Chapter 1
Introduction

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1.1 Advantages of Homogeneous Catalysis in Derivatisation of Renewables

In “green chemistry”, catalysis is a very helpful tool to convert basic chemicals into valuable fine and specialty products. By decreasing the energy of activation, the catalysts enable reactions which are not possible to carry out without the catalyst. This general rule is valid both for classical petrochemicals and of course for renewables. Depending on the molecular structure of the renewables (see Sect. 1.2), the reaction types may differ but the basis ideas remain the same.

Catalysis can be divided into different sections depending either on mechanistic considerations or on the methods of application. Very useful is the distinction between heterogeneous and homogeneous catalysis, but also special areas as biocatalysis, organocatalysis, photocatalysis or electrocatalysis can be considered. In the present book, the homogeneous catalysis takes centre, especially the homogeneous catalysis with transition metal complexes. Homogeneous catalysts are always solved in a liquid which may be a fluid starting compound or a solvent.

The transition metals have—compared to the main group metals—a number of important advantages in catalysis: They have free d-orbitals or even f-orbitals, through which they are able to interact with many reactants and with numerous ligands. Thus, an “inactive” ethene or carbon monoxide molecule can bind on the catalyst metal and can react as an activated intermediate with further compounds. Transition metals can also easily change their coordination number and ligand field. Thus, the catalytic complexes can be “tailored” for the specific reaction with the desired molecule. Too, transition metals occur in different oxidation states which can be changed easily. Thus, oxidative addition reactions or reductive eliminations are readily done. All these advantages of organometallic chemistry can be applied in homogeneous transition metal catalysis.

A. Behr and A.J. Vorholt, *Homogeneous Catalysis with Renewables*,
Catalysis by Metal Complexes 39, DOI 10.1007/978-3-319-54161-7_1

The row of valuable catalyst metals starts from the left side of the periodic table to the right: group 3 and group 4 metals are very useful for homogenous catalysed polymerisations, group 5 till 7 metals are often applied in oxidations or metathesis reactions, and the group 8 metals, especially the noble metals rhodium, palladium, iridium and platinum, are applied extensively e.g. in hydrogenations or carbonylations. Many of these catalytic complexes are easily synthesised by reproducible protocols, and their stoichiometry and structure are well known and readily analysable. As analytic methods in homogeneous catalysis, often spectroscopic techniques are used. Because all reactants and products, but also the starting catalyst and the catalytic intermediates are solved in a liquid phase, the classical organic analysis methods such as NMR, IR or UV-VIS can be adopted thus giving a deep insight into the mechanistic pathway of the reaction. If the mechanism is well known, the chemist can further optimise the reaction, often via adjustment of the reaction conditions, the reactor type or the composition of the catalytic complex e.g. via ligand tailoring.

The high variability of the complex ligand field is one of the big advantages of homogeneous transition metal catalysis. The number of ligands is overwhelming: monodentate ligands, carbenes, hemilabile ligands, chelates or higher multidentate ligands can be used; ligands with phosphorus, nitrogen, oxygen or other elements as binding atoms can be applied. Ligands with different electronic and steric properties can steer the reaction into the right direction.

This “steering effect” of the ligand field is the “plus point” of homogeneous catalysis: reactions can be carried out with very high selectivities, such as chemo-, regio-, stereo- or even enantioselectivities. Enantioselective reactions are of high importance in fine and specialty chemistry, e.g. for pharmaceuticals or agrochemicals. Enantioselective ligands date from the “chiral pool” of nature or can be synthesised in the laboratory. Chiral catalysis enables the directed synthesis only of the active components without formation of unwanted by-products, thus preserving our resources and avoiding harmful waste.

A further advantage of homogenous transition metal catalysis is the fact that this kind of catalysis often operates under very smooth conditions. Metal complexes are usually not stable at higher temperatures; thus, the catalytic reactions must occur at low temperatures e.g. in the range of room temperature till 150 °C. Also the pressures used in homogeneous catalysis are generally low, e.g. in the range of 1–40 bar. Thus—in comparison with many heterogeneous catalysed reactions—energy can be saved, and the apparatus can be constructed at relatively low costs. Renewables such as sugars or unsaturated fats are often sensitive against high temperature and pressures. Thus, homogeneous catalysis is a useful tool to convert them without unwanted breaking of bonds.

In chemical industry besides of activity and selectivity of the transition metal catalysts also the stability and lifetime of the catalyst is of high importance. In classical laboratory optimisations, this point is often insufficiently considered. To the comprehensive development of a catalyst, also the stability has to be tested in detail, for instance in continuously operated miniplants (see Chaps. 8–11) in which the homogeneous catalyst is monitored for a longer reaction period e.g. for several days or even weeks. Catalyst recycling is absolutely required to make the catalytic reaction economically feasible, especially if noble metals or valuable ligands are used. Only the results of such detailed investigations allow the decision of the industrial use of a new catalyst.

Catalysis and renewables are the two important pillars of "green chemistry". By using this combination, atom economic reactions can be carried out without significant by-products. Because of high selective reactions waste can be prevented. Homogeneous catalysis also enables the minimising of the energetic requirements of a chemical process: some reactions can even be conducted at ambient temperature and pressure. Thus, the catalytic reactions of renewables may lead to an enlarged number of valuable chemical products without damage of the environment and at acceptable costs.

