Antinutritional, toxic and other bioactive compounds

Compounds in food

beneficial indifferent antinutritive toxic

- natural antinutritive and toxic compounds
- foreign substaces
  - food additives
  - pollutants
    - exogenic
    - endogenic, processing

special case

microbial toxines (bacterial toxin and mycotoxins)

antinutritive compounds — **interference with nutrients**

toxic compounds

- natural toxic compounds — **toxins**
- products of anthropogenic activity — **xenobiotics**

toxic effects

- acute
- late (chronic)

the risk level

- contaminants
- toxins
- additive
- antinutritional substances

legislation

feeding experiments → NOAEL (No Observed Adverse Effect Level) → ADI (Acceptable Daily Intake) = NOAEL/100 (mg/kg), safety factor (100 or more)

anti-nutritive substances

plant origin, potential risk

- **enzyme inhibitors,**
  anti-enzymes
- **substances interfering with metabolism of vitamins,**
  anti-vitamins, antagonists of vitamins
- **substances interfering with metabolism**
  of metals
- **phenol compounds (tannins) reaction with proteins**
- **galactooligosaccharides (α-galactosides) causing flatulence**

anti-enzymes

inhibitors of proteases (anti-proteases),

inhibitors of serine proteases (trypsin, chymotrypsin, elastase)

weight loss of domestic animals, inactivation by heat (proteins)

anti-vitamins

- **structure analogues (oxythiamine, linatin)**
- **enzymes (ascorbase, thiaminase, lipoxygenase)**
- **formation of non-utilisable complexes (avidin)**

mineral binding compounds

♦ phytic acid and phytine	Fe, Zn
♦ oxalic acid	Ca
♦ glucosinolates and their degradation products	I

tannins

slow growth of domestic animals

decrease of protein digestibility and of minerals absorption

α-galactosides

raffinose, higher homologues, gastrointestinal problems

toxic compounds

plant and animal origin, real risk

- developing food intolerance

toxic to certain individuals

- developing intoxication

toxic to all individuals

food developing food intolerance

0,3-7% population

allergy (immunological reaction), alergenes (imunogenes),
non developing formation of IgE

celiac disease
non gluten diet (<100 mg/kg dry matter gliadin)

intolerance (non-immunological manifestation),
malfunction of metabolisms, hypersensitiveness (anaphylaxis),
averse effects (idiosyncrasy)

lactose intolerance

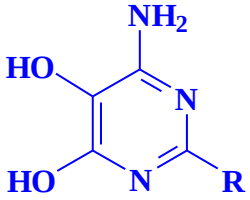
foods with low content (<10 g/kg)
lactose free (100 mg/kg)

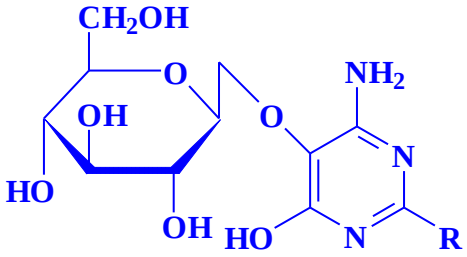
phenylketonuria,

protein hydrolysates without Phe

favism

fava beans (*Vicia faba*)





divicine, R = NH_2
isouramil, R = OH

vicine, R = NH_2
convicine, R = OH

toxins and other compounds developing intoxication

classification

- according to structure
- according to origin
- according to toxic effects

main groups of toxins

alkaloidy

- alkaloids
- saponins
- cyanogens
- glucosinolates
- lectins
- estrogenic substances
- phototoxic substances
- toxic amino acids and their products (biogenic amines)

+ others

anti-nutritive and toxic compounds of legumes

- inhibitors of proteases and amylases
- α-galactosides
- substances developing favism
- lectins
- cyanogenic glycosides
- estrogens
- saponins
- lathyrogens

toxic compounds of mushrooms

- proteins
- peptides
- amino acids
- amines
- hydrazines
- alkaloids
- terpenoids

alkaloids

classification

- **true alkaloids**

(*N*-heterocycles, derived from amino acids)

pyridine (nicotinic)	tobacco a.
piperideine	pepper a.
pyrrolizidine	senecioic (necins) a.
quinolizidine	lupine a.
quinoline	quinine (bark of cinchona tree) a.

- **pseudoalkaloids**

(*N*-heterocyclic, derived from others precursors)

purine	coffee, tee, cocoa a.
terpenoid (glycoalkaloids)	potato, tomato a.

- **Protoalkaloids**

(non N-heterocycles, derived from amino acids)

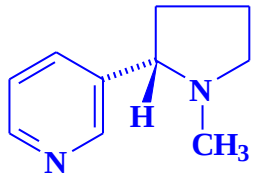
capsaicinoids	bell pepper and chilli pepper a.

