

Organic Chemistry

3.1 Introduction

Organic chemistry provides the foundation for understanding the transformation of plant materials into biofuels and biobased products. This chapter provides an overview to the subject for readers who are not familiar with the topic or require a brief review. More detailed descriptions can be found in the references at the end of this chapter.

The original distinction between inorganic and organic compounds was their source in nature. Inorganic compounds were derived from mineral sources, whereas organic compounds were obtained from plants or animals. Advances in chemical synthesis since the eighteenth century have made obsolete these definitions: the vast majority of organic chemicals commercially produced today are made from petroleum. The common feature of organic compounds is a skeleton of carbon atoms that include lesser amounts of other atoms, especially hydrogen, oxygen, and nitrogen, but also sulfur, phosphorus, and halides.

The high chemical valence of carbon allows for complex structures and large numbers of organic compounds. These include compounds consisting of chains of carbon atoms, referred to as acyclic or aliphatic compounds, and compounds containing rings of carbon atoms, known as carbocyclic or simply cyclic compounds. Some of these rings contain at least one atom that is not carbon (known as heteroatoms). These compounds are called heterocyclic compounds. Carbocyclic compounds are further classified as either aromatic compounds, in which electrons are shared among atoms to produce a particularly stable ring, or alicyclic compounds, which includes all non-aromatic cyclic compounds.

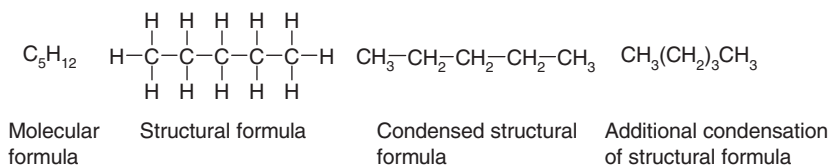
3.2 Classification of Reactions

A variety of reactions can occur among organic compounds. *Addition* reactions occur when two reactants combine to give a single product. *Elimination* reactions

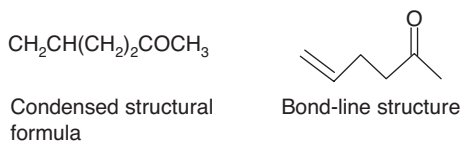
involve the splitting of a single compound into two compounds. Most elimination reactions form a product with a double bond containing the majority of the atoms found in the reactant. *Substitution* reactions involve replacement of one atom or group of atoms by a second atom or group of atoms. *Hydrolysis* is a particularly important instance of substitution reactions involving the action of water in splitting a large reactant molecule into two smaller product molecules. One product molecule is bonded to the hydrogen atom from the water, while the other product molecule is bonded to the hydroxyl group derived from the water. *Condensation* reactions involve two reactants combining to form one larger product with the simultaneous formation of a second, smaller product. Dehydration is a particularly important instance of condensation reactions in which water is the second, smaller product. Note that dehydration is the opposite of hydrolysis. *Rearrangement* reactions result from the reorganization of bonds within a single reactant to give an isomeric product.

3.3 Structural Formulas and Chemical Nomenclature

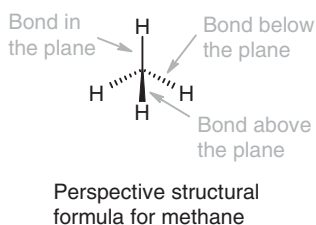
The molecular formula of a compound indicates its atomic composition. For example, the molecular formula for pentane is C_5H_{12} . Structural formulas show the arrangement of atoms and bonds. The number of lines between atoms in structural formulas indicates the number of bonds between them. For example, a carbon–hydrogen bond is represented by C–H, a carbon–carbon double bond is represented by C=C, and a carbon–carbon triple bond is written C≡C. Condensed structural formulas show only specific bonds; other bonds are left out but implied. The degree of condensation of structural formulas is somewhat arbitrary. Commonly, C–H bonds are not shown because they can only form single bonds. Additional condensation of structural formulas can be achieved by omitting C–C bonds.



Bond-line structures are an extreme shorthand for representing molecules. Carbon atoms are omitted, but carbon–carbon bonds are illustrated in a zigzag arrangement. Carbon–hydrogen bonds are omitted, while bonds of carbon atoms to other atoms or molecular groups are shown explicitly.

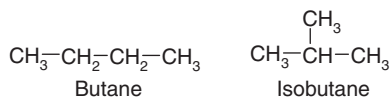


Sometimes it will be important to distinguish the three-dimensional structure of a molecule. In this case, perspective structural formulas are employed, with wedges indicating bonds that project out of the plane of the drawing. Solid wedges indicate bonds projecting above the plane of the drawing, while wedges shaded with parallel lines indicate bonds projecting below the plane of the drawing.

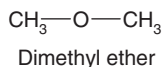
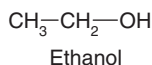


Organic compounds are named according to a system devised by the International Union of Pure and Applied Chemistry (IUPAC). The IUPAC name consists of three parts: prefix, parent, and suffix. The parent identifies the main carbon chain. The suffix identifies most of the functional groups present in the molecule. The prefix specifies the location of functional groups identified in the suffix as well as identifies some other atoms or groups of atoms attached to the main carbon chain. The nomenclature of organic compounds is further elaborated in the subsequent discussions on various functional groups. Many compounds continue to be known by their common names either because of long usage or to avoid the unwieldy nomenclature of some compounds derived from biological sources.

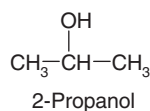
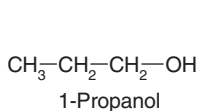
Compounds that have the same molecular formula but different structures are isomers. Isomers that differ in their carbon skeleton are called skeletal isomers. For example, butane and isobutane both have the molecular formula of C_4H_{10} , but butane is a straight-chain hydrocarbon, whereas isobutane includes a short side-chain.



Isomers that have different functional groups are called functional group isomers. For example, the molecular formula $\text{C}_2\text{H}_6\text{O}$ represents both ether, which has a functional group in the form of divalent oxygen, and an alcohol, which has a functional group in the form of monovalent hydroxyl group (OH).



Positional isomers have the same molecular formulas and functional groups. They differ only in the location of the functional groups in the carbon chains. For example, 1-propanol and 2-propanol are alcohols of molecular formula $\text{C}_3\text{H}_7\text{OH}$, but the former has its single hydroxyl group located at the end of the carbon chain, whereas the latter has its hydroxyl group at the middle of the chain.



3.4 Classification of Organic Compounds

Organic compounds are conveniently classified according to functional groups—the molecular structures that give the compounds distinctive chemical and physical properties. Those functional groups of particular interest to the chemistry of biobased products are summarized in Table 3.1. The rest of this section describes the chemistry of these functional groups.