In this book, important homogenously catalysed reactions and their application in continuously operated miniplants are highlighted. Hydrogenation, hydroformylation, aminations, telomerisations and oxidations were chosen as platforming reactions, in which homogeneous catalysis plays a role. Metatheses were recently reviewed; therefore, these reactions are subsumed in the chapter tandem reactions. Here, combinations of reactions can transform renewables in one preparative step into valuables. The rarely reported developments of homogenous catalysed reactions into continuously operated miniplants are differentiated also by reaction type, telomerisation, codimerisation, hydroamination and hydroformylation.

1.2 Introduction into the Chemistry of Renewables

Renewables are defined as natural compounds which grow again every year. They are produced in agriculture and forestry and are applied (predominantly) in the non-food area. These applications can be in chemistry or in producing energy. Especially, organic waste materials are of special interest for the use in industry, for instance saw mill waste or straw. Also, material of marine origin e.g. seaweed belongs to the big group of renewables. Instead of "renewables", the term "biomass" is generally used, and the non-food biomass is called, too, "industrial biomass". Besides herbal, animal feedstocks can also be utilised for instance tallows from slaughterhouses which can be processed to soaps.

The source of all these renewables is finally the light of the sun: by **photosynthesis,** carbon dioxide and water react to carbohydrates and oxygen as shown in Eq. 1.1:

$$nCO_2 + nH_2O => (CH_2O)_n + nO_2 \tag{1.1}$$

In biology, one distinguishes between primary and secondary substances. **Primary substances** are materials which are essential for the growth and the reproduction of the plants. They are responsible for the stability and elasticity of the plants or serve as energy buffer. For instance, sugar beets store their energy supply as sucrose in their roots. Important primary substances of plants are carbohydrates, lignin, fats and oils and proteins:

- The most common **carbohydrates** in nature are the macromolecular compounds cellulose, chitin, starch and hemicelluloses and the low-molecular carbohydrates mono- and disaccharides. Cellulose and hemicelluloses occur in wood and natural fibres, chitin in the shell of crabs and cancers, starch in many crop plants such as potatoes, corn, wheat and peas and mono- and disaccharides such as glucose, fructose or sucrose in numerous fruits, in beet roots and in sugar cane.
- **Lignin**—a macromolecular compound with aliphatic and aromatic structures—is a main component of wood.
- **Fats and oils** are triglycerides which appear in crops such as soy bean, rapeseed, sunflower or coconuts.
- **Proteins** are polyamides formed by amino acids. They are also found in numerous crops e.g. in soy beans.

The most important **secondary substances** occur only in small amounts in nature; however, they are important for the plant to repel aggressors or to attract dusting insects. Prominent examples are as follows:

- **Terpenoids** such as mono- or polyterpenes which occur in pins or rubber trees.
- Natural **colourants** such as alizarin or indigo.
- Natural **scents** such as essential oils of rose, jasmine or violets.
- Natural **drugs** such as pyrethroids, alkaloids or steroids.
- **Vitamins** such as the water-soluble vitamin C or the oil-soluble vitamin E.

It was estimated that 170 billion tons of renewables are formed by nature every year. The highest percentage of this huge amount forms the cellulose with about 39%, and all other carbohydrates sum up to 26%. The next 30% is given by lignin; the remaining 5% are all other renewables including the group of fats and oils. Till now, manhood is using only 6 billion tons of this biomass annually that means about 3.5 weight-percentage.

At the present time, chemical industry is using predominantly crude oil and natural gas as feedstocks for the production of organic chemicals; however, these fossil feedstocks are confined and must be replaced gradually by renewables. Currently, the chemical industry is already using renewables in a certain amount: in Germany, 17 Mio t of petrochemicals were produced in 2006, compared to 2.7 Mio t of products on the basis of renewables. Therefore, the fraction of renewables is at about 14 weight-percentage which is a little bit higher in Germany than in most other countries. Interestingly, the main part of renewables used in industry is herbal or animal fats and oils. The reason for this high share is the fact that fats and oils are chemically relatively simple molecules which resemble in their structure to the well-known petrochemical basic chemicals: the hydrocarbon chains of fatty compounds enable similar chemical conversions as with petrochemicals, and especially, catalytic conversions can be easily accomplished with fats and oils.

However, although the share of biomass is increasing in the last decades, the use of renewables in industry has also some **limitations**: one important problem can be the **acquisition** of the renewable feedstocks. Whereas crude oil and natural gas can be excavated in a relatively efficient manner on particular places, the renewables must be collected with high effort in a widespread agricultural or forest area. The same problem occurs if natural waste material must be collected, for instance saw dust from numerous saw mills or straw from a great number of harvested grain fields. Acquisition of renewables means often expansive and time-consuming transport arrangements. This fact influences substantially the economics of a chemical process using renewables.

Another problem is connected with the molecular structure and elemental composition of certain renewables. The big group of carbohydrates contains large amounts of oxygen e.g. in terms of aldehyde or hydroxyl groups which make the compounds very hydrophilic i.e. water soluble. Whereas common petrochemistry works preferentially with water-insoluble hydrocarbons, the handling of carbohydrates requires totally other reaction concepts. One alternative is to "defunctionalise" the carbohydrates by dehydration or hydrogenative dehydration yielding compounds similar to the well-known petrochemical hydrocarbons. Here, the fats and oils as well as the terpenoids have great advantages because they have similar structures to petrochemicals.

