

Phenylpropanoids comprise a multitude of plant secondary metabolites and cell wall components

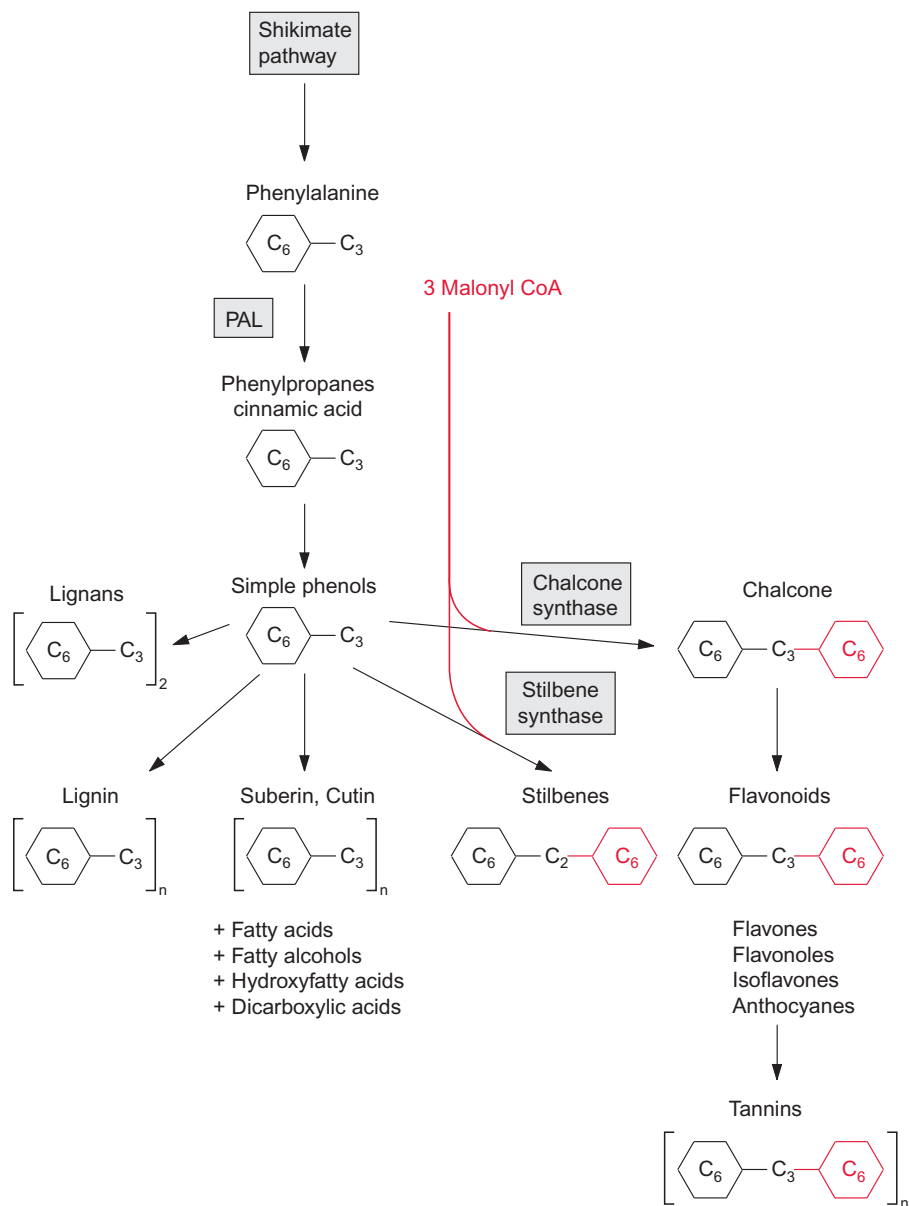
Plants contain a large variety of phenolic derivatives, which contain a phenyl ring and a C₃ side chain and are collectively termed **phenylpropanoids**. As well as simple phenols, these comprise flavonoids, stilbenes, tannins, lignans and lignin (Fig. 18.1). Together with long chain carboxylic acids, phenylpropanoids are also components of suberin and cutin. These rather structurally divergent compounds have important functions as antibiotics, natural pesticides, signal substances for the establishment of symbiosis with rhizobia, attractants for pollinators, protective agents against ultraviolet (UV) light, insulating materials to make cell walls impermeable to gases and water, and structural material to assist plant stability (Table 18.1). All these substances are derived from phenylalanine, and in some plants also from tyrosine. Phenylalanine and tyrosine are synthesized by the **shikimate pathway**, described in section 10.4. The flavonoids, including flavones,

Table 18.1: Some functions of phenylpropanoids

Coumarins	Antibiotics, toxins against browsing animals
Lignan	Antibiotics, toxins against browsing animals
Lignin	Cell wall constituent
Suberin and cutin	Formation of impermeable layers
Stilbenes	Antibiotics, especially fungicides
Flavonoids	Antibiotics, signal for interaction with symbionts, flower pigments, light protection substances
Tannin	Tannins, fungicides, protection against herbivores

isoflavones, and also anthocyanidins inherit the phenylpropane structure, and additionally a second aromatic ring that is built from three molecules of malonyl CoA (Fig. 18.1). This also applies to the stilbenes, but here, after the introduction of the second aromatic ring, one C atom of the phenylpropane is split off.

Figure 18.1 Overview of products of the phenylpropanoid metabolism. Cinnamic acid, synthesized from phenylalanine by phenylalanine ammonia lyase (PAL), is the precursor for the various phenylpropanoids. In some plants, 4-hydroxycinnamic acid is synthesized from tyrosine in an analogous way (not shown in the figure). An additional aromatic ring is built either by chalcone or stilbene synthase from three molecules of malonyl CoA.



18.1 Phenylalanine ammonia lyase catalyzes the initial reaction of phenylpropanoid metabolism

Phenylalanine ammonia lyase, abbreviated **PAL**, catalyzes a deamination of phenylalanine (Fig. 18.2): a carbon-carbon double bond is formed during the release of NH_3 , yielding *trans*-cinnamic acid. In some grasses, tyrosine is converted to 4-hydroxycinnamic acid in an analogous way by **tyrosine ammonia lyase**. The released NH_3 is probably refixed by the glutamine synthetase reaction (section 10.1).

PAL is one of the most intensively studied enzymes of plant secondary metabolism. The enzyme consists of a tetramer with subunits of 77 to 83 kDa. The formation of phenylpropanoid **phytoalexins** after fungal infection involves a very rapid induction of PAL. PAL is inhibited by its product *trans*-cinnamic acid. The phenylalanine analogue aminooxyphenylpropionic acid (Fig. 18.3) is also a very potent inhibitor of PAL.

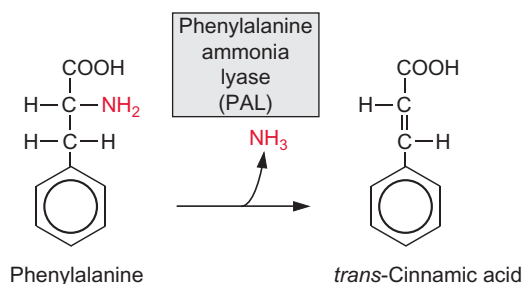


Figure 18.2 Synthesis of *trans*-cinnamic acid.