3.4.1 Alkanes

The simplest organic compounds consist only of carbon and hydrogen atoms and are known as hydrocarbons. Hydrocarbons containing only carbon–carbon single bonds are classified as alkanes and conform to the general chemical formula of $\text{C}_n\text{H}_{2n+2}$. Alkanes are also called paraffins. A hydrocarbon that contains only carbon–carbon single bonds is said to be saturated.

Alkanes with a continuous chain of carbon atoms are normal alkanes. The names and molecular formulas for normal alkanes containing up to 10 carbon atoms are listed in Table 3.2. Note that all end in the suffix “-ane.” The first four names are based on common names, while those with more than four carbon atoms are derived from Greek numbers that indicate the number of carbon atoms. Familiar alkanes include the fuels—methane (CH_4), propane (C_3H_8), and butane (C_4H_{10}). Gasoline is a mixture of higher boiling point alkanes.

A normal alkane molecule minus one hydrogen atom is known as an alkyl group; for example, “ $\text{CH}_3\text{—}$ ” is the methyl group. As shown in Table 3.2, the names of the alkyl groups conform to the names of the corresponding alkanes. The short hand for an alkyl group is “R–” (i.e., “remainder of molecule”). The number of alkyl groups attached to hydrocarbons is a convenient way to classify them.

Branched alkanes result when carbon atoms in the chain bond to other carbon atoms, forming side chains. These still have the general formula $\text{C}_n\text{H}_{2n+2}$ and thus

Table 3.1 Classification of organic compounds based on functional groups


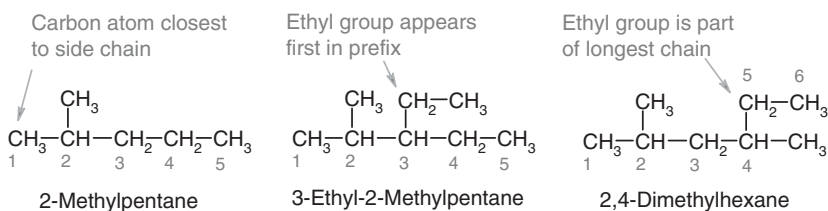
Class	General Formula	Functional Group	Suffix to Chemical Name
Alkane	RH	$\begin{array}{c} \text{C}-\text{H} \\ \\ \text{C}-\text{C} \end{array}$	-ane
Alkene	RCH=CH ₂ RCH=CHR R ₂ C=CHR R ₂ C=CR ₂	$\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	-ene
Alkyne	RC≡CH RC≡CR	—C≡C—	-yne
Aromatic hydrocarbon	ArH		—
Alcohol or phenol	ROH	—O—H	-ol
Ether	ROR	$\begin{array}{c} \quad \\ -\text{C}-\text{O}-\text{C}- \\ \quad \end{array}$	—
Aldehyde	RCHO	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{H} \end{array}$	-al
Ketone	RCOR	$\begin{array}{c} \text{O} \\ \\ -\text{C}- \end{array}$	-one
Carboxylic acid	RCOOH	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{H} \end{array}$	-oic acid
Ester	RCOOR	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}-\text{C}- \\ \quad \end{array}$	-oate
Amine	RNH ₂	$\begin{array}{c} \text{H} \\ \\ -\text{N}-\text{H} \end{array}$	-amine
Amide	RCONH ₂	$\begin{array}{c} \text{O} \quad \text{H} \\ \quad \\ -\text{C}-\text{N}-\text{H} \end{array}$	-amide

Table 3.2 Names of alkanes and alkyl groups

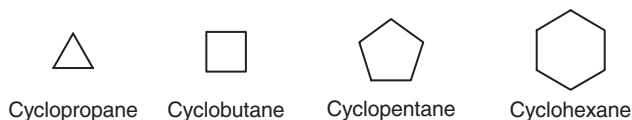
Number of Carbon Atoms	Alkane		Alkyl Group	
	Name	Molecular Formula	Name	Molecular Formula
1	Methane	CH ₄	Methyl	CH ₃ —
2	Ethane	C ₂ H ₆	Ethyl	C ₂ H ₅ —
3	Propane	C ₃ H ₈	Propyl	C ₃ H ₇ —
4	Butane	C ₄ H ₁₀	Butyl	C ₄ H ₉ —
5	Pentane	C ₅ H ₁₂	Pentyl	C ₅ H ₁₁ —
6	Hexane	C ₆ H ₁₄	Hexyl	C ₆ H ₁₃ —
7	Heptane	C ₇ H ₁₆	Heptyl	C ₇ H ₁₅ —
8	Octane	C ₈ H ₁₈	Octyl	C ₈ H ₁₇ —
9	Nontane	C ₉ H ₂₀	Nonyl	C ₉ H ₁₉ —
10	Decane	C ₁₀ H ₂₂	Decyl	C ₁₀ H ₂₁ —

represent isomers of the normal alkanes. They are named such that the longest continuous chain is the parent part of the IUPAC name. The name and position of the alkyl groups making up the side chains are included in the suffix part of the IUPAC name. Positions of alkyl groups are specified by numbering carbon atoms along the main carbon chain, with the lowest numbered carbon atom appearing at the end of the chain closest to the first branch chain. The prefix specifies all alkyl groups attached to the main chain, with the prefixes listed alphabetically rather than by location on the main chain. Two or more groups of the same name are indicated by the prefix di-, tri-, tetra-, etc. For example, an alkane consisting of five carbon atoms in the main chain with a methyl group attached to the carbon atom second to the end of the main chain is called 2-methylpentane. Replacement of an ethyl group for one of the hydrogen atoms attached to the third carbon of 2-methylpentane is called 3-ethyl-2-methylpentane. Note that if the ethyl group had been attached to the fourth carbon atom, it would not be called 4-ethyl-2-methylpentane because the ethyl group now becomes part of the longest chain in the molecular structure. Instead, it should be considered as consisting of a six-carbon main chain with two methyl groups attached to the second and fourth carbon atoms, which is called 2,4-dimethylhexane.



Closely related to the alkanes are the cycloalkanes, which contain carbon–carbon single bonds in a ring structure and conform to the general chemical formula of C_nH_{2n} . The simplest cycloalkanes are cyclopropane (C_3H_6) in a triangular ring, cyclobutane (C_4H_8) in a rectangular ring, cyclopentane (C_5H_{10}) in a pentagonal ring, and cyclohexane (C_6H_{12}) in a hexagonal ring.