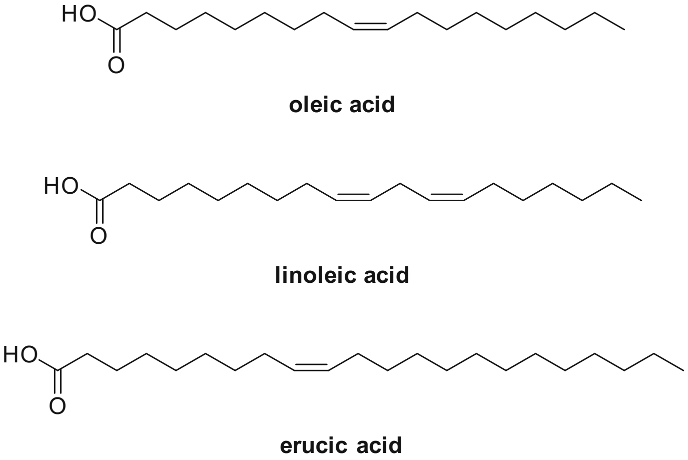
1.3 Introduction into the Main Groups of Renewables

1.3.1 Oleochemicals

Fats and oils are triglycerides i.e. esters of long-chain carboxylic acids with glycerol (1,2,3-propane triol). These carboxylic acids are called "fatty acids". By hydrolysis of triglycerides with water, the so-called fat splitting or fat hydrolysis, the fatty acids can be set free. In triglycerides, the three fatty acids can be identical, but also different. In nature, almost exclusively even fatty acids occur; their chain length is usually in the range of C12 till C22. They can be not only saturated such as palmitic acid (C16) or stearic acid (C18), but also unsaturated. Important unsaturated fatty acids (Fig. 1.1) are as follows:

- Oleic acid (C18) with one *Z* double bond in C9-position
- Linoleic acid (C18) with two *Z* double bonds in the C9- and C12-positions
- Linolenic acid (C18) with three *Z* double bonds in the C9-, C12- and C15-positions
- Erucic acid (C22) with one *Z* double bond in C13-position.

These double bonds are of great importance of the reactivity of the molecules, because unsaturated fatty acids or esters cannot only react on the carboxyl group but can catalytically be converted, too, to interesting follow-up products via addition on



oleic acid

linoleic acid

erucic acid

Fig. 1.1 Important unsaturated fatty acids

their CC-double bonds. Also, saturated fatty compounds can be functionalised on the alkyl chain, however, usually not selectively via radical substitution reactions.

The most important **fats and oils** (by mass of production) are palm oil, soy bean oil, rape seed oil and sunflower oil. Besides these four big fat resources, palm kernel oil, coconut oil and animal fats such as tallow and grease are also of importance for use in chemical industry.

- **Palm oil** and **palm kernel oil** arise in the same source, the fruits of the oil palm. The numerous fruits contain a soft pulp which contains triglycerides with predominantly saturated and unsaturated C16- and C18 fatty acids. The kernel of the oil palm fruit, however, contains a fat with a high amount of triglycerides with short-chain carboxylic acids such as lauric acid (C12) and myristic acid (C14). Oil palms have origin in the rain forests of Guinea, but today they grew predominantly in plantations of Indonesia and Malaysia.
- The **coconut palm** provides the coconut oil, which contains triglycerides which resemble very much the palm kernel oil. Once again, the short-chain fatty acids (C12–14) predominate (65%); the remaining acids are C16- and C18 acids. Similar to oil palms, coconut palms also grew in the equatorial zone.
- **Rape seed oil** is an important oil which stems from the temperate zones. The classical rape seed contains a great amount (50%) of erucic acid which is not convenient as human food. By breeding, a new type of rape seed oil was developed, the 00-type of rapeseed oil. It contains high amounts of oleic acid and linoleic acid and can therefore be used as food.
- **Soy bean oil** stems from soy beans which contain high amounts of proteins (40%) and a lower amount of oil (20%). This oil is obtained by extraction and contains 50% of linoleic acid, 30% of oleic acid and 3–11% of linolenic acid. It also contains lecithins which can be used as emulsifiers both in food preparation

and in technical applications. The residue of the extraction contains the proteins and the carbohydrates and is used as food in soy milk, in soy flour and in tofu. For technical applications, the high content of linoleic acid is of importance: varnishes and paints, lubricants and plasticizers are made on the basis of soy oil. In recent years, polyols stemming from soy oil are used as starting compounds for bio-polyesters and bio-polyurethanes.

- **Sunflower oil** derives from sunflowers which originally occurred in Northern America but came to Europe in the sixteenth century. The flower contains thousands of sunflower seeds whose content of oil amounts to 57%. The "old" sunflower oil contains predominantly linoleic acid (44–70%) and oleic acid (14–43%) and can be used for soaps and varnishes. By breeding, the "new" high oleic type was established yielding oleic acid in high yield (91%) and purity. Thus, this type is very suitable for the production of detergents, paints and cosmetics.
- Important **animal fats** are tallow, grease and fish oils. The grease is a collective name for spreadable fats stemming from pigs and geese. Tallow is a fat predominantly from cows or wethers. Grease and tallow contain especially oleic, palmitic and stearic acids. Fish oils are only produced in small amounts for food applications and contain useful polyunsaturated fatty acids, the so-called PUFAs.