Structural types of basic skeleton	Occurrence	Precutsors	Example
True alkaloids			
Pyridine	Tobacco leaves	Nicotinic acid, Orn, Lys	Nicotine, nornicotine, anatabine, anabasine
Piperidine	Black pepper seeds	Lys	Piperine
Pyrrolizidine	Ragworts, goundsels	Orn, Ile	Senecionine
Quinolizidine	Lupin seeds	Lys	Lupanine, Lupinine, Sparteine
Quinoline	Cinchona bark	Trp	Quinine, quinidine
Pseudoalkaloids			
Purine	Coffee, tea, cocoa	Purines	Coffeine, theobromine, theophylline
Steroid (terpenoid)	Potatoes, tomatoes	Mevalonic acid	Solanine, tomatine
Protoalkaloids			
Capsaicinoides (vanillylamides)	Chili pepper	Phe, Leu, Val	Capsaicine

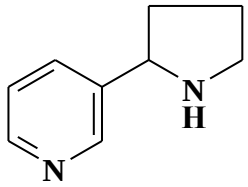
pyridine alkaloids

nicotine and minor alkaloids (~ 20 compounds)

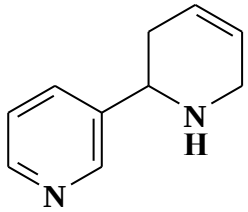
tobacco



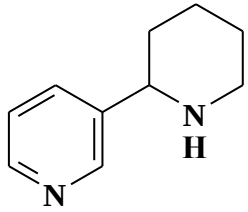
nicotine



nornicotine



anatabine



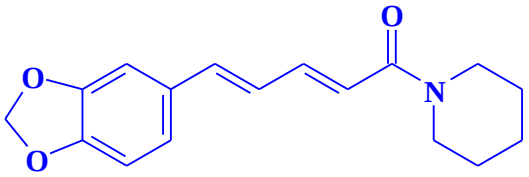
anabasine

obligation to declare their content on tobacco products, warning

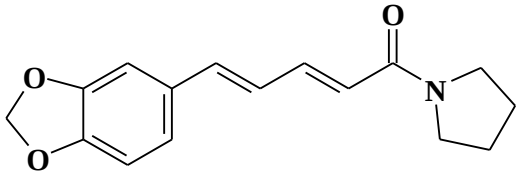
piperidine alkaloids

piperine – pungent strong, sharp smell

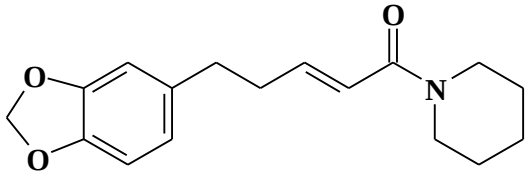
homologues, geometric isomers



piperine

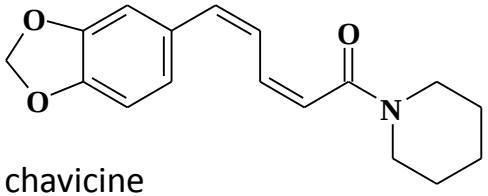


piperyline

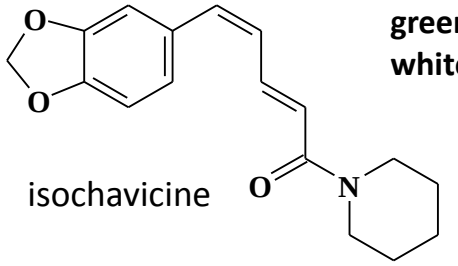


piperanine

light

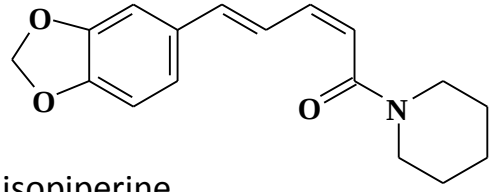


chavicine



isochavicine

nearly tasteless



isopiperine

Black pepper (*Piper nigrum*)
4.6-9.7% of piperine

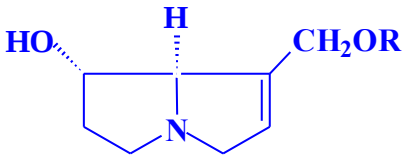
black pepper (cooked and dried unripe fruit)
green pepper (dried unripe fruit)
white pepper (ripe fruit seeds)

- once ground, pepper's aromatics can evaporate quickly; most culinary sources recommend grinding whole peppercorns immediately before use for this reason