Bond-line drawings of cycloalkanes

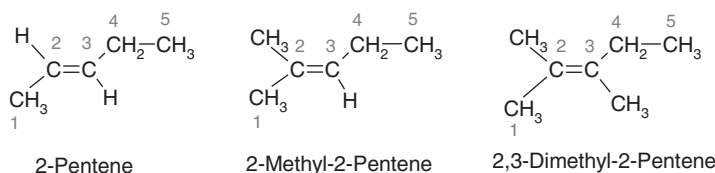


Because C–H bonds are nonpolar, alkanes are nonpolar, with implications for the physical properties of these hydrocarbons. Alkanes are not soluble in water, a highly polar compound (following the rule-of-thumb that “like dissolves like”). The absence of polarity also means that alkane molecules do not strongly interact; thus, boiling points of alkanes are relatively low compared to other organic

compounds, increasing with molecular weight. The C–C and C–H bonds of alkanes are not very reactive with the exception of oxidation. The high heats of oxidation make alkanes attractive as fuels.

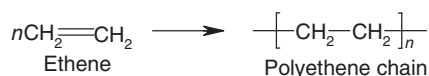
3.4.2 Alkenes and Alkynes

Hydrocarbons with carbon–carbon double bonds are called alkenes and conform to the general chemical formula of C_nH_{2n} . The IUPAC nomenclature follows that of the alkanes (see Table 3.2) except the suffix “-ene” is used instead of “-ane.” Like alkanes, alkenes can have branched chains. The longest continuous chain containing the double bond is the parent. Carbon atoms are numbered consecutively from the end nearest to the double bond. Isomers are distinguished by including the number of the first carbon atom in the double bond in the prefix to the parent name. The prefix also specifies the type and location of all alkyl groups attached to the main chain, with the prefixes listed alphabetically rather than by location on the main chain. Two or more groups of the same name are indicated by the prefix di-, tri-, tetra-, etc.



Common names are often employed in the chemical industry. For example, the simplest alkene, ethene (C_2H_4), is commonly known as ethylene. Ranked first among organic chemicals in annual production in the United States, ethene is produced from natural gas liquids.

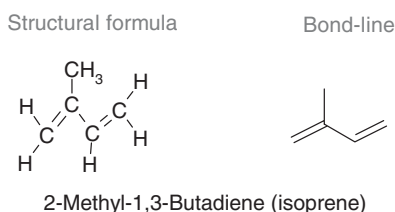
Alkenes are widely used in the production of polymers, a high-molecular-weight compound created by the repetitive reaction of low-molecular-weight molecules, known as monomers, to form long carbon chains. Polymerization of alkenes occurs by addition reactions—carbon chains are lengthened by addition of monomers without the formation of other products. For example, ethene, at elevated pressures and temperatures and in the presence of a trace amount of oxidant, yields a polymeric chain of molecular mass of 50 000 to 300 000 known as polyethene (familarly known as polyethylene), a low-density plastic used in the manufacture of plastic bags and squeeze bottles.



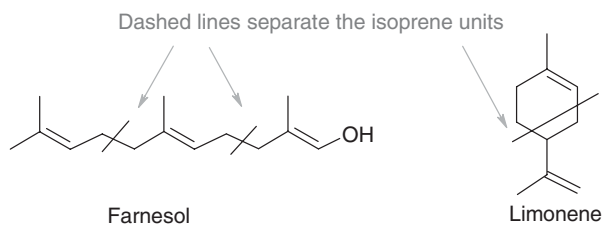
Other polymers from alkenes include polypropene, commonly called polypropylene and spun into fibers for carpets and ropes; polychloroethene, also known as

polyvinyl chloride, widely used in making both rigid plastic products, such as pipe and floor tiles, as well as flexible plastic products, such as shower curtains and garden hoses; polydichloroethene, used in plastic wrap; polytetrafluoroethene, the basis of Teflon; polyacrylonitrile, used in synthetic fibers; polystyrene, used in Styrofoam; and polymethyl methacrylate, used in Plexiglass.

If more than one double bond appears in a molecule, the location of each double bond is indicated in the prefix, and the suffix becomes -diene, -triene, -tetraene as appropriate to indicate the number of double bonds. Alkadienes, containing two double bonds, are commonly called dienes. If the two double bonds of a diene are separated by one single bond, the resulting compound, known as a conjugated diene, has chemical properties distinct from other alkenes (if separated by more than one single bond, the double bonds are unconjugated dienes and have properties similar to other alkenes). An important example of a conjugated diene is 2-methyl-1,3-butadiene, commonly known as isoprene.



Isoprene is the basis for many important natural chemicals. Both terminal carbon atoms can bond with terminal carbon atoms of other isoprenes to form a variety of cyclic and acyclic compounds with different degrees of saturation and various functional groups attached. Terpenes, compounds of two or more isoprene units joined together with the generic formula $(C_5H_8)_n$, have distinctive odors and flavors. They are responsible for the fragrant odors of pine trees and the bright colors of tomatoes and carrots. Terpenes are classified by the number of isoprene units they contain—monoterpenes have two isoprene units, sesquiterpenes have three isoprene units, and diterpenes, triterpenes, and tetraterpenes contain four, six, and eight isoprene units, respectively. Examples include farnesol, an acyclic sesquiterpene first isolated from roses and citronella, and limonene, a cyclic monoterpene with a distinctive lemon odor.



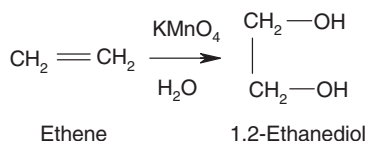
Hydrocarbons with carbon–carbon triple bonds are called alkynes and conform to the general chemical formula C_nH_{2n-2} . The nomenclature follows that of the alkanes (see Table 3.2) except the suffix “-yne” is used instead of “-ane,” although common names are often employed in the chemical industry. For example, the simplest alkyne, ethyne (C_2H_2), is commonly known as acetylene, the fuel for many high-temperature cutting torches. Compounds with multiple triple bonds are diynes, triynes, and so on. Compounds with both double and triple bonds are called enynes; numbering of these compounds starts from the end nearest the first multiple bond.

The presence of double and triple bonds in alkenes and alkynes, respectively, makes them unsaturated hydrocarbons. These unsaturated compounds are often classified according to the number of alkyl groups (R–) attached to the double or triple bond unit, which is known as the “degree of substitution.” As an example, various degrees of substitution are illustrated in Table 3.3 for an alkene and an alkyne.