1.3.2 Terpenes

Terpenes are very well known since hundreds of years, especially because of their widespread applications as flavours and fragrances. They are extracted from trees, fruits and flowers via different methods. According to Wallach's rule, terpenes are composed of isoprene, i.e. branched C5-units. Hence, a distinction is drawn between monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20) and triterpenes (C30). Also, longer terpenes are known, for instance the polyterpene natural rubber, which is a *cis*-poly(isoprene), and the gutta-percha, which is the isomeric *trans*-poly(isoprene). The structure of the terpenes can be very variable: there are a great number of acyclic hydrocarbons, but also mono-, bi- to pentacyclic derivatives exist. The reason why they are interesting for homogeneous catalysis is the fact that most of them are unsaturated and contain CC-double bonds which can coordinate to metal complexes. Acyclic monoterpenes like myrcene contain three double bonds, monocyclic monoterpenes like limonene contain two double bonds, and bicyclic monoterpenes such as α-pinene, β-pinene, 3-carene or camphene contain only one double bond (Fig. 1.2).

However, not only saturated terpenes exist in nature, such as pinane, but also functionalised terpenes occur such as terpene alcohols (such as nerol, geraniol, citronellol and menthol), terpene aldehydes (such as citronellal and citral) or terpene ketones (such as carvone or camphor) (Fig. 1.3).

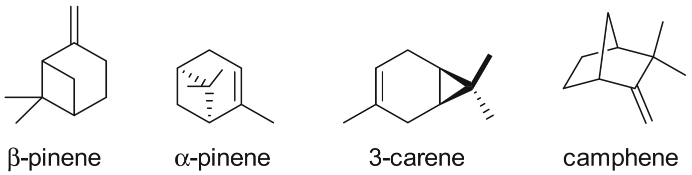


Fig. 1.2 Acyclic and cyclic monoterpene hydrocarbons

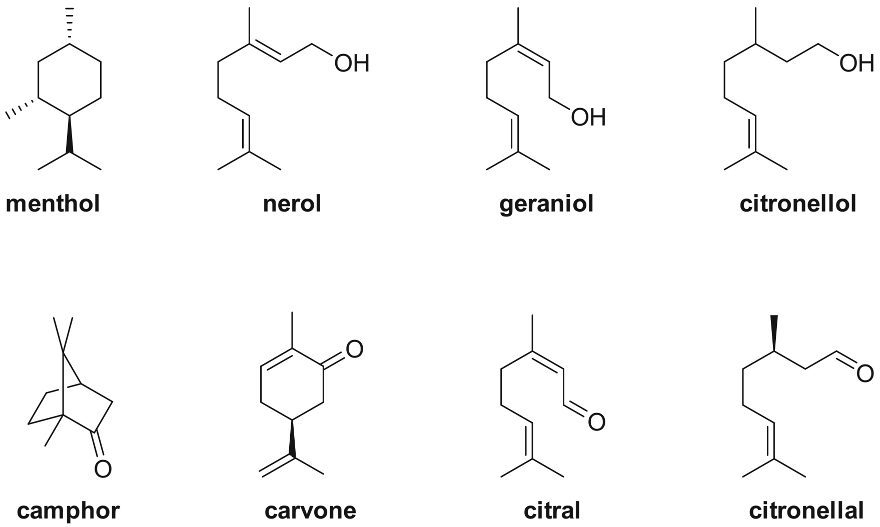


Fig. 1.3 Functionalised monoterpenes

Important higher terpenes are e.g. the sesquiterpenes bisabolene and farnesene as well as the diterpene retinol (Fig. 1.4):

- **Bisabolenes** (with different positions of the double bonds) are present in the essential oils of lemon and oregano. They function also as pheromones of different insects.
- **α-Farnesenes** occur in apple skins and cause the typical odour of green apples. The isomeric **β-farnesenes** can be found in different essential oils. Certain potato species use it as natural insect repellent.
- **Retinol** is an essential fat soluble vitamin (Vitamin A_1) and occurs in numerous animal and plant food.

Respective to the quantity, the most important source of terpenes is turpentine which is a broad mixture of volatile terpene compounds stemming from the tree resin of conifers. Depending on the starting material and the production method, the turpentine is classified into three categories:

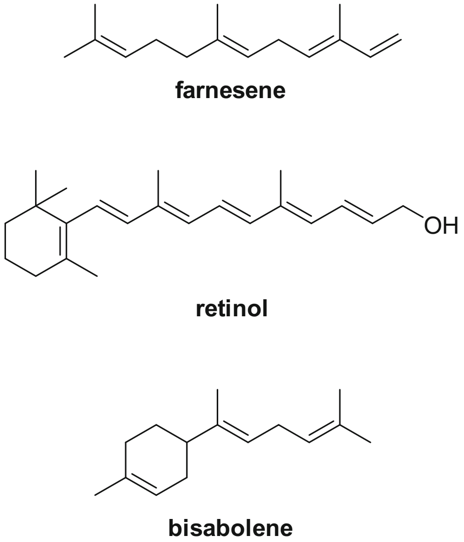


Fig. 1.4 Examples for sesqui- and diterpenes

- **Wood turpentine** is obtained via steam distillation or extraction with hydrocarbons or chlorohydrocarbons of old chopped wood stumps. This process is based on the fact that the resin level is particularly high in the lower trunk section. However, because of the dwindling supply of tree stumps, this route has become less important.
- **Gum turpentine** derives from the balsam of living trees. An incision is made into the trunks to collect the crude balsam in bottles or bags. For example, black pines afford annually up to 5 kg balsam. The further processing takes place via vacuum distillation, where colophony remains as residue. Because of its high purity gum, turpentine is very suitable for further syntheses. The main producer worldwide is the PR China; the biggest producer in Europe is Portugal.
- **Sulphate turpentine** is a cheap by-product in pulp production via the sulphate process ("Kraft process"). In this process, wood chips of cut trees are partially solubilised in NaOH by addition of Na_2S, Na_2SO_4 and Na_2SO_3. The crude sulphate turpentine is obtained from the condensate of the waste gas. However, also after further purification and oxidation steps, sulphate turpentine still contains some contaminations with sulphur compounds. The biggest producer worldwide is the USA; great producers in Europe are Scandinavia and Russia.

The most abundant ingredients of turpentine are the two pinenes (see Fig. 1.2) which serve as starting compounds for the synthesis of flavours, fragrances and pharmaceuticals. A major part is used for the industrial manufacture of camphor which is applied as plasticizer in celluloid production. A certain amount is used for the synthesis of myrcene via pinene pyrolysis at a temperature of 450–500 °C. This isomerisation occurs with a very short retention time (5 s) followed by a quick quenching step. The maximum myrcene yield amounts to 85%. Myrcene has both isolated and conjugated double bonds and is therefore an interesting model compound for homogeneous catalysed reactions.

A great number of terpenes are isolated from fruits, flowers and herbs, e.g. from citrus fruits, coriander, roses, cloves, violets, salvia and rosemary. The essential oils are obtained via steam distillation, extraction and "enfleurage" which is an absorption of the volatile terpenes in a layer of fat. To get very pure individual terpenes, a careful fractionated distillation has to be performed. Some important examples of the production of functionalised monoterpenes are as follows:

- **Nerol** is isolated from lavender and essences of roses
- **Geraniol** and **citronellol** are extracted especially from geranium
- **Citronellal** stems from lemons and limes
- **Citral** is the main component of lemon grass
- **Menthol** occurs in mint and peppermint plants.

1.3.3 Carbohydrates

The name "carbohydrates" originally stems from the expression "hydrates of carbon", which was used because of the elementary composition $C_nH_{2n}O$. In a formal way, this formula can also written as $C_n(H_2O)_n$, thus explaining this (wrong) denomination. Today, often the name "saccharides" is chosen and one differentiates between:

- Monosaccharides (such as glucose and fructose)
- Disaccharides (such as sucrose and lactose)
- Further oligosaccharides (like the trisaccharide raffinose) and
- Polysaccharides (such as cellulose and starch).

The low-molecular saccharides, the sugars, are water soluble and have a sweet flavour, whereas the polysaccharides are water insoluble and tasteless. By definition, the saccharides contain one aldehyde or one keto group and at least two hydroxy groups. A typical example for a hydroxyaldehyde is D-glucose; an example for a hydroxyketone is D-fructose (see Fig. 1.5).

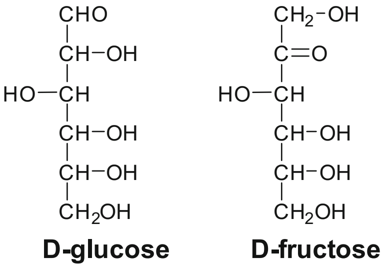


Fig. 1.5 Linear formulas of D-glucose and D-fructose

Saccharides which contain an aldehyde group are called aldoses; saccharides with keto groups are ketoses. The monosaccharides contain three to six carbon atoms and have the names trioses (3 C), tetroses (4 C), pentoses (5 C) and hexoses (6 C). Using this nomenclature, the glucose belongs to the group of aldohexoses and fructose to the group of ketohexoses. Both exist in two enantiomeric isomers: in nature exists only the D-glucose, whereas the non-natural L-glucose is only available synthetically and is of no importance. Also, fructose exists in D- and L-enantiomers.

D-Glucose ($C_6H_{12}O_6$), also named "grape sugar" or "dextrose", is the main product of photosynthesis and is stored in nature in polymers as starch (in plants) or as glycogen (in animals). It is already frequently used in chemical industry especially in fermentations. Starting from D-glucose, both ethanol and amino acids, citric acid and lactic acids are accessible by fermentation reactions. Also, metal catalysed conversions of D-glucose are carried out e.g. the hydrogenation of D-glucose to the sugar alcohol D-sorbitol which is both a low-caloric sweetening agent and an important starting compound for the synthesis of vitamin C.

The ketohexose **D-fructose** is also called "fruit sugar", because it is found in many tree fruits, vine fruits, melons, beets and berries. D-Fructose has a very sweet taste (about 1.7 times sweeter than sucrose). In industry, starch is disintegrated enzymatically to D-glucose which is than isomerised (also enzymatically) to a mixture of D-fructose (45%) and D-glucose (55%). This "high-fructose corn syrup" (HFCS) is often used as sweetener in foods and drinks. A non-food application of fructose is the dehydration to 5-(hydroxymethyl) furfural, which is widely discussed as platform compound in chemical industry.