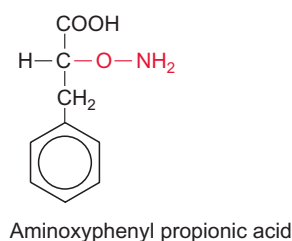
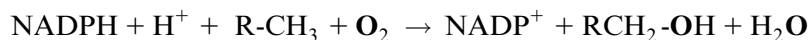


Figure 18.3 Aminooxyphenylpropionic acid, a structural analogue of phenylalanine, inhibits PAL.

18.2 Monooxygenases are involved in the synthesis of phenols

The introduction of the hydroxyl group into the phenyl ring of cinnamic acid (hydroxylation, Fig. 18.4) proceeds via a **monooxygenase catalyzed reaction** utilizing cytochrome P₄₅₀ as the O₂ binding site according to:



In this reaction, electrons are transferred from NADPH via FAD (Fig. 5.16) to cytochrome-P₄₅₀ (pigment with absorption maximum at 450 nm) and subsequently to O₂. From the O₂ molecule, only one O atom is incorporated into the hydroxyl group; the remaining O atom is reduced to yield H₂O. Since both O atoms are incorporated into two different molecules, it is a **monooxygenase reaction**. Like cyt-*a*₃ (section 5.5), cyt-P₄₅₀ can bind CO instead of O₂. Therefore, P₄₅₀-monooxygenases are inhibited by CO.

P₄₅₀-monooxygenases are widely distributed in the animal and plant kingdoms. Genomic analyses of the model plant *Arabidopsis thaliana*

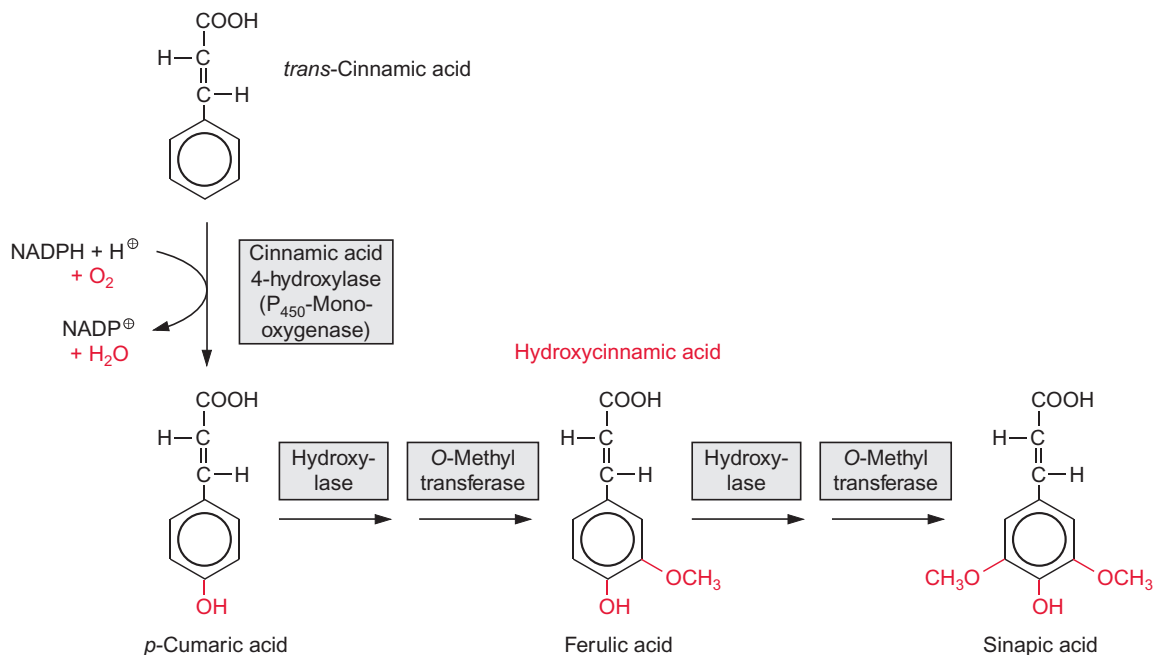


Figure 18.4 Synthesis of various hydroxycinnamic acids from *trans*-cinnamic acid.

revealed about 300 different genes that encode P₄₅₀-proteins. It seems to be the largest gene family in plants. The majority of these proteins is probably involved in the generation of hydroxyl groups for the synthesis of plant hormones and secondary metabolites, but they also play an important role in detoxification processes (e.g., the detoxification of herbicides) (section 3.6).

Like all P₄₅₀-monooxygenases, the cinnamic acid hydroxylase is bound at the membranes of the endoplasmatic reticulum. *p*-Coumaric acid can be hydroxylated further at positions 3 and 5 by hydroxylases, again by the P₄₅₀-monooxygenase reaction type. The -OH groups thus generated are methylated mostly via *O*-methyl transferases with **S-adenosylmethionine** as the methyl donor (Fig. 12.10). In this way ferulic acid and sinapic acid are synthesized, which, together with *p*-coumaric acid, are the precursors for the synthesis of lignin (section 18.3).

Benzoic acid derivatives, including **salicylic acid** as well as a derivative of benzaldehyde, **vanillin** (the aroma substance of vanilla), are formed by cleavage of a C₂ fragment from the phenylpropanes (Fig. 18.5). Under the trade name aspirin, the acetyl ester of salicylic acid is widely used as a remedy against pain, fever, and other illnesses and is probably the most frequently used pharmaceutical worldwide. The name salicylic acid is derived from *Salix*, the Latin name for willow, since it was first isolated from the bark of the willow tree, where it accumulates in high amounts. Since ancient times, the salicylic acid content of willow bark was used as medicine in the Old and New Worlds. In the fourth century BC Hippocrates gave women willow bark to chew to relieve pain during childbirth. Native Americans also used extracts from willow bark as pain killers.

Salicylic acid also affects plants. It has been observed that tobacco plants treated with aspirin or salicylic acid have enhanced resistance to pathogens, such as the *Tobacco mosaic virus*. Many plants show an increase in their salicylic acid content after being infected by viruses or fungi, but also after being exposed to UV radiation or ozone stress. Salicylic acid is an important signal component of signal transduction chains that lead to the expression of enzymes involved in **defense reactions** against viruses, bacteria, and fungi (sections 16.1 and 19.9). *Arabidopsis* mutants, which have lost the ability to produce salicylic acid, are more prone to infection, while a dose of salicylic acid can give better protection against pathogens. This principle is now used commercially. A salicylic acid analogue with the trade name **Bion** (Syngenta) is being sprayed on wheat to prevent mildew infection.

However, salicylic acid not only triggers defense reactions, but can also induce blooming in some plants. By stimulating the mitochondrial alternative oxidase (section 5.7), it activates the production of heat in the spadix of the voodoo lily, emitting a carrion-like stench.