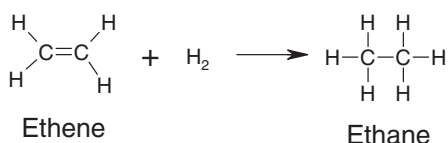
Both alkenes and alkynes are nonpolar compounds with physical properties similar to those for alkanes. However, the double and triple bond components in alkenes and alkynes are weaker than the single bond in alkanes, making them more chemically reactive than alkanes. Unsaturated compounds are easily oxidized without destroying the carbon chain. For example, potassium permanganate readily oxidizes ethene to 1,2-ethanediol, commonly known as ethylene glycol, familiar as automotive anti-freeze.

Table 3.3 Examples of substitutions of alkyl groups in alkenes and alkynes

Substitution	Ethene	Ethyne
Unsubstituted	$\begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$
Mono-substituted	$\begin{array}{c} \text{R} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array}$	$\text{R}-\text{C}\equiv\text{C}-\text{H}$
Di-substituted	$\begin{array}{c} \text{R} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{R} & & \text{H} \end{array}$	$\text{R}-\text{C}\equiv\text{C}-\text{R}$
Di-substituted	$\begin{array}{c} \text{R} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{R} \end{array}$	
Tri-substituted	$\begin{array}{c} \text{R} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{R} & & \text{R} \end{array}$	
Tetra-substituted	$\begin{array}{c} \text{R} & & \text{R} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{R} & & \text{R} \end{array}$	

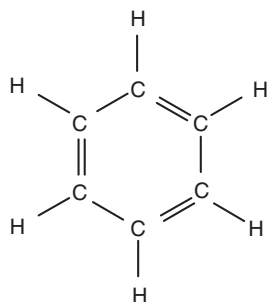


An important reduction reaction, known as hydrogenation, is the conversion of a C=C bond in an alkene or the C≡C bond in an alkyne to a C–C bond by the addition of hydrogen in the presence of a catalyst.

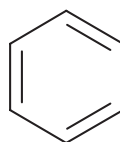


3.4.3 Aromatic Compounds

Among the most important cyclic hydrocarbon structures is the benzene ring, consisting of six carbon atoms in an extremely stable hexagonal structure.



Benzene: structural formula

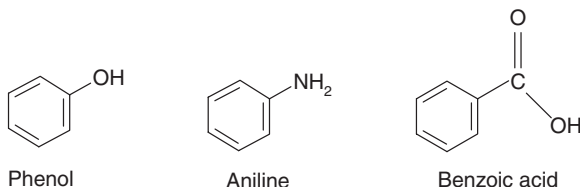


Benzene: bond-line structure

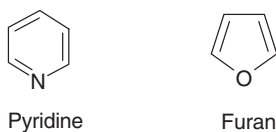
This stability is the result of the sharing of electrons (delocalization) among all the atoms of the ring, a condition that can be predicted by the Hückel rule. Compounds that satisfy the Hückel rule are known as aromatic compounds because many of these compounds have distinctive fragrances, such as vanilla and oil of wintergreen. Compounds based on the six-carbon ring of benzene are not the only cyclic compounds classified as aromatic, but they are among the most important compounds in organic chemistry.

Substitution of various chains or ring structures for the hydrogen atoms yields a tremendous variety of chemical compounds with a range of useful properties. For example, substitution with a hydroxyl group yields phenol, a crystalline acidic compound used in the manufacture of phenolic resins and readily produced by the pyrolysis of biomass. Substitution with an amine group yields aniline, the basis of the synthetic dye industry in the nineteenth century. Substitution with a carboxylic

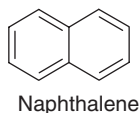
group yields benzoic acid, a white crystalline acid found naturally in cranberries and used especially as a preservative of foods.



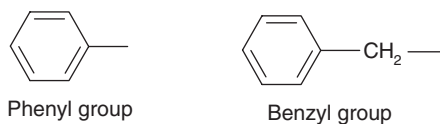
If one or more of the carbon atoms in the ring of an aromatic compound are substituted by another atom, usually nitrogen, sulfur, or oxygen, the resulting compound is said to be a heterocyclic aromatic compound. Examples include pyridine, a pungent, water-soluble flammable liquid that is the parent of many naturally occurring organic compounds, and furan, a five-member ring (unsaturated) ether obtained by dehydrating (removal of water) and decarbonylating (removal of carbon monoxide) carbohydrate obtained from woody or herbaceous biomass.



Aromatic compounds consisting of two or more rings “fused” together are known as polycyclic aromatic hydrocarbons. These compounds are planar, that is, all atoms in the rings and those atoms directly attached to the rings are in a plane. A prominent example is naphthalene, often used in the manufacture of mothballs.



An aromatic ring attached to a larger parent structure is an aryl group, often symbolized by “-Ar,” just as the alkyl group is symbolized by R-. Examples of aryl groups derived from benzene are the phenyl group and the benzyl group.

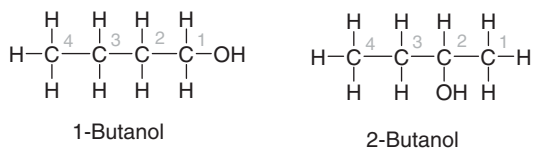


3.4.4 Alcohols and Phenols

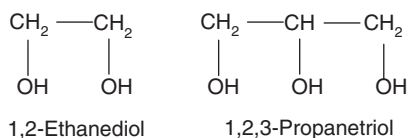
Hydrocarbons, compounds of only carbon and hydrogen, make up only a small fraction of plant material. Most plant material incorporate large amounts of oxygen and, thus, functional groups containing oxygen play important roles in the

chemistry of biobased products. Organic compounds that have functional groups containing oxygen include alcohols, phenols, ethers, aldehydes, ketones, acids, esters, and amides.

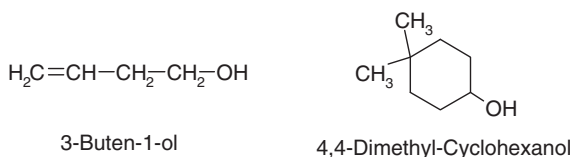
The hydroxyl group, “-OH,” characterizes alcohol, which are named according to the longest carbon chain containing the hydroxyl group. The parent name is obtained by adding “-ol” to the name of the alkyl group attached to the hydroxyl group. The location of the hydroxyl group in the parent chain is specified by prefixing to the name a number corresponding to the carbon atom to which the hydroxyl group is attached. The lowest numbered carbon atom is the one at the end of the carbon chain that is located closest to the hydroxyl group. For example, an alcohol formed from the attachment of a hydroxyl group to the end of the butyl group is known as 1-butanol, whereas a hydroxyl group attached to the second of the four carbon atoms in the butyl group is called 2-butanol.