Both aldohexoses and ketohexoses exist not only in a linear structure (see Fig. 1.5), but also in cyclic structures. This is shown in the following on the example of D-glucose: the aldehyde function can react with the hydroxy group on position 5, thus yielding a hemiacetal (Fig. 1.6). By this reaction, a new hydroxy

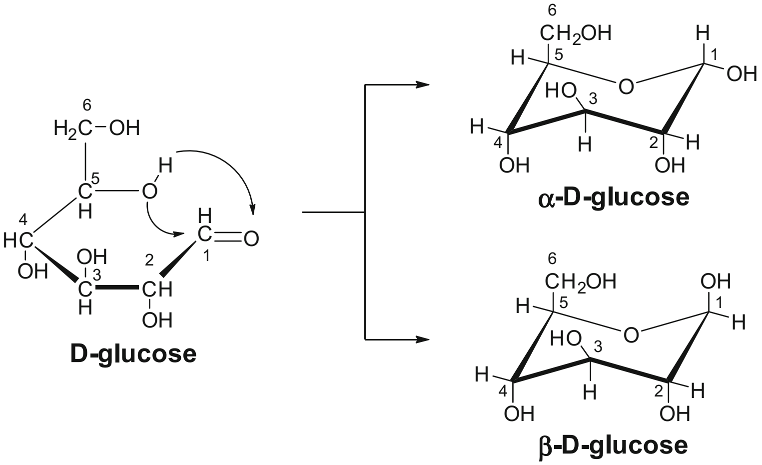


Fig. 1.6 The anomers α-D-glucose and β-D-glucose

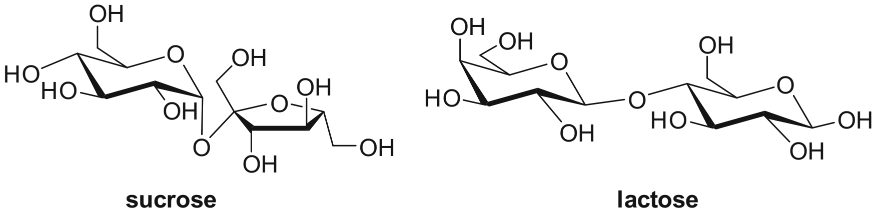


Fig. 1.7 Formula of the disaccharides sucrose and lactose

group is formed on carbon atom 1 which can be oriented in α- or in β-position. Thus, we have to differentiate between the isomers α-D-glucose and β-D-glucose which are called "anomers".

The most important disaccharide is **sucrose** which is simply named "sugar" in everyday life. It is produced from sugar cane and sugar beet in an amount of about 180 million tons per year (2014/15). In sucrose, the α-D-glucose is linked with β-fructose as shown in Fig. 1.7. Many industrial applications of sucrose are based on fermentation reactions. The splitting of the sucrose molecule into its monosaccharides succeeds by using the glucoside hydrolase enzyme "invertase" yielding the "invert sugar syrup". Sucrose can also be converted into sucralose, a zero-calorie artificial sweetener, or into isomaltose, a tooth-friendly sucrose replacement especially for diabetics.

The disaccharide **lactose** can be found in milk and dairy products. The molecule consists of the two monosaccharides β-galactose and β-glucose which are bound through a β-1,4-glycosidic linkage (see also Fig. 1.7). Lactose is applied in infant nutrition and as matrix material in the pharmaceutical industry. Also, a number of chemical conversions of lactose are well known, e.g. hydrogenations, oxidations and isomerisations.

Cellulose consists of some hundreds up to 10,000 monomeric β-D-glucose units which are linked together in a β-1,4 manner (Fig. 1.8). This polysaccharide is unbranched, and therefor, the cellulose chains can easily have contact to each other via hydrogen bridging bonds. The key resource of cellulose is wood in which the cellulose occurs together with hemicelluloses and lignin (see Sect. 1.3.4). More than 2 billion tons of wood are lumbered every year whereof a great part is used as timber or firewood. Only 13% of the wood is processed further, e.g. by the "Kraft process" in which the cellulose is separated from hemicelluloses and lignin by a mixture of sodium sulphide and sodium hydroxide. The resulting cellulose or

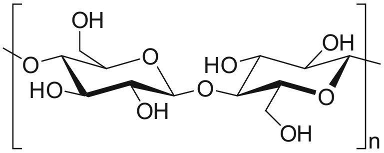


Fig. 1.8 Molecular structure of cellulose

"pulp" is predominantly used for the production of paper and cardboards, and only 4% are used for chemical conversions.

Important secondary products of cellulose are as follows:

- Cellulose esters (such as cellulose acetate or cellulose nitrate)
- Cellulose ethers (such as carboxymethyl cellulose or ethyl cellulose)
- Regenerated cellulose which is applied to make fibres (e.g. rayon) or films (e.g. cellophane).

Starch is—like cellulose—also composed of monomeric β-D-glucose units; however, the linkage is done in an α-1,4-manner. The linear polymer formed is called amylose. Depending on the source of the starch, also branched polymer chains occur. By additional α-1,6-glycosidic linkages, the amylopectin molecules are formed (Fig. 1.9).