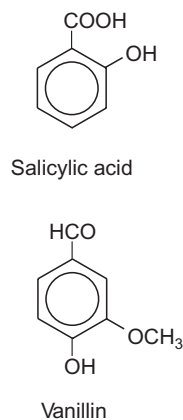
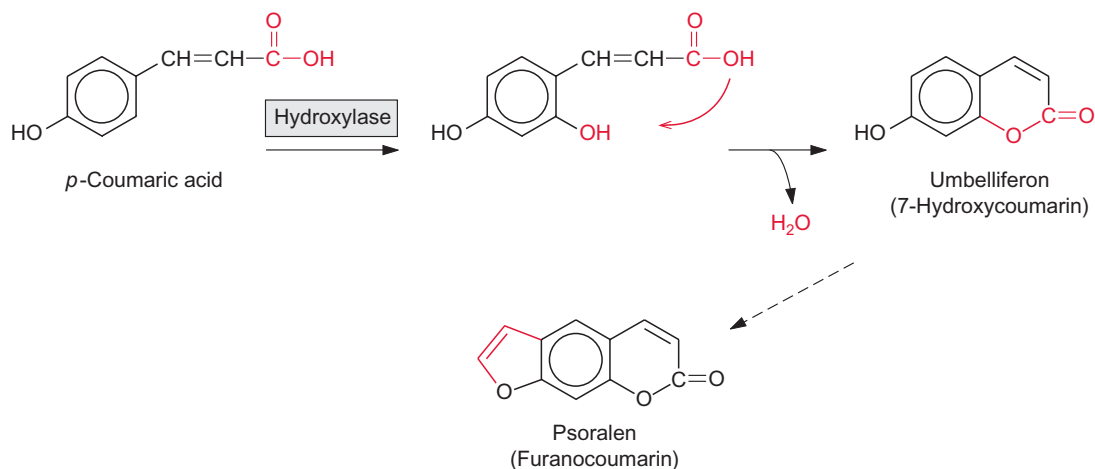


Figure 18.5 Salicylic acid and vanillin are phenylpropanoids.

**Figure 18.6**

Umbelliferone, which is the precursor for the synthesis of the defense compound psoralen, is formed by hydroxylation of *p*-coumaric acid and the formation of a ring.

7-Hydroxycoumarin, also called **umbelliferone**, is synthesized from *p*-coumaric acid by hydroxylation and the formation of an intermolecular ester, a lactone (Fig. 18.6). The introduction of a C_2 group into umbelliferone yields psoralen, a **furanocoumarin**. Illumination with UV light turns psoralen into a toxic compound. The illuminated psoralen reacts with the pyrimidin bases of the DNA, causing blockage of transcription and DNA repair mechanisms, which finally results in the death of the cell. As mentioned in section 16.1, some celery varieties contain very high concentrations of psoralen and caused severe skin inflammation of workers involved in the harvest. Many furanocoumarins have antibiotic properties. In some cases, they are constitutive components of the plants, whereas in other cases, they are formed only after infection or wounding as phytoalexins.

18.3 Phenylpropanoid compounds polymerize to macromolecules

As mentioned in section 1.1, after cellulose, **lignin** is the second most abundant natural substance on earth. The basic components for lignin synthesis are *p*-coumaryl, sinapyl, and coniferyl alcohols, which are collectively termed **monolignols** (Fig. 18.7). Synthesis of the monolignols requires reduction of the carboxylic group of the corresponding acids to an alcohol. In the discussion on the glyceraldehyde phosphate dehydrogenase reaction in section 6.3, it was shown that a carboxyl group can be reduced by NADPH

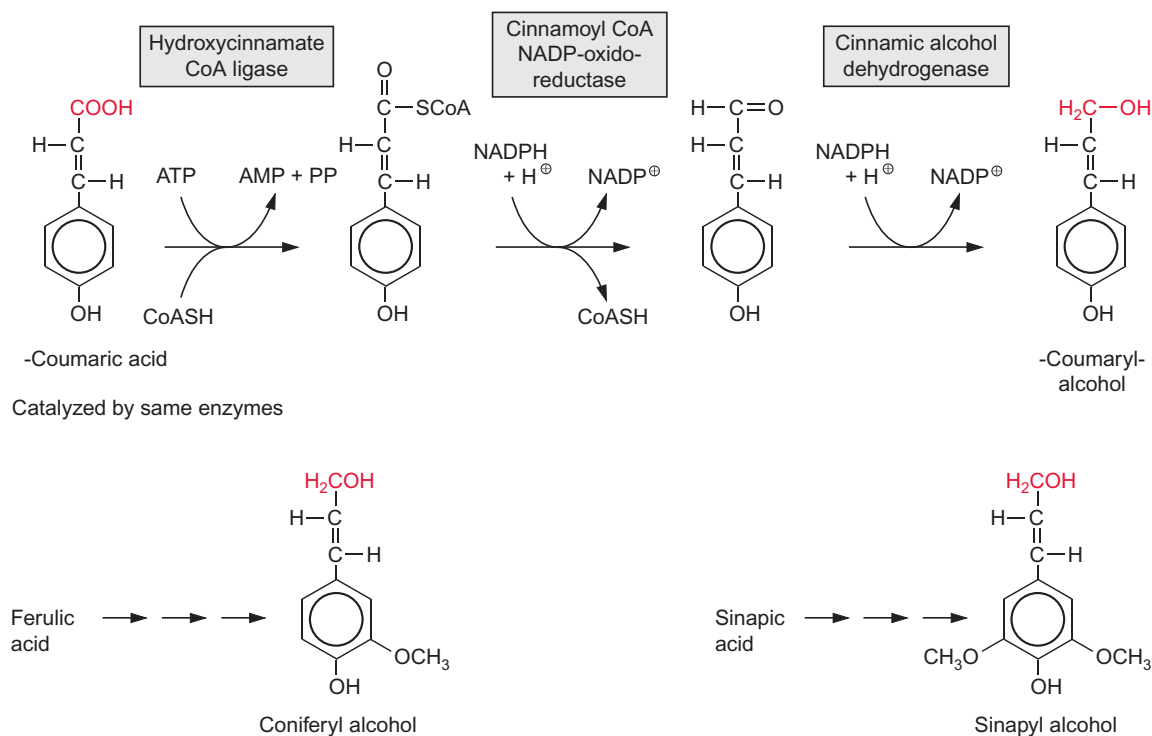


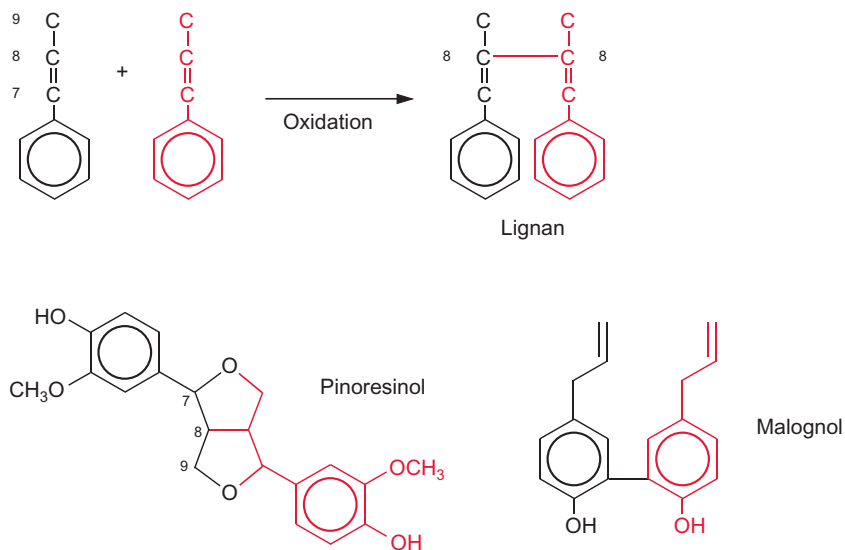
Figure 18.7 Reduction of the hydroxycinnamic acids to the corresponding alcohols (monolignols).