Some alcohols, known as polyols, contain two or more hydroxyl groups. They are named by retaining the “-e” in the name of the parent alkane and adding -diol, -triol, and so forth to indicate the number of hydroxyl groups attached, although many polyols have common names. For example, 1,2-ethanediol consists of two hydroxyl groups attached to an ethane background. Commonly known as ethylene glycol, it is used both as anti-freeze and as an important chemical in the manufacture of the synthetic fiber Dacron[®] and Mylar[®] film. An example of a triol is 1,2,3-propanetriol, which consists of three hydroxyl groups attached to a propane chain. Commonly known as glycerol, it is the backbone of fats and oils.



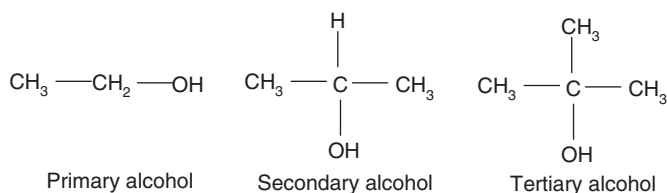
Alcohols are also formed by attaching hydroxyl groups to ring structures and carbon chains containing double or triple bonds. The carbon atoms on ring structures are numbered starting with the carbon atom attached to the hydroxyl group and continuing around the ring in the direction that gives the lowest numbers to atoms attached to substituents. Alcohols containing double and triple bonds are named by including a prefix number that labels the position of the double bond and a suffix that combines the position of the hydroxyl group along with the designation -ol.



The hydroxyl group is responsible for several prominent physical properties of alcohols. The hydroxyl group serves as both a hydrogen bond donor and a hydrogen bond acceptor, resulting in large intermolecular forces between alcohol molecules. The large energy required to separate these bonds is responsible for high boiling points of alcohols compared to alkanes of similar molecular weight. Like water, lower-molecular-weight alcohols are highly polar, resulting in high solubility in water and polar organic compounds.

Alcohols can serve as both proton donors and proton acceptors. When an alcohol loses a proton, a conjugate base called an alkoxide ion, $\text{R}-\text{O}^-$, is produced. Alcohols are very weak acids. When an alcohol accepts a proton, a conjugate acid called an oxonium ion, $\text{R}-\text{OH}_2^+$, is produced. Alcohols are very weak bases, forming only under the action of a very strong acid.

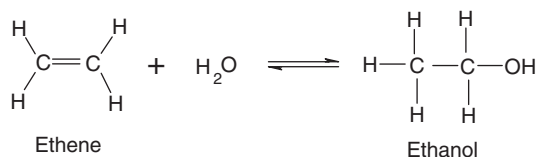
Alcohols are classified as primary, secondary, or tertiary alcohols depending upon how many carbon atoms are attached to the carbon atom that is bonded to the hydroxyl group.



Removal of a water molecule from an alcohol is a dehydration reaction, which is an example of an elimination reaction. This reaction requires an acid catalyst, such as sulfuric acid or phosphoric acid, and is illustrated by the formation of ethylene from ethanol.

Primary alcohols, which have the general formula of RCH_2OH , can be oxidized to aldehydes, a class of organic compounds with the general formula of RCHO ; the reaction is accompanied by the removal of two hydrogen atoms. The resulting aldehydes can be further oxidized to carboxylic acids, a class of organic compounds with the general formula of RCOOH ; the oxidized molecule gains an oxygen atom. Secondary alcohols, which have the general formula of R_2CHOH , are oxidized to ketones, a class of organic compounds with the general formula of RCOR , which cannot be further oxidized because there is no hydrogen atom on the oxygen bearing carbon atom of the ketone. Tertiary alcohols, which have the general formula R_3COH , cannot be readily oxidized because the carbon atom bearing the hydroxyl group has no hydrogen atom.

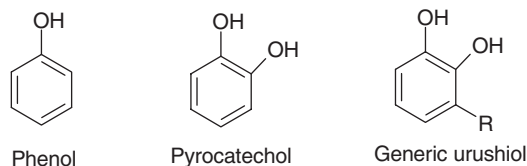
Alcohols can be synthesized from alkenes by hydration (addition of water). Conversely, alkenes can be dehydrated (removal of water) to form alcohols. For example, the equilibrium expression for hydration of ethene and dehydration of ethanol is given by



The direction of the reaction is controlled by Le Chatelier's principle. Thus, excess water will drive the reaction toward alcohol formation, whereas a deficiency in water will drive the reaction toward alkene formation. This latter condition is achieved by reaction in concentrated sulfuric acid, where water concentration is very low.

The attachment of a hydroxyl group to benzene forms an important class of compounds known as phenols. Both alcohols and phenols can be considered organic analogs of water and undergo reactions that are similar to water, such as reaction with alkali metals to form hydrogen gas. However, the delocalization of electrons in the benzene ring makes the C–O bond in phenols much stronger than the C–O bond in alcohols, resulting in important chemical differences between these two classes of compounds. In alcohols, the hydroxyl group is readily displaced, whereas the strong C–O bond in phenol prevents this from occurring except under extreme conditions.

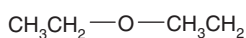
Examples of phenolic compounds include phenol with one hydroxyl group attached to the benzene ring; pyrocatechol, containing two adjacent hydroxyl groups and originally obtained from pyrolysis of biomass; and urushiols, a mixture of pyrocatechol derivatives with saturated and unsaturated side chains of 15 or 17 carbon atoms, which is the oily irritant in poison ivy. Phenol is used to manufacture epoxy resins and polymers such as Bakelite and nylon. It is also used in the manufacture of dyes, herbicides, and disinfectants.



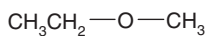
3.4.5 Ethers

Ethers contain two groups, which may be alkyl or aryl groups, bonded to an oxygen atom. The smaller alkyl group and the oxygen atom constitute an alkoxy

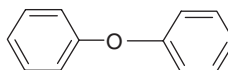
group (R–O). Similarly, an aryl group and the oxygen atom constitute a phenoxy group (Ar–O). The alkoxy and phenoxy groups are considered substituents on the larger parent alkyl or aryl group. These groups can form either symmetrical ethers or unsymmetrical ethers, depending upon whether the same or different alkyl or aryl groups are attached to the two oxygen bonds. Ethers are named by listing the alkyl or aryl groups in alphabetical order and appending the name ether.



Diethyl ether
(symmetrical ether)



Ethyl methyl ether
(asymmetrical ether)



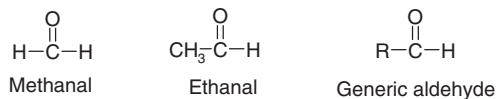
Diphenyl ether
(symmetrical ether)

The two C–O bonds result in substantial dipole moments for ethers. They are more polar than alkanes but less polar than alcohols. Thus, they are more soluble in water than alkanes of similar molecular weight. This functional group has no hydrogen bond donors; thus, boiling points are substantially less than for alcohols of comparable molecular weight and similar to alkanes of comparable molecular weight. Ethers are stable compounds that do not react with most common reagents. Ethers have found applications as solvents and anesthetics.