Starch can be isolated from different plants e.g. from corn, wheat, rice, barley, potatoes or manioc. It is used frequently in the paper, thickener and binder industry. It can be applied not only in the production of biodegradable thermoplastic materials, but also in the pharmaceutical, cosmetic or food sector. By enzymes or acids, starch can be hydrolysed selectively to oligomers or to the monomer D-glucose. By oxidation, complexing agents can be synthesised which are used in the detergent industry. Just as cellulose, starch can also be converted into starch esters (e.g. acetates or phosphates) or ethers (e.g. carboxymethyl starch or hydroxyethyl starch).

1.3.4 Lignin

Lignin is a major component of wood. Depending on the type of wood, it contains 20–30% lignin, 40–55% cellulose and 30–35% hemicelluloses. Thus, wood is a

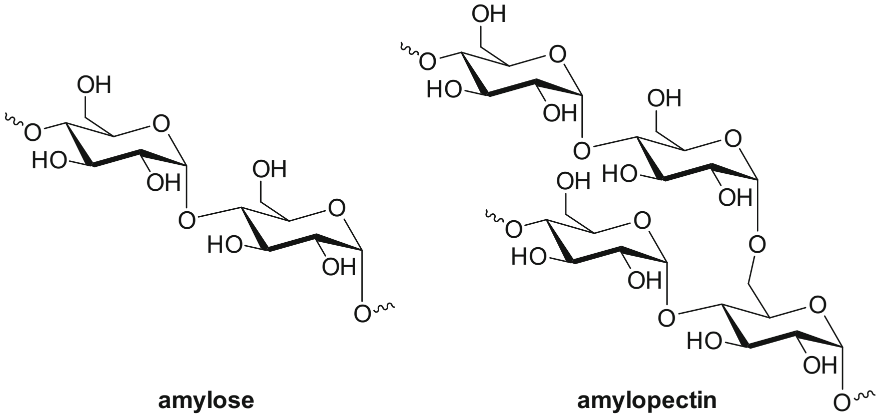


Fig. 1.9 Molecular structures of amylose and amylopectin

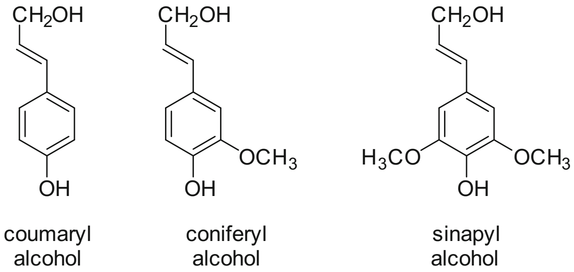


Fig. 1.10 Monomeric lignin constituents

composite material in which the lignin is basically responsible for the stability. Lignin is a macromolecule which is formed from aromatic monomers, especially coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Fig. 1.10).

Lignin is water insoluble, and only partially soluble in acids, bases or special solvents like pyridine. In the manufacture of cellulose (see Sect. 1.3.3), lignin is a side product which is produced in amounts of more than 55 million tons per year. However, it is usually not isolated, but burnt to provide the thermal energy for the paper mills. The types of linkage in the macromolecule lignin are very diverse, and it is a big challenge to open selectively these linkages, thus yielding valuable aromatic compounds e.g. phenol or substituted phenols. There are some decomposition methods which use not only acids (e.g. nitric, acetic or formic acid) or bases (e.g. sodium hydroxide, ammonia or ethanol amine), but also solvents such as ethanol or methanol or special activators like anthrachinone. Also, hydrogenation of lignin or enzymatic methods are under investigation. So far, the use of lignin is comparatively limited: one application is the production of vanillin via oxidative treatment with strong bases or the formation of duromeric resins. Because of the dispersing and emulsion-stabilising properties of lignin, it is also used in cement applications, water treatment or oilfield applications.

1.3.5 Peptides

In peptides, α-amino acids are linked together forming amides. Two amino acids form a dipeptide; molecules with a greater number of amino acids are called oligopeptides. If the molecular weight is in the range of about 6000 to about 1 million, these substances are polypeptides or proteins (Fig. 1.11). In nature, all proteins are formed from 22 natural occurring α-amino acids. The simplest α-amino

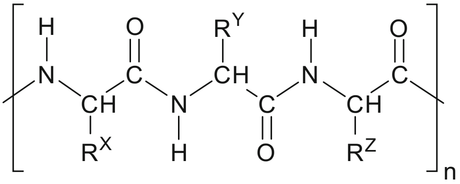


Fig. 1.11 General molecular structure of proteins

acid is the amino acetic acid glycine. In all other α-amino acids, the α-C-atom is an asymmetrically substituted carbon atom, thus yielding chiral molecules. Natural proteins are formed by L-amino acids e.g. by leucine, valine, tyrosine or methionine.

The sequence of the L-amino acids gives the primary structure of the protein. However, by the formation of hydrogen bridges, secondary structures are formed like the α-helix structure or the β-pleated sheet structure. Additional bonds can be formed like disulphide bridges between two cysteine units.

Proteins can be synthesised from the amino acids via stepwise condensation reactions with the elimination of water. In nature, this composition of the protein structure is regulated by the desoxyribonucleic acids of the genes. Vice versa, the proteins can be hydrolysed into the amino acids both by strong acids and by specific enzymes.