to an aldehyde only if it is activated via the formation of a thioester. For the reduction of *p*-coumaric acid by NADPH (Fig. 18.7) a similar activation occurs. The required thioester is formed with CoA at the expense of ATP in a reaction analogous to fatty acid activation described in section 15.6. The cleavage of the energy-rich thioester bond drives the reduction of the carboxylate to the aldehyde. In the subsequent reduction to an alcohol, NADPH is again the reductant. The synthesis of sinapyl- and coniferyl alcohols from sinapic and ferulic acids follows the same principle, but there are specific enzymes involved. Alternatively, coniferyl and sinapyl alcohols can also be formed from *p*-coumaryl alcohol by hydroxylation followed by methylation (Fig. 18.4).

Lignans act as defense substances

The dimerization of monolignols leads to the formation of **lignans** (Fig. 18.8). This takes place mostly by a reductive 8,8-linkage of the side chains, but

Figure 18.8 Lignans are formed by dimerization of monolignols. Pinoresinol and malagnol are examples of two lignans.



sometimes also by a condensation of the two phenol rings. The mechanism of lignan synthesis is still not clear. Probably free radicals are involved (see next section). Plant lignans also occur as higher oligomers. In the plant world, lignans are widely distributed as defense substances. The lignan **pinoresinol** is a constituent of the resin of forsythia and is formed when the plant is wounded. Its toxicity to microorganisms is caused by an inhibition of cAMP phosphodiesterase. Pinoresinol thus averts the regulatory action of cAMP, which acts as a messenger component in many organisms (whether also in plants is still undecided (section 19.1)). Malagnol inhibits the growth of bacteria and fungi.

Some lignans have interesting pharmacological effects. Two examples may be used to illustrate this: podophyllotoxin, from *Podophyllum*, a member of the Berberidaceae family growing in America, is a mitosis toxin. Derivatives of podophyllotoxin are used to combat cancer. Arctigenin and tracheologin (from tropical climbing plants) have antiviral properties. Investigations are under way to try to utilize this property to cure AIDS.

Lignin is formed by radical polymerization of phenylpropanoid derivatives

Lignin is formed by polymerization of monolignols, in angiosperms primarily of sinapyl and coniferyl alcohol, and in gymnosperms mainly of coniferyl alcohol. The synthesis of lignin takes place outside the cell, but the mechanism by which the monolignols are exported from the cell for lignin synthesis is still not known. There are indications that the monolignols are

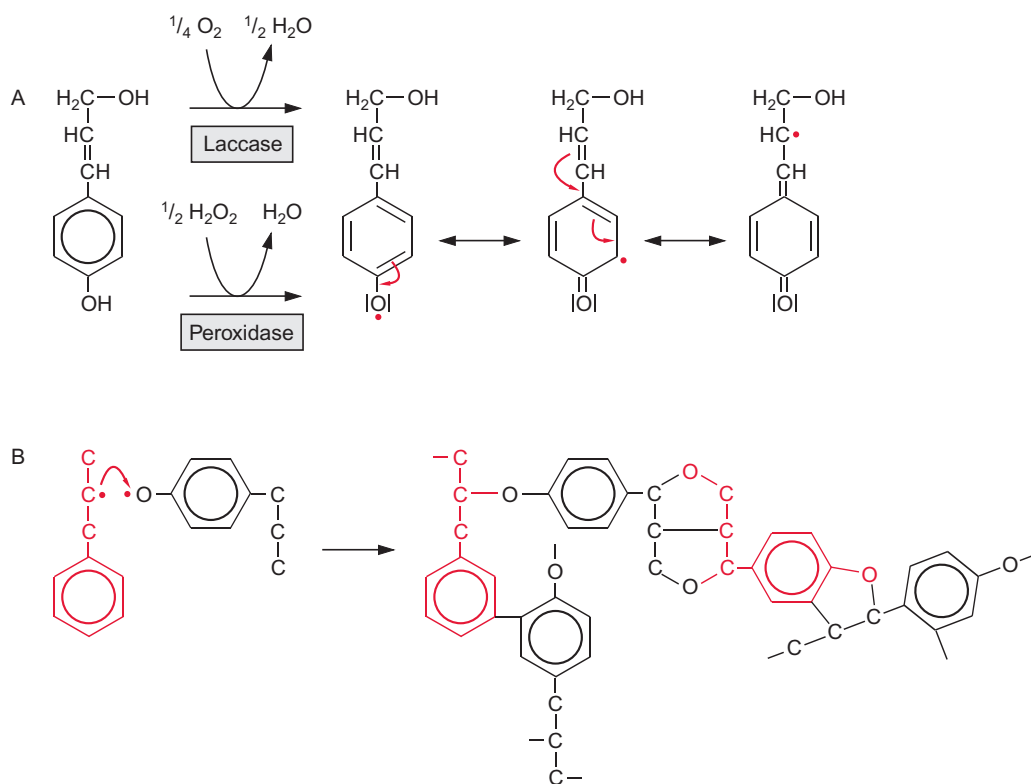


Figure 18.9 A. Oxidation of a monolignol by laccase or a peroxidase results in the formation of a phenol radical. The unpaired electron is delocalized and can react with various resonance structures of the monolignol. B. Two monolignols can form a dimer and polymerize further. Finally, highly branched lignin is formed.

exported as glucosides that are hydrolyzed outside the cell by glucosidases, but this is still a matter of controversy. The mechanism of lignin formation also remains unclear. Both **laccase** and **peroxidases** probably play a role in the linkage of the monolignols. Laccase is a **monophenol oxidase** that oxidizes a phenol group to a radical and transfers hydrogen via an enzyme-bound Cu^{++} ion to molecular oxygen. The enzyme was given this name as it was first isolated from the lac tree (*Rhus vermicifera*), which grows in Japan. In the case of peroxidases, H_2O_2 functions as an oxidant, but the origin of the required H_2O_2 is not certain. As shown in [Figure 18.9A](#), the oxidation of a phenol by H_2O_2 presumably results in the formation of a resonance-stabilized phenol radical. These phenol radicals can dimerize nonenzymatically and finally polymerize nonenzymatically ([Fig. 18.9B](#)). Due to the various resonance structures, many combinations are possible in the polymer. Monolignols react to form several C-C or C-O-C linkages,

building a highly branched phenylpropanoid polymer. Free hydroxyl groups are present in only a few side chains of lignin and sometimes are oxidized to aldehyde and carboxyl groups.