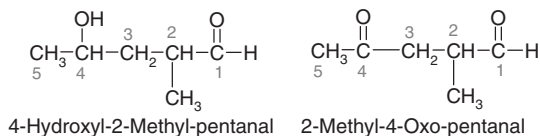
3.4.6 Aldehydes and Ketones (Carbonyl Compounds)

Aldehydes and ketones are characterized by the carbonyl functional group, which consists of an oxygen atom double-bonded to carbon (C=O). The carbon atom of the carbonyl group is called the carbonyl carbon atom, and the oxygen atom is called the carbonyl oxygen atom. The carbonyl group is prevalent in compounds isolated from plants. Aldehydes and ketones, collectively known as carbonyl compounds, often have pleasant odors and are responsible for the fragrant smell of flowers. At one time, plants were the sole source of aldehydes and ketones used in such products as perfumes.

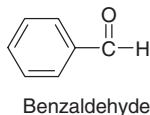
An aldehyde is a carbonyl group with the carbonyl carbon atom bonded to a hydrogen atom and either another hydrogen atom or an alkyl or aryl group. The aldehydes are named by addition of the suffix “-al” to the root alkyl name corresponding to the longest continuous carbon chain containing the carbonyl group. For example, methanal is a carbonyl group (C=O) bonded to two hydrogen atoms. Methanal is more commonly known as formaldehyde, a preservative for biological specimens. Ethanal, containing two carbon atoms, consists of a carbonyl group bonded to one hydrogen atom and one methyl group (CH₃). Ethanal is more commonly known as acetaldehyde, a compound found in a variety of fruits and vegetables.



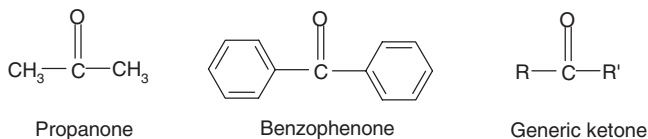
The alkyl group attached to the carbonyl group may also have side chains, which must be indicated in the name. This is done by specifying the location and type of alkyl group as a prefix to the parent name. Carbon atoms in the parent chain are numbered starting with the carbonyl carbon atom. The presence of carbonyl side chains (C=O) is designated with the prefix “oxo-.”



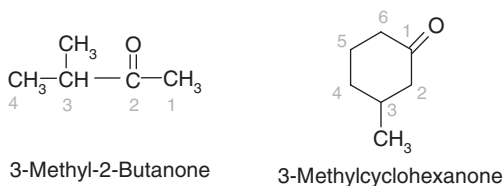
An example of an aldehyde incorporating an aryl group is benzaldehyde, consisting of a carbonyl group bonded to a hydrogen atom and a phenyl group (i.e., a benzene ring). Benzaldehyde is known as oil of almonds and used in flavorings and perfumes.



When the carbonyl carbon atom is bonded to two other carbon atoms, the compound is known as a ketone. These other carbon atoms can be part of either an alkyl group or an aryl group. The ketones are named by addition of the suffix “-one” to the root alkyl name corresponding to the longest continuous carbon chain containing the carbonyl group. Replacing the hydrogen bond in ethanal, for example, with another methyl group yields the solvent propanone (commonly known as acetone), while replacing the hydrogen bond in benzaldehyde with another phenyl group yields benzophenone, a component in the manufacture of perfumes and sunscreens.



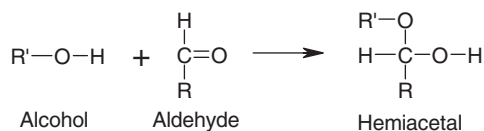
For more complicated ketones, the location of the carbonyl carbon atom and the position and type of side chains must be specified. The carbon atoms are numbered from the end of the parent chain closest to the carbonyl carbon atom. Cyclic ketones are called cycloalkanones. The carbonyl carbon atom is designated as the first carbon atom in the ring.



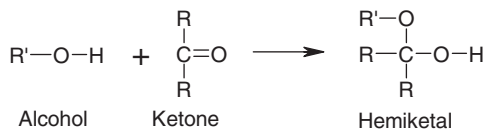
The carbonyl group is polar; thus, carbonyl compounds have boiling points that are higher than alkanes of similar molecular weight. The carbonyl group cannot act as a hydrogen donor, but the carbonyl oxygen atom can serve as a hydrogen acceptor, allowing aldehydes and ketones to form hydrogen bonds with water. Accordingly, lower-molecular-weight compounds containing the carbonyl group are miscible in water. For the same reason, alcohols and carboxylic acids are soluble in these compounds. Several ketones are excellent solvents for polar organic compounds.

Aldehydes can be synthesized by the controlled oxidation of primary alcohols, while ketones can be prepared by oxidation of secondary alcohols. Carbonyl compounds can participate in a variety of chemical reactions including oxidation to carboxylic acids, reduction to alcohols, and condensation to give a group of compounds known as aldols, which contain both aldehyde and alcohol functional groups. They also participate in acid-catalyzed addition reactions with alcohol to form compounds very important to carbohydrate chemistry.

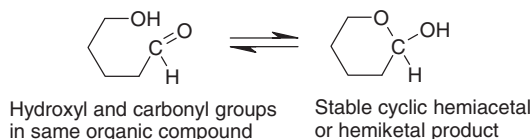
In the addition reaction of alcohol with a carbonyl compound, the hydrogen atom from the hydroxyl group of the alcohol adds to the carbonyl oxygen atom, whereas the remaining “-R” fragment from the alcohol, known as the alkoxy group, adds to the carbonyl carbon atom. The product is called hemiacetal if the carbonyl compound in the reactants is aldehyde.



The product is called hemiketal if the carbonyl compound in the reactants is ketone.

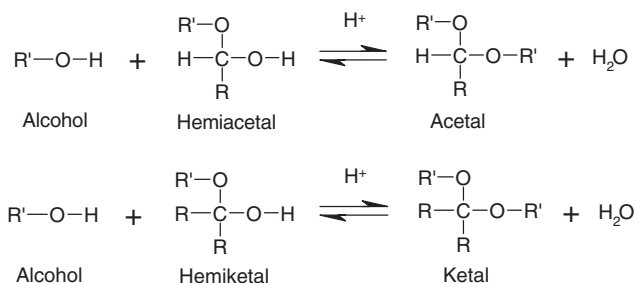


The equilibrium constant for the formation of either hemiacetal or hemiketal is less than 1; thus, these compounds are usually unstable. However, if the hydroxyl and carbonyl groups are part of the same molecule, a stable cyclic product forms.