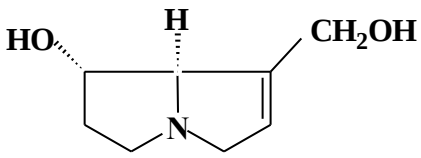
pyrrolizidine alkaloids

mono-, di-, macrocyclic esters of plants

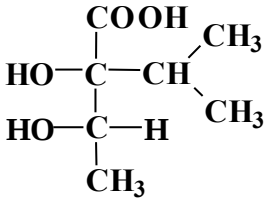
hepatotoxic compounds



echinatine



heliotridine



viridifloric acid

Symphytum officinale

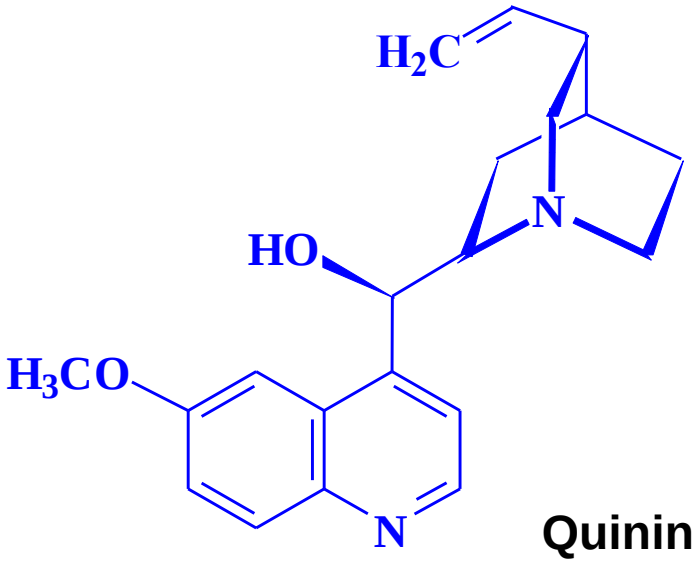
Viper's Bugloss

Petasites hybridus

Tussilago

quinoline alkaloids

cinchoma tree



Quinine

purine alkaloids

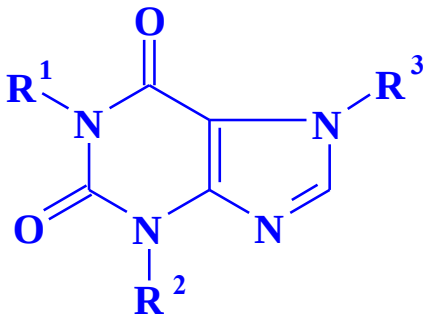
group of similar compounds

coffee, tee, cocoa (chocolate), mate, guarana

caffeine	$R^1 = R^2 = R^3 = CH_3$
theobromine	$R^1 = H,\ R^2 = R^3 = CH_3$
theophylline	$R^1 = R^2 = CH_3,\ R^3 = H$

~~theine~~

guaranine



alkaloids content in green coffee beans

Alkaloid	Content in dry matter (%)		
	Coffea arabica	*Coffea canephora*	*Coffea liberica*
Coffeine	0.53-1.45	2.11-2.72	1.28-1.35
Theobromine	< 0.005	< 0.005-0.01	< 0.005
Theophylline	< 0.005	< 0.005-0.01	0.01
Trigonelline	0.97-1.31	0.57-0.88	0.25-0.29

The European Commission Directive 2002/67/EC states only that if a beverage intended for consumption contains caffeine in a proportion in excess of 150 mg/l, the product must have on the label message 'High caffeine content'.