Although until now the primary structure of lignins has not been fully established in all its details, it is recognized that even in a single cell lignins of **different structure** are deposited in **discrete sections of the cell wall**. It has been postulated that certain extracellular glycoproteins, termed **dirigent proteins**, control the polymerization of monolignol radicals in such a way that defined lignin structures are formed. It is still a matter of debate to what extent lignin is formed by chance and formed specifically through the action of dirigent proteins.

The composition of lignin varies greatly in different plants. Lignin of conifers, for instance, has a high coniferyl content, whereas the coumaryl moiety prevails in the straw of cereals. Lignin is covalently bound to cellulose in the cell walls. **Lignified cell walls** have been compared with **reinforced concrete**, in which the cellulose fibers are the steel and lignin is the concrete. In addition to giving mechanical strength to plant parts such as stems or twigs, or providing stability for the vascular tissues of the xylem, lignin has a function in defense. Its mechanical strength and chemical composition make plant tissues difficult for herbivores to digest. In addition, lignin inhibits the growth of pathogenic microorganisms. Lignin is synthesized in many plants in response to wounding. Only a few bacteria and fungi are able to cleave lignin. A special role in the **degradation of lignin** is played by **woodrot fungi**, which are involved in the rotting of tree trunks.

Often one-third of dry wood consists of lignin. For the production of cellulose and paper, this lignin has to be removed, which is very costly and the methods used ultimately contribute significantly to the pollution of rivers. Attempts are being made to reduce the content of lignin in wood by means of genetic engineering. Experiments have shown that it is possible to lower the lignin content of wood by antisense constructs (section 22.5) that inhibit the expression of genes encoding lignin biosynthesis enzymes.

Suberins form gas- and water-impermeable layers between cells

Suberin is a polymeric compound formed from phenylpropanoids, long chain fatty acids and fatty alcohols (C_{18} – C_{30}), as well as hydroxyfatty acids and dicarboxylic acids (C_{14} – C_{20}) (Fig. 18.10). In suberin, the phenylpropanoids are to some extent linked with each other as in lignin. However, most of the 9'-OH groups are not involved in these linkages and instead form esters with fatty acids. Often two phenylpropanoids are connected by

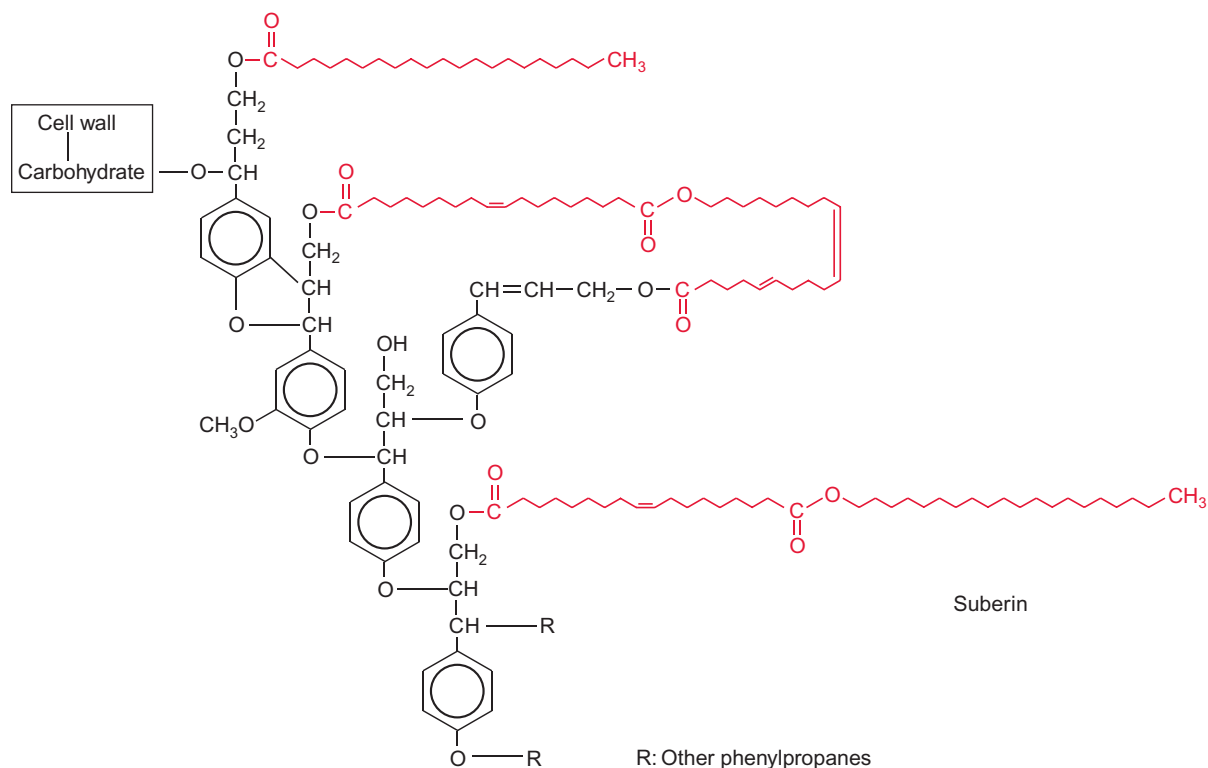


Figure 18.10 In suberin, the monolignols are connected similarly as in lignin, but the 9'-OH groups usually remain free. Instead they form esters with long-chain fatty acids and hydroxyfatty acids. Carboxylic acid esters provide a link between two monolignols.

dicarboxylic acids via ester linkages, and fatty acids and hydroxyfatty acids also can form esters with each other. Although the mechanism of suberin synthesis is to a large extent still not known, it appears that peroxidases are also involved in this process.

Suberin is a cell wall constituent that forms gas- and watertight layers. It is part of the **Casparian strip** of the root endodermis, where it acts as a diffusion barrier between the apoplast of the root cortex and the central cylinder. Suberin is present in many C_4 plants as an impermeable layer between the bundle sheath and mesophyll cells. Cork tissue, consisting of dead cells surrounded by alternating layers of suberin and wax, has a particularly high suberin content. **Cork cells** are found in a secondary protective layer called the periderm and in the bark of trees. Cork layers containing suberin protect plants against loss of water, infection by

microorganisms, and heat exposure. Due to this, some plants even survive short fires and are able to continue growing afterwards.

Cutin is a gas- and water-impermeable constituent of the cuticle

The epidermis of leaves and shoots is surrounded by a gas- and water-impermeable cuticle (Chapter 8). It consists of a cell wall that is impregnated with cutin and in addition is covered by a wax layer. **Cutin** is a polymer similar to suberin, but with a relatively small proportion of phenylpropanoids and dicarboxylic acids, mainly composed of esterified hydroxyfatty acids (C₁₆–C₁₈).