Carbohydrates contain both hydroxyl and carbonyl groups and commonly form such cyclic hemiacetals or hemiketals, as will be discussed in a later section.

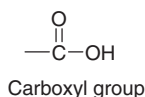
Note that the resulting hemiacetal or hemiketal contains a new hydroxyl group. In an acidic solution, this hydroxyl group can be replaced by another alkoxy group derived from alcohol to form acetal and ketal, respectively.



The position of the equilibrium can be shifted toward formation of acetal or ketal by adding alcohol or removing water from the reaction. Note that the reverse reactions are acid-catalyzed hydrolysis of acetal or ketal to form carbonyl compounds and alcohol. Cyclic hemiacetals and cyclic hemiketals react with alcohols to form cyclic acetals and cyclic ketals, respectively.

3.4.7 Carboxylic Acids

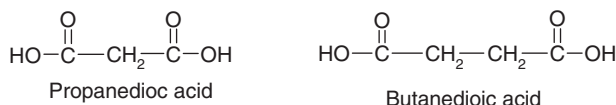
The carboxyl group, a combination of carbonyl group and hydroxyl group, characterizes carboxylic acids.



The carbonyl group and hydroxyl group modify the behavior of each other; thus, the behavior of carboxylic acids differs from that of carbonyl compounds and alcohols.

Carboxylic acids are named by replacing the “-e” in the root alkyl name corresponding to the longest continuous carbon chain containing the carboxyl group. For example, attached to a hydrogen atom, it forms methanoic acid, commonly known as formic acid, a pungent liquid secreted by ants when disturbed; attached to the methyl group, it forms ethanoic acid, commonly known as acetic acid, the main ingredient of vinegar and important in the manufacture of polymers;

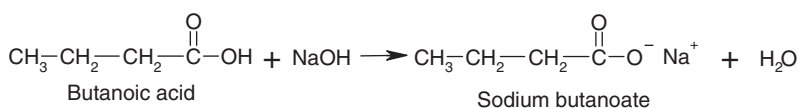
Carboxylic acids containing a $-\text{COOH}$ group at each end of the carbon chain are known as dicarboxylic acids or simply diacids. They are named by adding -dioic acid to the end of the alkyl root name. Examples include propanedioic acid, commonly known as malonic acid, and butanedioic acid, commonly known as succinic acid, both of which are being proposed as precursors in the synthesis of biobased polymers.



The boiling points of carboxylic acids are high because the formation of hydrogen-bonded dimers causes the molecules to interact very strongly. Carboxylic acids serve both as hydrogen bond donors and as hydrogen bond acceptors; thus, carboxylic acids are soluble in water. Liquid carboxylic acids have sharp, unpleasant odors.

The carboxyl group readily serves as a proton donor; thus, carboxylic acids are relatively strong acids compared to alcohols, able to react with some metals to liberate hydrogen and react with metallic carbonates to liberate carbon dioxide, but they are rather weak acids compared to mineral acids.

The reaction of carboxylic acid with a base yields the conjugate base RCOO^- known as the carboxylate ion, which is named by replacing the -oic acid ending with -oate. The salt of a carboxylic acid is named by preceding the name of the carboxylate ion by the name of the metal ion.

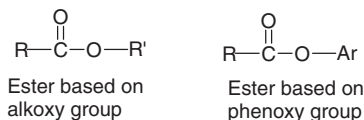


Because they are ionic, carboxylates are more soluble than their corresponding carboxylic acids. This feature is often used to separate carboxylic acids from other nonpolar organic compounds.

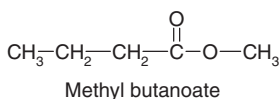
3.4.8 Esters

The RCO unit in a carboxylic acid is called an acyl group. A number of carboxylic acid derivatives result by replacing the hydroxyl group that is attached to the acyl group of a carboxylic acid with other atoms or functional groups, which are known as substituents.

If an alkoxy group ($\text{R}-\text{O}$) or phenoxy group ($\text{Ar}-\text{O}$) are bonded to the acyl group, the derivative is called an ester.

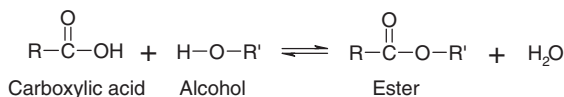


Esters are named by adding the suffix “-oate” to the parent name of the corresponding carboxylic acid and adding a prefix appropriate to the alkoxy or phenoxy group. For example, the acyl group from butanoic acid combined with the alkoxy group derived from the methyl group yields methyl butanoate, a chemical that gives apples their aroma.



Esters are polar molecules; however, because there is no intermolecular hydrogen bonding between the molecules, the boiling point of esters is lower than those of alcohols and carboxylic acids of comparable molecular weight. The oxygen atoms in esters can form hydrogen bonds to the hydrogen in water; thus, esters are slightly soluble in water. They are less soluble than carboxylic acids, though, because they have no hydrogen to form a hydrogen bond to the oxygen in water. Esters have pleasant fruity smells that are responsible for the aroma of many fruits.

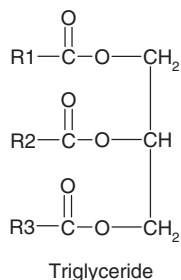
Esters are synthesized from carboxylic acids by condensation reactions with alcohols in the presence of an acid catalyst. In these condensation reactions, known as esterification, the carboxylic acid supplies the hydroxyl group, while the alcohol supplies the hydrogen to form water. According to Le Chatelier’s principle, distilling water out of the reaction mixture can increase the yield of ester. Likewise, reacting in the presence of excess alcohol can increase the ester yield.



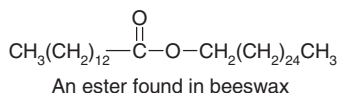
Hydrolysis of esters, catalyzed by a strong acid, is the reverse reaction of esterification, yielding a carboxylic acid and an alcohol as products. However, if hydrolysis occurs in the presence of a strong base, the conjugate base of the carboxylic acid, known as a carboxylate ion, forms instead of the acid. This process is called saponification, from the Latin word for soap, because soaps are the salts of long-chain carboxylic acids (metal carboxylates).

