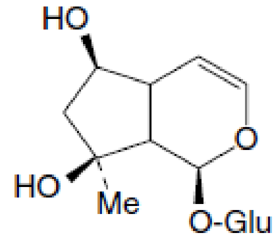
The name derives from *Iridomyrmex, a genus of ants which produces* these compounds as a defensive secretion. In a series of reviews covering the years up to December 1989 several hundred iridoids, classified originally into 10 groups, have been listed. Junior **has reviewed (146 refs) the isolation and structure elucidation** of these compounds. Most occur as glycosides; some occur free and as bis compounds. There are many seco-iridoids, see secologanin, in which the pyran ring is open, and in a few the pyran ring oxygen is replaced by nitrogen.



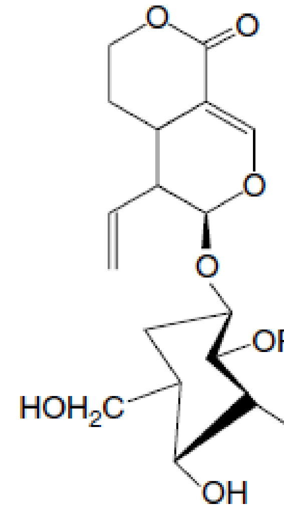
Aucubin–a common iridoid-glycoside



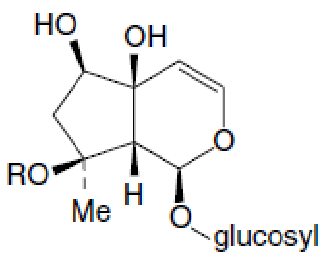
Gentiopicroside–a seco-iridoid of gentian



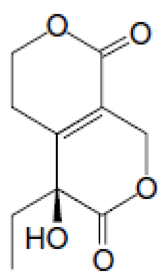
Leonuride



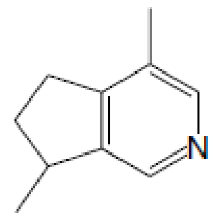
Sweroside; R1 = H, R2 = H
Centapicrin;
R1 = *m*-hydroxybenzoyl
R2 = acetyl



Harpagide; R = H
Harpagoside; R = Cinnamoyl

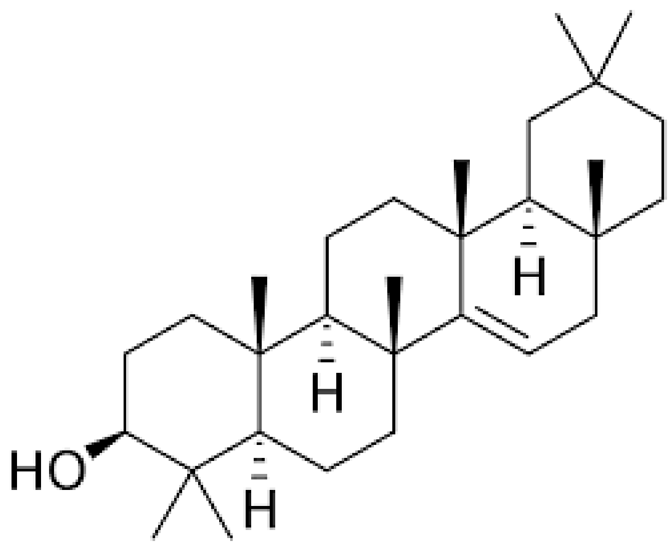


(+)-(*S*)-Gentiolactone



Actinidine–a simple monoterpenoid alkaloid

Bitter substances, or bitters, are nitrogen-free, non-poisonous glycosides with a strong bitter taste that have long been used to stimulate the appetite. They are distinguished from bitter alkaloids by their non-poisonous nature and by their lack of nitrogen.
Chemically, they are poorly understood owing to the difficulty of isolating them in their pure form. This group of glycosides contains a number of terpenoid derivatives as an aglycon. For example, taraxerol, a bitter substance of dandelion root, contains as a glycon the polysaccharide inulin, and the aglycon is a pentacyclic triterpenoid. In the composition of shamrock contains flavonoids and terpene derivatives such as menyanthin as an aglycon. In these glycosides, the aglycon is represented by iridoids, which are derivatives of monoterpenes.



taraxerol,

Bitter glycosides, depending on the composition of the plant material, can be subdivided into aromatic bitters - **Amara aromatica**, where bitter substances occur together with essential oils and are studied in theessential oil plants, and pure bitters - **Amara pura**, predominantly iridoids.

Common Dandelion roots - Taraxaci officinalis radices
Common Dandelion - Taraxacum officinale Wigg.
Family Asteraceae

Taraxacum officinale,
the **dandelion** or **common dandelion**, is a flowering herbaceous perennial plant of the dandelion genus in the family Asteraceae . The common dandelion is well known for its yellow flower heads that turn into round balls of many silver-tufted fruits that disperse in the wind. These balls are usually called "clocks" in both British and American English. The name "blowball" is also used.