18.4 The synthesis of flavonoids and stilbenes requires a second aromatic ring derived from acetate residues

Probably the largest group of phenylpropanoids is that of the flavonoids, in which a second aromatic ring is linked to the 9'-C atom of the phenylpropanoid moiety. A precursor for the synthesis of flavonoids is chalcone (Fig. 18.11), synthesized by **chalcone synthase (CHS)** from *p*-coumaroyl-CoA and three molecules of malonyl-CoA. This reaction is also called the **malonate pathway**. The release of three CO₂ molecules and four CoA molecules makes chalcone synthesis an irreversible process. In the overall reaction, the new aromatic ring is formed from three acetate residues. Since CHS represents the first step of flavonoid biosynthesis, this enzyme has been thoroughly investigated. In some plants, one or two different isoforms of the enzyme have been found, while in others there are up to nine. CHS is the most abundant enzyme protein of phenylpropanoid metabolism in plant cells, probably because this enzyme has only a low catalytic activity. As in the case of phenylalanine ammonia lyase (section 18.1), the *de novo* synthesis of CHS is subject to multiple controls of gene expression by internal and external factors, including elicitors.

Some stilbenes are very potent natural fungicides

Some plants, including pine, grapevine and peanuts, possess a **stilbene synthase** activity, by which *p*-coumaroyl-CoA reacts with three molecules of

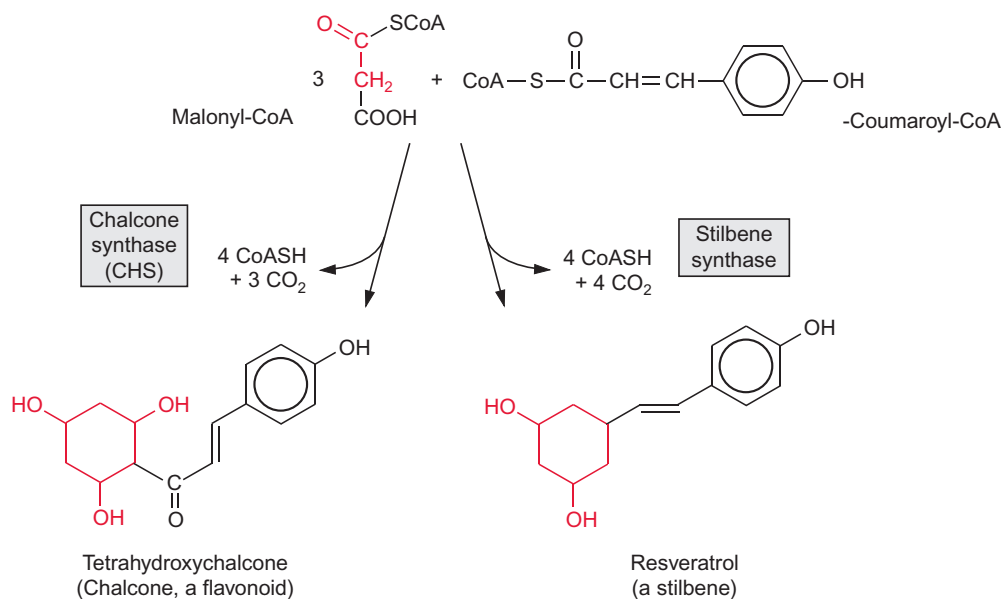


Figure 18.11 An additional aromatic ring is formed by chalcone synthase and stilbene synthase.

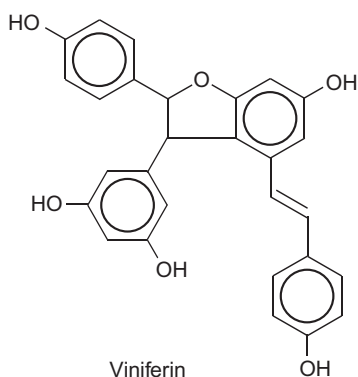


Figure 18.12 A natural fungicide from grapevine.

malonyl CoA. In contrast to CHS, the 9'-C atom of the phenylpropane is released as CO_2 (Fig. 18.11). **Resveratrol**, synthesized by this process, is a phytoalexin belonging to the stilbene group. A number of very potent plant fungicides are stilbenes, including **viniferin** (Fig. 18.12), which is contained in grapevine. The elucidation of stilbene synthesis has opened new possibilities to combat fungal infections. A gene from grapevine for the formation of resveratrol has been expressed by genetic engineering in tobacco, and the

resultant transgenic tobacco plants were resistant to the pathogenic fungus *Botrytis cinerea*.

18.5 Flavonoids have multiple functions in plants

Chalcone is converted to flavanone by **chalcone isomerase** (Fig. 18.13). As a key enzyme of flavonoid synthesis, the synthesis of the enzyme protein of chalcone isomerase is subject to strict control. It is induced like PAL and

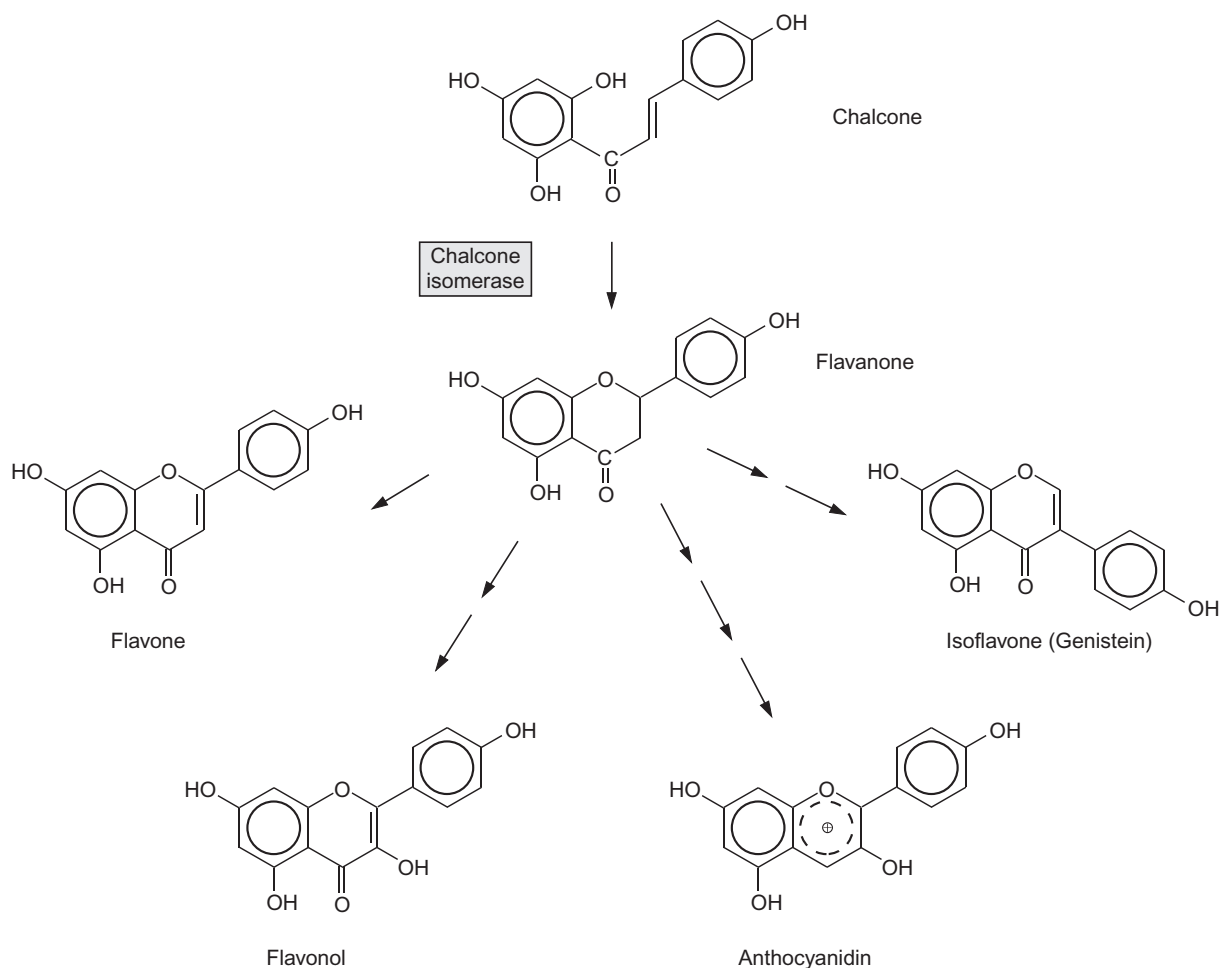


Figure 18.13 Chalcone is the precursor for the synthesis of various flavonoids.