steroid glycoalkaloids

row of relative compounds

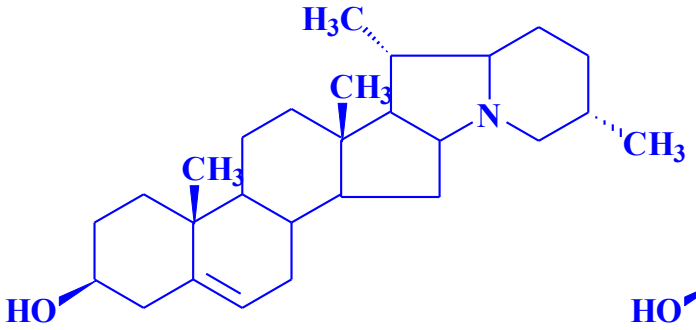
potato, tomato, eggplant

heteroglycosides, aglycones, sugars

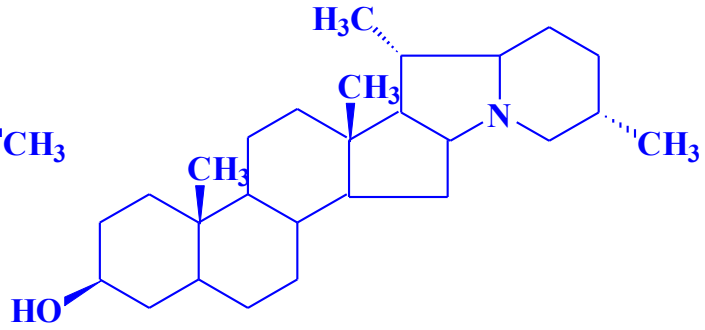
potato: ~ 95%

α-solanine = solanidine + β-solatriose

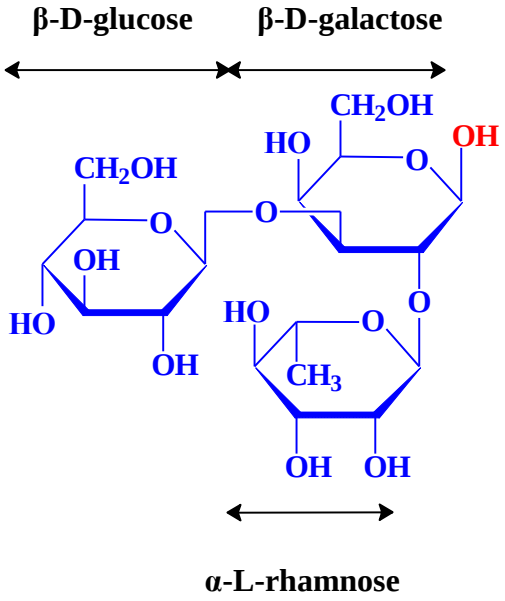
α-chaconine = solanidine + β-chacotriose



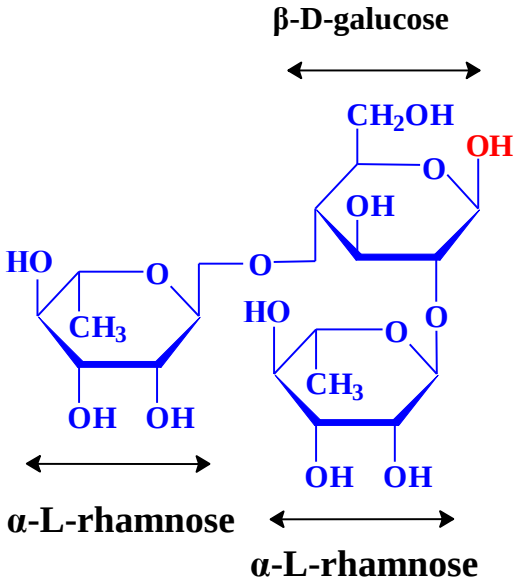
solasodine



demissidine



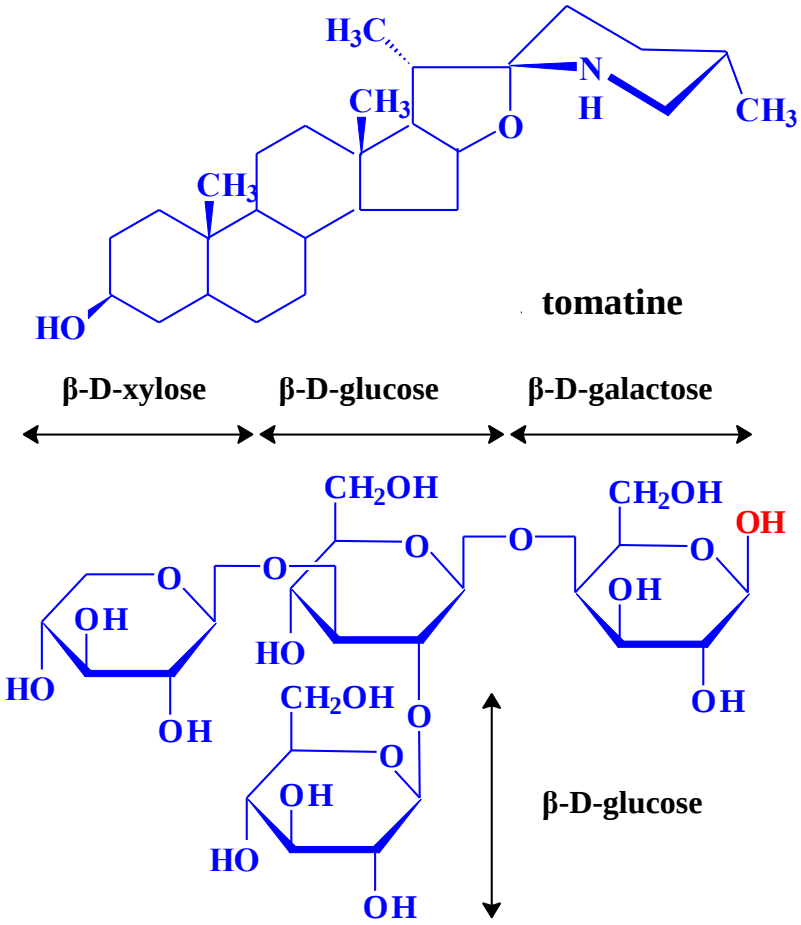
β-solatriose



β-chacotriose

tomato:

tomatine = tomatidine + β-lycotetraose



legislation: 200 mg/kg, teratogenic

distribution and content of glycoalkaloids in potatoes

part of tuber	content $mg.kg^{-1}$ (fresh weight)
Unpeeled	75
Peel (2-3% of tuber weight)	300-600
Peel (10-15% of tuber weight)	150-300
Peel with germ (ϕ 3 mm)	300-500
Peeled	12-50