Taraxacum officinale grows from (generally unbranched) taproots and produces several hollow, leafless flower stems: 470 that are typically 5–40 centimetres tall, but sometimes up to 70 cm in tall. The stems can be tinted purplish, they are upright or lax, and produce flower heads that are held as tall or taller than the foliage. The foliage may be upright-growing or horizontally spreading; the leaves have petioles that are either unwinged or narrowly winged. The stems can be glabrous or sparsely covered with short hairs. Plants have milky latex and the leaves are all basal; each flowering stem lacks bracts and has one single flower head. The yellow flower heads lack receptacle bracts and all the flowers, which are called florets, are ligulate and bisexual.

The leaves are 5–45 cm in long and 1–10 cm in wide, and are oblanceolate, oblong, or obovate in shape, with the bases gradually narrowing to the petiole. The leaf margins are typically shallowly lobed to deeply lobed and often lacerate or toothed with sharp or dull teeth.

The fruits, called cypselae, range in color from olive-green or olive-brown to straw-colored to grayish, they are oblanceoloid in shape and 2–3 mm in long with slender beaks. The fruits have 4 to 12 ribs that have sharp edges. The silky pappi, which form the parachutes, are white to silver-white in color and around 6 mm wide.

The plant is widely distributed throughout almost all of Russia, except in the Arctic and the highlands. It grows near settlements, along roadsides, in meadows, pastures, vegetable gardens, parks and sometimes as a weed in crops.

Chemical composition. The roots of the dandelion contain bitter glycosides -Taraxacin and Taraxacerin, polysaccharides, among which inulin is characteristic (up to 25%). Triterpene compounds (β-amyrin, arnidiol, faradiol), and sterols - β-sitosterol and stigmasterol. The milky juice contains resinous substances of a rubbery nature.

Standardisation. The authenticity of raw materials and their quality is regulated by GF XIV. For the whole, crushed raw material the extractive substances extracted with water should not be less than 40%.

Dandelion roots are harvested in autumn, dug out with a spade or plough, shaken off the ground, cut off the above-ground part, the rhizomes ("neck") and small roots, then washed immediately in cold water, after the roots are left to air-dry for a few days (until the micaceous juice stops oozing when the roots are cut). Dry in well-ventilated attics, under sheds. May be dried in ovens or dryers at 40-50°C. Repeated harvesting of the raw material from the same plantations.
Repeated harvesting of the raw material from the same bush should be done at an interval of 2 to 3 years.

Whole raw material is represented by tap root, sparse branching roots,Solid or broken, 2-15 cm long and 0.3-3 cm thick. The rootsare longitudinally-wrinkled, sometimes helically twisted. The fracture is granular; in the centre of the root there is yellow wood, surrounded by broad grayish-white bark.surrounded by a broad grayish-white bark. The bark (under a magnifying glass) shows groups of sponges, arranged in concentric bands. The outer surface is light brown to dark brown, dark brown on the outside. It has no smell. The taste is bitter with a sweet aftertaste.

The roots are used in the form of an infusion as a bitter to stimulate the appetite, as a choleretic, and as a mild laxative for constipation. They are included in appetizing, stomachic and diuretic herbals.

Western phytotherapists use the leaves for some diseases. In China they use the whole plant.

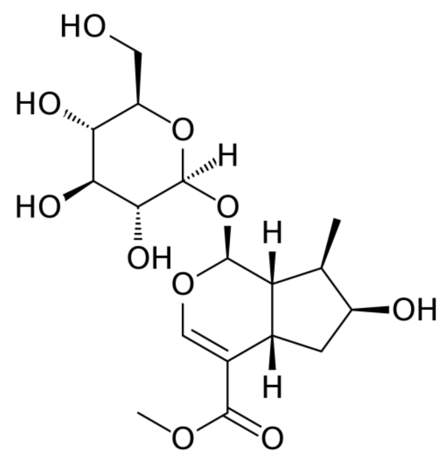
bogbean leaves - Menyanthidis trifoliatae folia
bogbean (buckbean) - Menyanthes trifoliate L.
Family Menyanthaceae

It is a wetland herbaceous plant with a long, creeping rhizome that takes root.
A herbaceous plant with a long, creeping rhizome that takes root in muddy substrates.in muddy substrate.
The top of the rhizome is elevated and bears leaves and flowers above the water.
The leaves have very long petioles (up to 20 cm) that contain aerenchyma and therefore float easily.

Leaves are alternate, deeply tripartite. Leaf lobes elliptic or oblong-obovate, entire margins. The peduncle is long, with air cavities, bearing a dense cluster of five-membered pinkish-white flowers. Corolla funnel-shaped, densely pubescent inside. The fruit is a capsule. Seeds elliptic, compressed on both sides, glossy.

Widespread throughout the European part, except in the southern. In the north it penetrates the tundra zone, reaching the coast of the Arctic Ocean. It also grows throughout the Asian part of the country, with the exception of Central Asia and the Far North. Central Asia and the Far North.