CHS by elicitors. The middle ring is formed by the addition of a phenolic hydroxyl group to the double bond of the carbon chain connecting the two phenolic rings. Flavanone is the precursor for a variety of flavonoids; the details of the synthesis pathways of flavonoids will not be described here.

The flavonoids include protectants against herbivores and many are phytoalexins. An example of this is the poisonous isoflavone dimer **rotenone**, an inhibitor of the respiratory chain (section 5.5), which accumulates in the leaves of a tropical legume. Aboriginals in South America used to kill fish by flinging the leaves of these plants into the water. The isoflavone **medicarpin** from alfalfa (*Medicago sativa*) is a phytoalexin (Fig. 18.14). Flavonoids also serve as signals for interactions of the plant with symbionts. Flavones and flavonols are emitted from leguminous roots in order to attract rhizobia by chemotaxis and to induce in these the genes required for the nodulation (section 11.1).

Flavones and flavonols have an absorption maximum in the UV region. As **protective pigments**, they shield plants from the damaging effect of UV light. The irradiation of leaves with UV light induces a strong increase in flavonoid biosynthesis. Mutants of *Arabidopsis thaliana*, which, because of a defect in either chalcone synthase or chalcone isomerase, are not able to synthesize flavones, are extremely sensitive to the damaging effects of UV light. In some plants, fatty acid esters of sinapic acid (section 18.2) can also act as protective pigments against UV light.

Many flavonoids are **antioxidants** in acting as radical scavengers for reactive oxygen species (ROS), thus preventing the peroxidation of lipids. As constituents of nutrients, they are assumed to be protectants against cardiovascular diseases and cancer. For this reason, nutrients containing flavonoids (e.g., green tea, soy sauce, and red wine) have been regarded as beneficial for health.

Recently, particular attention has been focused on certain isoflavones that are found primarily in legumes. It had been observed earlier that sheep became infertile after grazing on certain legumes. It turned out that these forage plants contained isoflavones, which in animals (and in humans) have an effect similar to that of estrogens. For this reason, they have been named **phytoestrogens**. **Genistein**, shown in Figure 18.13, has a strong estrogen effect. Some of these phytoestrogens are used for medical purposes.

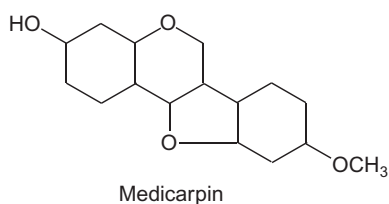
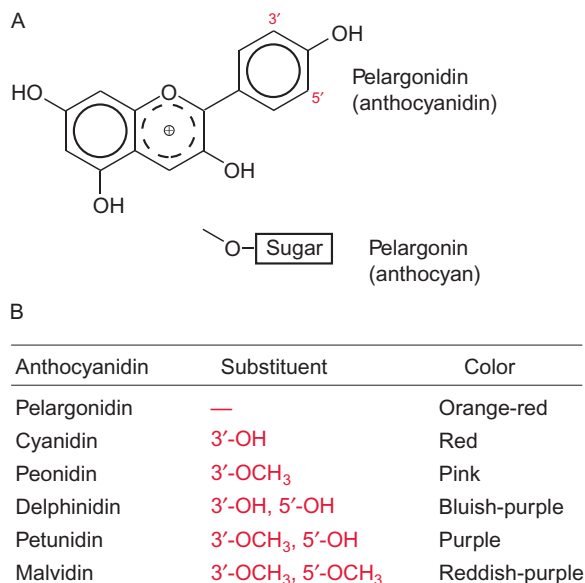


Figure 18.14 A phytoalexin from *Medicago sativa*.

Figure 18.15

A. Pelargonidin, an anthocyanidin, is a flower pigment. It is present in the petals as a glucoside, named pelargonin. B. More plant pigments are synthesized by additional -OH groups at 3' and 5' positions and subsequent methylation.



18.6 Anthocyanins are flower pigments and protect plants against excessive light

As discussed earlier, carotenoids provide yellow and orange flower pigments (section 17.6). Other widely distributed flower pigments are the yellow **chalcones**, light yellow **flavones**, and red and blue **anthocyanins**. Anthocyanins are glucosides of anthocyanidins (Fig. 18.15) in which the sugar component, consisting of one or more hexoses, is usually linked to the -OH group of the pyrylium ring. Anthocyanins are contained in the vacuole. They are transported as glutathione conjugates via the glutathione translocator to the vacuole (section 12.2) and are deposited there. The anthocyanin pelargonin, shown in Figure 18.15, contains **pelargonidin** as chromophore. The introduction of two -OH groups at 3' and 5' positions of the phenyl residue by P₄₅₀ dependent monooxygenases (section 18.2) and their successive methylation yields five additional flower pigments, each with a different color. Hydroxylations at other positions result in even more pigments. A change in the pH in the vacuole leads additionally to alterations of the color. This in part explains the change of color when plants fade. Moreover, the color of the pigment is altered by the formation of complexes with metal ions. Thus, upon complexation with Al⁺⁺⁺ or Fe⁺⁺⁺, the color of pelargonin changes from orange red to blue. These

various pigments and their mixtures lead to the multitude of color nuances of flowers. With the exception of pelargonidin, all the pigments listed in [Figure 18.15](#) are found in the flowers of petunia. To date, 35 genes that are involved in the coloring of flowers have been isolated from petunia.