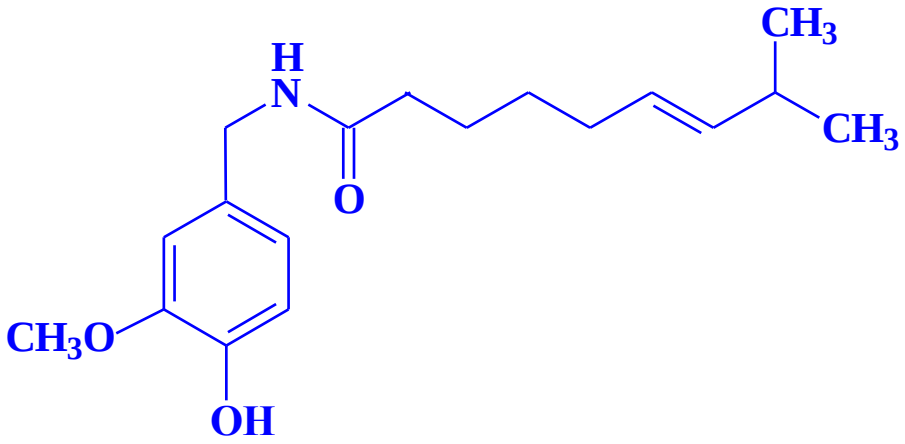
tomatine content in tomatoes

state of ripeness (days after flowering)	content $mg.kg^{-1}$ (fresh weight)
Small and green (10)	795
Large and green (20)	49
Pink (30)	20
Light red (40)	1.5
Red ans ripe (50)	3.7

capsaicinoids

capsaicin, homologues, bell and chilli peppers (pungent compounds)

influence of technological procedures



capsaicin, (E)-8-methyl-*N*-vanillylnon-6-enamide

saponins

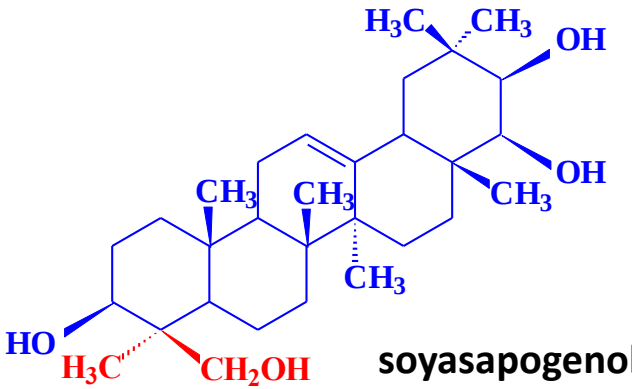
many similar compounds of plant origin

heteroglycosides, aglycone, sugar

aglycone = sapogenin (sapogenol),

- **triterpenoic alcohols**

sterols (4-demethylsterols)



soyasapogenol A

saponins content in legumes and onther plants

plant	content %
soya bean	0.22-5.6
common bean	0.35-1.6
peanut	0.01-1.6
spinach	4.7
beet	5.8
liquorice	2.2-15.0

biological effects

erythrocyte hemolysis, damage of intestinal mucose

- **toxic for cold-blooded animals**
- **bitter taste**
- **detergents activity, emulsion (o/v)**
- **fungicide, antioxidant, anti-carcinogenic , anti-cholesterolemic activities**

usage

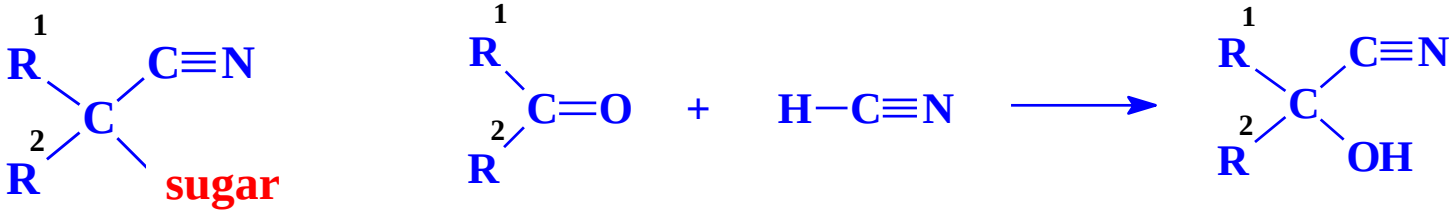
- **foaming compounds (cosmetics)**
- **emulsifiers (cosmetics)**
- **sweeteners (glycyrrhizin, liquorice: 0,2-5,6% saponins)**