All animal or plant cells contain proteins. Typical animal protein sources are meat, fish, eggs, milk, cheese and yoghurt; plant protein sources are e.g. soy beans, beans, manioc, lentils or chick peas.

1.3.6 Carbon Dioxide

In a certain way, also carbon dioxide is a “renewable”. It is consistently formed by nature in the biospheric cycle: The plants die off and are reconverted to CO_2 and water via microorganisms. In addition, mankind uses fossil raw materials such as oil, gas and coal especially for energy production, thus producing great amounts of anthropogenic carbon dioxide. In the last 150 years, the emissions of CO_2 have increased in a nearly exponential manner, and mankind is trying to stop and reduce these emissions as good as possible. One (small) possibility is to use carbon dioxide as a C1 source for chemical applications. The anthropogenic emission of CO_2 is estimated to 30 billion tons per year; the range of use of carbon dioxide in chemical industry is (today) only estimated to 0.2 billion tons per year.

The problem is that carbon dioxide is a very stable molecule: this colourless and inodorous gas is extremely inert and resists also high temperatures. It presents the highest oxidation state of carbon and is difficult to reduce or to functionalise. But there are some possibilities to activate CO_2:

- The reduction with hydrogen gas e.g. to formic acid or its stable derivatives
- The reaction with molecules which have high energy-containing groups such as epoxides, dienes or alkines
- The reaction to products which are very stable, e.g. salts

There are already some applications of carbon dioxide in chemical industry, in parts for many years (Fig. 1.12):

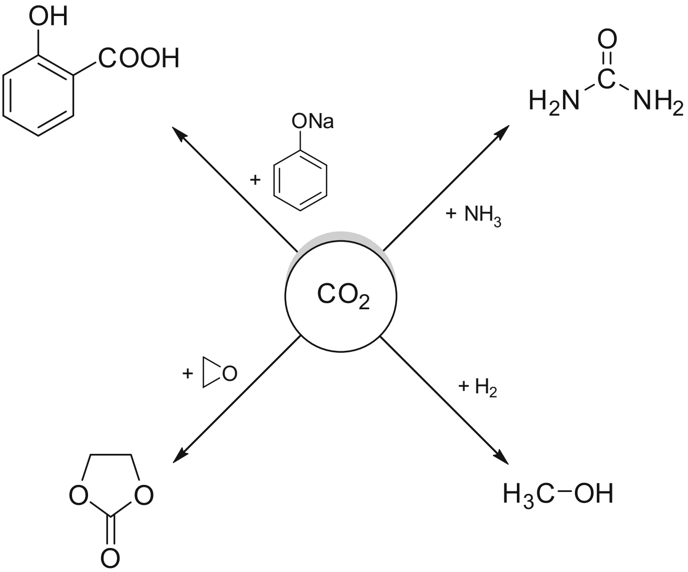


Fig. 1.12 Today' applications of carbon dioxide

- The synthesis of urea from carbon dioxide and ammonia (more than 100 Mio t/a)
- The supplement of CO_2 to synthesis gas which is used for methanol production (2 Mio t/a)
- The reaction of CO_2 with epoxides to cyclic carbonates or to polycarbonates (50.000 t/a)
- The conversion with sodium phenolate to salicylic acid (25.000 t/a).

However, one important tool to activate carbon dioxide is not yet fully investigated: the activation by transition metal catalysis. By coordination to metal complexes, the linear and stable CO_2 molecule is influenced by the electron field of the metal and is bound e.g. in nonlinear way which enables the reaction with other molecules. There are a number of interesting catalytic applications under investigation (Fig. 1.13):

- The nickel catalysed conversion of ethene with CO_2 to acrylic acid
- The palladium catalysed telomerisation of 1,3-butadiene with CO_2 yielding lactones
- The nickel or rhodium catalysed reaction of CO_2 with alkines to pyrones
- The ruthenium catalysed hydroformylation of alkenes with CO_2/H_2 mixtures to aldehydes
- The ruthenium catalysed hydrogenation of CO_2 to formic acid
- The iron or cobalt catalysed co-polymerisation of CO_2 with epoxides.

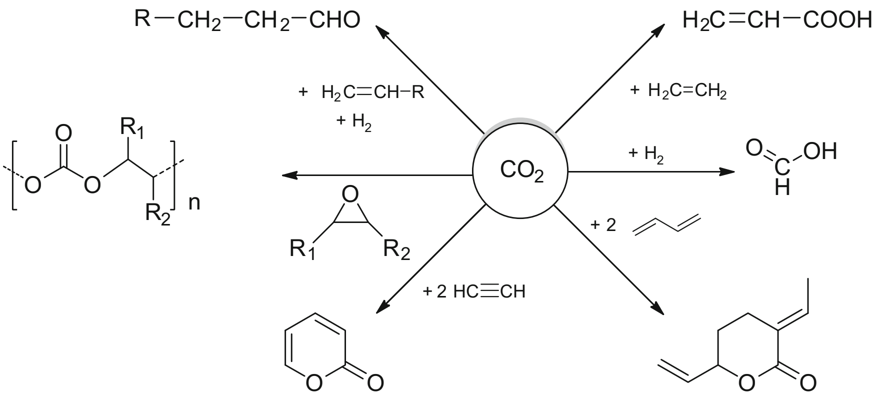


Fig. 1.13 Carbon dioxide applications under investigation

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