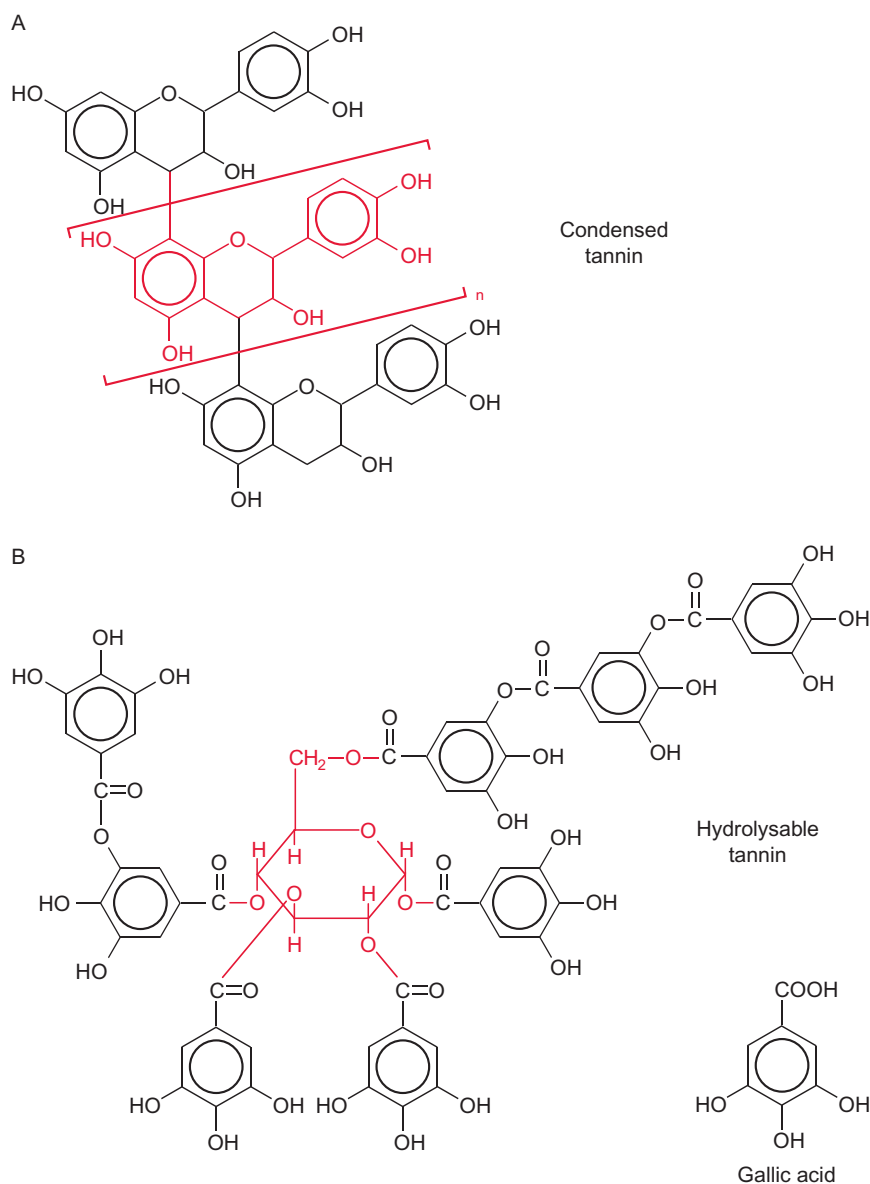
Anthocyanins not only contain flower pigments to attract pollen-transferring insects, but also function as protective pigments for shading leaf mesophyll cells. Plants in which growth is limited by environmental stress factors, for instance phosphate deficiency, chilling, or high salt content of the soil, often have red leaves, due mainly to the accumulation of anthocyanins. Stress conditions, in general, reduce the utilization of NADPH and ATP, which are provided by the light reactions of photosynthesis. Shading the mesophyll cells by anthocyanins decreases the light reactions and thus prevents overenergization and overreduction of the photosynthetic electron transport chain (see section 3.10).

18.7 Tannins bind tightly to proteins and therefore have defense functions

Tannins are a collective term for a variety of plant polyphenols used in the tanning of rawhides to produce leather. Tannins are widely distributed in plants and occur in especially high amounts in the bark of certain trees (e.g., oak) and in galls. Tannins are classified as condensed and hydrolyzable tannins ([Fig. 18.16A](#)). The **condensed tannins** are flavonoid polymers and thus are products of phenylpropanoid metabolism. Radical reactions are probably involved in their synthesis, but few details of the biosynthesis pathways are known. The **hydrolyzable tannins** consist of **gallic acids** ([Fig. 18.16B](#)). Many of these gallic acids are linked to hexose molecules. Gallic acid in plants is synthesized from shikimate ([Fig. 10.19](#)).

The phenolic groups of the tannins bind very tightly to proteins by forming hydrogen bonds with the -NH groups of peptides and these bonds cannot be cleaved by digestive enzymes. In the tanning process, tannin binds to the collagen of the animal hides and thus produces leather that is able to withstand the attack of microorganisms. Tannins have a sharp unpleasant taste; binding of tannins to the proteins of the mucous membranes and saliva draws the mouth together. In this way animals are discouraged from eating plant leaves that accumulate tannin. When an animal eats these leaves, the destruction of leaf cells results in the binding of tannins to plant proteins, which renders the leaves less digestible and thus unsuitable as fodder. Tannins also react with enzymes of the herbivore digestive tract. For

Figure 18.16 A. Composition of a condensed tannin ($n = 1-10$). The terminal phenyl residue can also contain three hydroxyl groups. B. Example of hydrolyzable tannin. The hydroxyl groups of a hexose are esterified with gallic acids (from *Anarcadia* plants).



these reasons, tannins are very effective in protecting leaves from being eaten by animals. To illustrate this: in the South African savannah, the leaves of the acacia are the main source of food for the kudu antelope. These leaves contain tannin, but in such low amounts that it does not affect the nutritional quality. Trees injured by feeding animals emit volatile ethylene

(section 19.5), and within 30 minutes the synthesis of tannin is induced in the leaves of neighboring acacias. If too many acacia leaves are eaten, the tannin content can increase to such a high level that the kudu could die when feeding from these leaves. Thus the acacias protect themselves from complete defoliation by a collective warning system. Investigations are in progress to decrease the tannin content of forage plants by genetic engineering.

Tannins also protect plants against attack by microorganisms. Infection of plant cells by microorganisms is often initiated by the secretion of enzymes for lytic digestion of plant cell walls. These aggressive enzymes are inactivated when tannins are bound to them.

Further reading

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Multiple signals regulate the growth and development of plant organs and enable their adaptation to environmental conditions

In complex multicellular organisms such as higher plants and animals, metabolism, growth, and development of the various organs are coordinated by the emission of signal compounds. In animals these signals can be hormones, which are secreted by glandular cells. Hormones are classified in paracrine hormones, which function as signals to neighboring cells, and endocrine hormones, which are emitted to distant cells (e.g., via the blood circulation). Also in plants, signal compounds are released from certain organs, often signaling to neighboring cells, but also to distant cells via the xylem or the phloem. All these plant signal compounds are termed **phytohormones**. Some of the phytohormones (e.g., brassinosteroids) resemble animal hormones in their structure, whereas others are structurally completely different. Like animal hormones, phytohormones also have many different signal functions. They control the adjustment of plant metabolism to environmental conditions, such as water supply, temperature, and day length, and regulate plant development. Light sensors including **phytochromes**, which recognize red and far-red light, and **cryptochromes** and **phototropin** monitoring blue light, control the growth and the differentiation of plants depending on the intensity and quality of light.

The signal transduction chain between the binding of a certain hormone to the corresponding receptor and its effect on specific cellular targets, such as the transcription of genes or the activity of enzymes, is now known for many animal hormones. In contrast, signal transduction chains have not been fully resolved for any of the phytohormones or light sensors. However,