cyanogenic glucosides

many compounds of similar structure **foods of plant origin**

heteroglycosides, aglycone, sugar,

aglycone = 2-hydroxynitril (cyanhydrin)



nitriles of 2-hydroxycarboxylic acids

substituents

- **aliphatic**
- **aromatic**

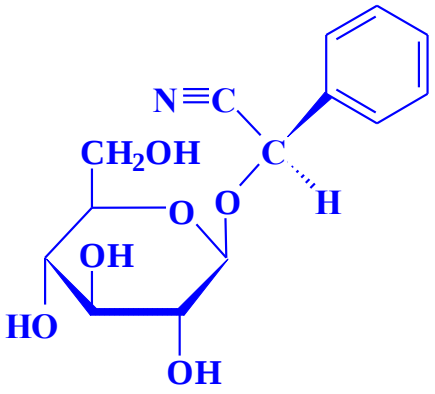
chirality

acetone, methyl(ethyl) ketone

benzaldehyde

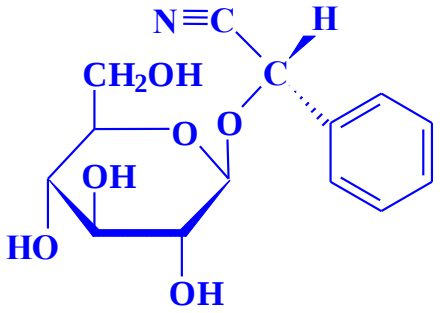
sugar

- **mostly Glu**
- **disaccharides: genciobiose and others**



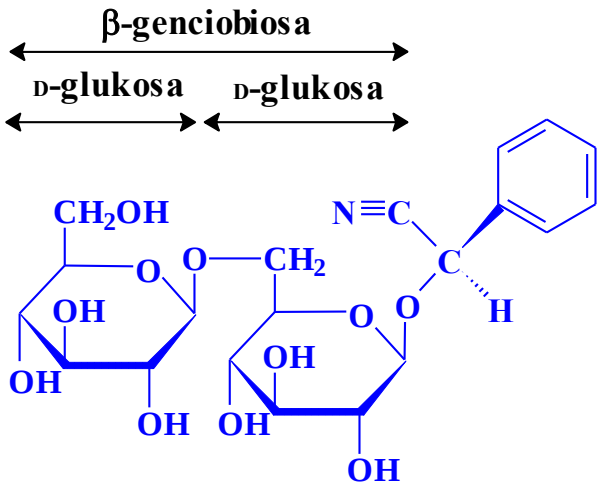
(*R*)-prunasin

plum seeds



(*S*)-sambunigrin

elderberry (leaves, unripe fruits)



(*R*)-amygdalin

plum seeds

properties

- **decomposition (β -glucosidase) → HCN**
- **toxicity (inhibition of cytochromoxidase)**

  actual intoxication,

  chronic intoxication (cassava, manioc)

LD_{50} = 0.5-3.5 mg/kg, i.e. 35-245 mg (70 kg)

origin	HCN (mg.kg^{-1} of fresh material)
cassava	
tuber bark	840-2450
whole tubers	550 (100-330)
bamboo	
unride shoots	3000
tops of unripe shoots	8000
stone fruits	
apricot stones	3200
sour cherry stones	3540
sour cherry flesh	10
sweet almonds	0-100
bitter almonds	2800-410
flax	
seeds	200-380

glucosinolates

thioglucosides (glucosides of mustard oils),

plum seeds,

foods of plant origin (*Brassica* plants))

heteroglycosides, sugar,

aglycone = thiohydroxamate-O-sulphonate, K^+ ion

substituents

- **aliphatic**
- **aromatic**
- **heterocyclic**

sugar

exclusively Glc

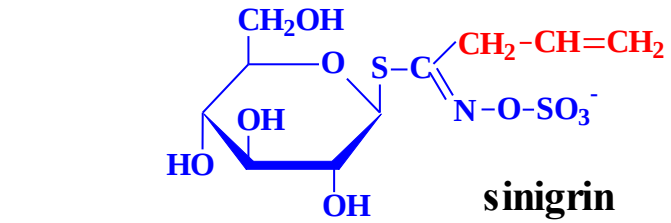
glucosinolate	substituent R	occurrence
sinigrim	prop-2-en-1-yl (allyl)	charlock, vegetable
progoitrin	(*R*)-2-hydroxybut-3-en-1-yl	rape, vegetable
glucoraphanin	4-methylsulfinylbutyl	radish
sanalbin	4-hydroxybenzyl	white mustard
glucobrassicin	3-indolylmethyl	vegetables

properties

- degradation (myrosinase) → isothiocyanates, nitriles and other products
- toxicity