Chemical composition. The main active substances in the leaves monoterpene bitternesses loganine, sveroside, menyanthine and traces of alkaloids are the main active substances in the leaves of the tricarp. They also contain the flavonoids rutin, hyperoside and Trifolin, which are choleretic agents. A small amount of tannins, carotenoids, ascorbic acid and some iodine.



loganine

According to GF XIV in the whole, crushed raw material content of the sum of flavonoids in terms of rutin should not be less than 1%.

Harvest the fully developed leaves with no more than 3 cm of petiole remaining. The raw material is harvested after the plant has finished flowering in July and August. It needs to be harvested in warm weather, as pickers have to go into thein the water. Do not cut the young and apex leaves, as they can get darker when dried. They tend to darken in the drying process.

The plants should not be pulled up by the root to avoid destroying the thickets. Repeat harvesting at the same repeat harvesting in the same location after a maximum of two to three years.

The harvested leaves are exposed to the wind for a few hours and then they are piled loosely in an open container and quickly left to dry. The leaves are dried in dried in a tumble drier at 40 to 50° C or in attics, barns or other well-ventilated areas, sheds or other well-ventilated areas. The leaves are spread in a thin layer, occasionally turn them upside down. Remove blackened leaves from the dried material leaves, petioles longer than 3 cm and foreign impurities are removed from the dried material.

The whole raw material is represented by the whole or partially shredded naked, deeply three-parted leaves with a residual petiole up to 3 cm long. The leaf lobes are elliptic or oblong-obovate, smooth-edged, sometimes with sparse denticles. Colour green. Odour faint. Taste very bitter (bitterness index 1:10000).

Pharmacological action. Bitterness (appetite stimulant and choleretic).

The leaves are used in the form of an infusion as an appetite booster and increases gastrointestinal secretion. Included in the collection -appetizing, choleretic. Produce a thick extract used for bitter tincture.

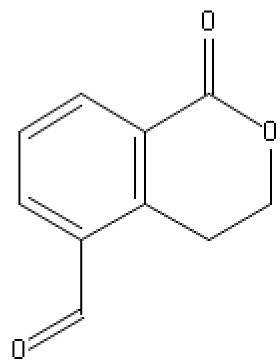
Centaury herb - Centaurii nerba
bachelor's button – Centaurium umbellatum, common centaury (European centaury) - Centaurium erythraea
Family Gentianaceae

This is an erect biennial herb which reaches half a meter in height. It grows from a small basal rosette and bolts a leafy, erect stem which may branch. The triangular leaves are arranged oppositely on the stem and the erect inflorescences emerge from the stem and grow parallel to it, sometimes tangling with the foliage. Each inflorescence may contain many flowers. The petite flower is pinkish-lavender and about a centimeter across, flat-faced with yellow anthers. The fruit is a cylindrical capsule.

Centaurium erythraea

This centaury is a widespread plant of Europe (including Scotland, Sweden and Mediterranean countries) and parts of western Asia and northern Africa. It has also naturalised in parts of North America, New Zealand, and eastern Australia, where it is an introduced species.

Chemical composition. The herb contains bitternesses which are monoterpene glycosides (iridoids): sveroside, gentiopycroside,erythrocentaurin, and 0.6 to 1% of alkaloids (gentianin or erythricin and other pyridine derivatives). The herb also contains tannins, ascorbic and oleanolic acids, and seven xanthones.



erythrocentaurin

According to the XIV Pharmacopoeia the content of the sum of xanthones in the terms of alpizarin should not be less than 1.5%.

Harvest during flowering while the root leaves are still in place. Cut the above-ground part of the plant with a knife or sickle above root leaves. The cut herbs are placed in baskets with the flowers on one side.one side. Dry herbs in drying rooms or in attics.

The herb is dried in a drying oven at 40 - 50°C or in attics, less often under well ventilated sheds, in a thin layer so that all the inflorescences are on the same side.

The whole raw material consists of flowering shoots. Stems are tetrahedral with obtuse or winged ribs, glabrous, branched at the top. Leaves opposite, sessile, with five veins, oblong obovate or lanceolate, glabrous, smooth-edged. Inflorescences calyx-shaped. Flowers are actinomorphic, pentamerous, with a double perianth. Corolla with a long cylindrical tube and a five-septate unguent. The colour of stems, leaves, calyx is yellowish-green, corolla pinkish-purple and yellow. The smell is faint. The taste is bitter.

Pharmacological action. Bitterness (appetite enhancer).

The medicinal use of Centaury is reported by Hippocrates, Theophrastus, Dioscorides and Avicenna. In modern medicine, it is used in the form of infusions and decoctionsas a bitter to stimulate the appetite, in gastritis with reduced secretion, some dyspepsia, liver, gallbladder and kidney ailments. The tincture of Centaury is part of a complex bitter tincture. The raw material is included in appetising herbal preparations. In high doses, preparations of Centaury can cause digestive upset.


Thank you
for your
attention