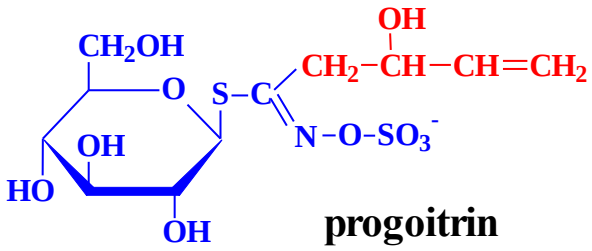
isothiocyanates and goitrin strumigenic,

nitriles hepatotoxic

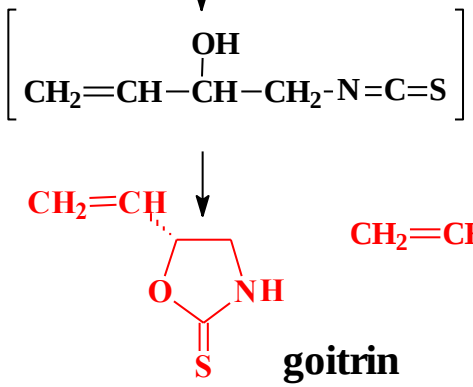


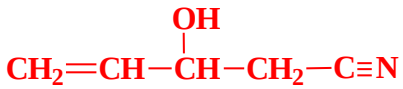
sinigrin

allyl isothiocyanate **allyl cyanide**



progoitrin

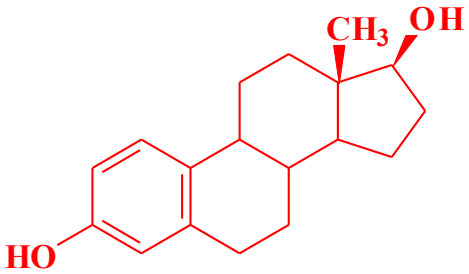




goitrin

plant phenols

estrogenic compounds

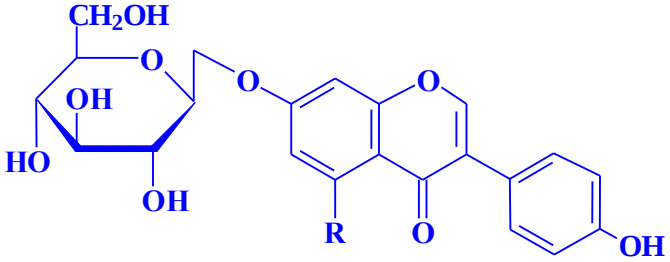


estradiol

- **phytoestrogenes** — food of plant origin

  isoflavones

  content in soy beans

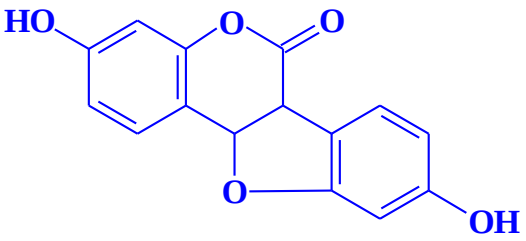


daidzin, R = H — aglycon daidzein

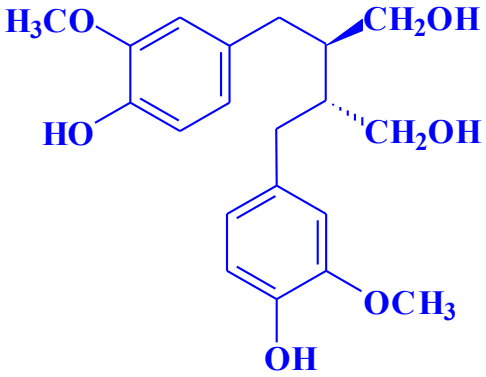
genistin, R = OH — aglycon genistein

content in soy beans (0.13 - 0.42%)

pterocarpanes
lignans



coumestrol
germinated soy beans



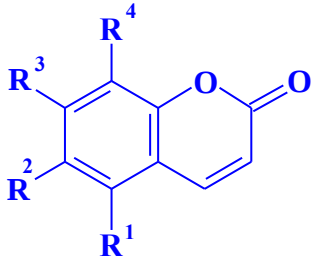
secoisolariciresinol
linseeds

- **mycoestrogenes**
- **xenoestrogenes**

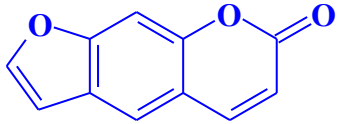
properties
simultaneously useful and harmful

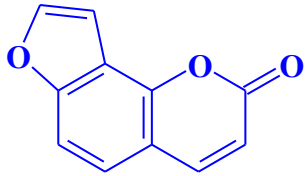
phototoxic compounds

- **cumarins** — **foods of plant origin**



cumarine





furanocumarine

linear psoralen **angular angelicin**

properties

- **phototoxicity (sensitivity of non pigmented skin, connection with skin cancer, acute dermatitis)**
- **phytoalexins (phytoncides, plant antibiotics, pesticides), blastocolines (inhibit germination of seeds)**
- **antimicrobial effects**
- **anticoagulant effects**
- **vasodilatory effects**
- **spasmolytic effects**

- **phototoxic pigments**

hypericin (St. John's wort), fagopyrin (buckwheat))

lectins

fytohematoglutinins

foods of plant origin (seeds and other parts of plants)

proteins with another centre than catalytic

- **merolectins (1 centre, catalytic no)**
- **hololectins (2 centres, catalytic no)**
- **chimerolectins (1-2 centres, catalytic yes)**

soy lectin

metaloprotein, 120 kDa,

bound N-acetyl-D-galactosamine

properties

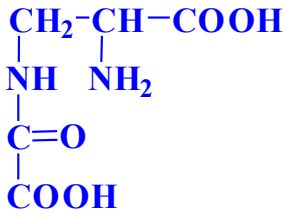
- precipitate of erythrocytes, interaction with sugar in glycoproteins and glycolipids membranes (protection mechanism of plants against predators, parasites)
- toxic intravenously, some orally, some not at all,
- some probiotics (garlic)

amino acids

lathyrogens

foods of plant origin (seeds of vetch)

amino acids (peptides, nitriles)



3-(N-oxalyl)-2,3-diaminopropionic acid

properties

- **structure appearance with proteinogenic amino acids, metabolic failure**
- **deformation of legs (osteolathyrism), above all farm animals**
- **injury of blood vessel (angiolathyrism),**
- **disorder of neural system (neurolathyrism), human**

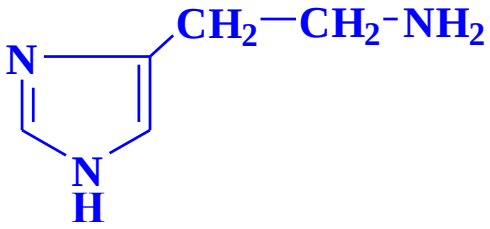
biogenic amines

aliphatic, aromatic, heterocyclic bases with biological activity

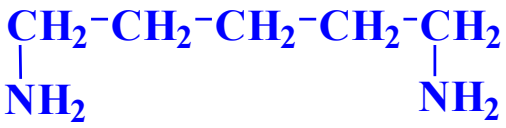
fermented and microbially adulterated plant and animal foods

formation

- **zfrom amino acids by microbial carboxylyases and transaminases**



histamine (His)



cadaverine (Lys)

food	histamine	cadaverine
meat		
pork	0-45	0-171
sausages	tr-550	tr-787
fish		
tuna	tr-8000	tr-447
sardine	4-2350	18-1050
cheeses		
emmental	tr-2000	0-460
roquefort	0-4100	42-905
other foods		
sauerkraut	1-200	1-311
soya sauce	0-274	-
beer	0-22	0-40
wine	0-30	3-108

tr = traces

properties

- hormones (allergic reaction, anaphylactic shock)
- psychoactive and vasoactive compounds

biogenic amine	original AA	biological activity
histamine	His	local tissue hormone, reduces blood pressure, effect on gastric juice secretion, participation in anaphylactic shock and allergic reactions
cadaverine	Lys	stabilisation of macromolecules (nucleic acids), subcellular structures (ribosomes), stimulation of cell differentiation, vegetable hormone
putrescine	Arg *via* Orn or Cit	stabilisation of macromolecules (nucleic acids), subcellular structures (ribosomes), stimulation of cell differentiation, vegetable hormone
agmatine	Arg	stabilisation of macromolecules (nucleic acids), subcellular structures (ribosomes), stimulation of cell differentiation, vegetable hormone
phenylethylamine	Phe	neuromodulator, neurotransmitter in mammalian central nervous systém
tyramine	Tyr	precursor of dopamine, local tissue hormone, increases blood pressure, effect on smooth muscle contraction
dopamine	DOPA	mediators of sympathetic nerves
tryptamine	Trp	local tissue animal and plant hormones (catecholamines), effect on blood pressure, intestinal peristalsis, mental functions