Triglycerides, also known as fats and oils, are a special class of esters that consist of three long-chain fatty (carboxylic) acids attached to a backbone of glycerol (1,2,3-propanetriol). The acid fractions of triglycerides can vary in chain length and degree of saturation. Fats, which are solid or semi-solid at room temperature, have a high percentage of saturated acids, whereas oils, which are liquid at room temperature,

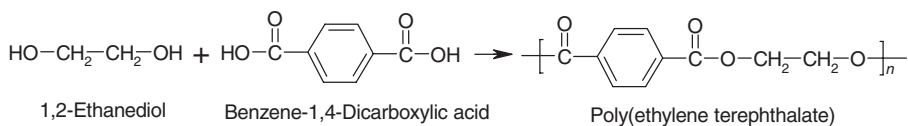
have a high percentage of unsaturated acids. Plant-derived triglycerides are typically oils containing unsaturated fatty acids, including oleic, linoleic, and linolenic acids.



Waxes are another class of esters consisting of fatty acids and long-chain alcohols containing an even number of carbon atoms. Waxes are low-melting solids that coat the surface of plant leaves and fruits, and also the hair and feathers of some animals. Waxes are usually a complex mixture of several esters. For example, hydrolysis of bees wax yields several fatty acids and a mixture of alcohols containing 24–36 carbon atoms.



Polyesters are produced by the reaction of carboxylic acids and alcohols that contain two or more functional groups. These acid-catalyzed condensation reactions yield long chains of repeating ester groups that represent an important class of synthetic polymers. One of the most important polyesters, poly(ethylene terephthalate) or PET, is produced by the reaction of 1,2-ethanediol (ethylene glycol) with benzene-1,4-dicarboxylic acid (terephthalic acid), which is spun into fibers and marketed as Dacron.



3.4.9 Other Functional Groups

Other carboxylic acid derivatives include amides, in which a substituent is linked to the acyl group by a nitrogen atom; thioesters, in which the substituent is linked to the acyl group by a sulfur atom; acyl chlorides, in which the substituent linked to the acyl group is a chlorine atom; and acid anhydrides, in which two acyl groups are linked by an oxygen atom.

Organic compounds with one or more carbon–nitrogen single bonds are amines. Compound with carbon–nitrogen double and triple bonds are imines and nitriles,

respectively. Sulfur forms single bonds to carbon in two classes of compounds. Thiols (also called mercaptans) and thioethers (also called sulfides) structurally resemble alcohols and ethers, which contain oxygen, another element in the same group of the periodic table as sulfur.

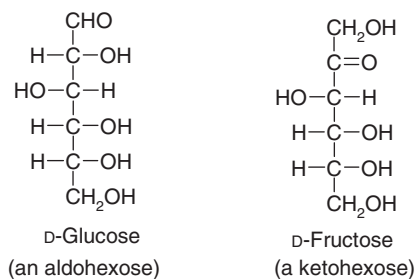
3.5 Chemistry of Lignocellulosic Plant Materials

3.5.1 Carbohydrates

Carbohydrates are polyhydroxy aldehydes, polyhydroxy ketones, or compounds that can be hydrolyzed from them. Carbohydrates, which are designated with the suffix “-ose,” range in size from molecules containing three carbon atoms to gigantic molecules containing thousands of carbon atoms. The smallest carbohydrates, those that cannot be hydrolyzed to smaller carbohydrate units, are called monosaccharides.

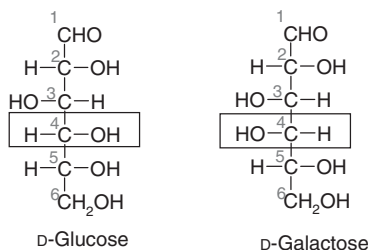
Carbohydrates consisting of a few monosaccharides are called oligosaccharides. Those consisting of two monosaccharides, which may be the same or different compound, are called disaccharides. Examples include lactose and maltose. Polysaccharides contain thousands of covalently linked monosaccharides. Starch and cellulose are examples of homopolysaccharides, which are polysaccharides containing only one kind of monosaccharide. Polysaccharides that contain different kinds of monosaccharides are called heteropolysaccharides. Acetal or ketal bonds link the monosaccharides in oligo- and polysaccharides; these can be hydrolyzed to yield the component monosaccharides.

Monosaccharides are classified according to their most highly oxidized functional group, either an aldehyde group or a ketone group. Aldoses contain a single aldehyde group, while ketoses contain a single ketone group. Monosaccharides are designated with the prefix aldo- or keto-, as appropriate, and the prefix tri-, tetra-, pent-, and hex- to indicate the number of carbon atoms. For example, D-glucose and D-fructose are 6-carbon monosaccharides isomers with the molecular formula of $C_6H_{12}O_6$. However, D-glucose contains an aldehyde group as the first carbon atom in the chain, making it an aldohexose, while D-fructose contains a ketone group as the second carbon atom in the chain, making it a ketohexose.



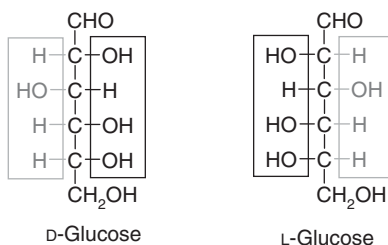
D-Glucose is the carbohydrate around which metabolism is based, and D-fructose is the sugar commonly found in fruits and honey. Because of the differences in functional groups, D-glucose and D-fructose qualify as functional isomers of one another.

The monosaccharides also include stereoisomers—those that have the same sequence of bonded atoms but differ only in the spatial location of atoms or functional groups around the carbon chain. Of particular interest are epimers, isomers that differ in spatial arrangement only about a single carbon atom in the chain. D-Galactose, like D-glucose, is an aldohexose with molecular formula $C_6H_{12}O_6$. They differ only in the position of the hydroxyl group attached to the fourth carbon atom (where carbon atoms are numbered starting at the end of the chain closest to the carbonyl carbon atom); thus, they are known as C-4 epimers. Although physical and chemical properties of epimers are essentially the same, biological activity can be quite different.

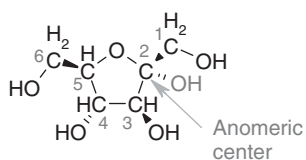


A special instance of positional isomers among monosaccharides is based on chirality. A molecule is chiral if it is not superimposable on its mirror image; otherwise, it is achiral. Chiral molecules have the same chemical formulas but can be arranged in two different ways corresponding to the mirror images of one another; these are known as enantiomers. In carbohydrate chemistry, enantiomers are designated by either the suffix D- or L-, the former being used for enantiomers that correspond to the chirality of the naturally occurring enantiomer of glyceraldehyde, a three-carbon monosaccharide. Because monosaccharides in nature are derived from the building block D-glyceraldehyde, nearly all naturally derived monosaccharides are of the D series. Thus, the D- or L-suffix is commonly discarded when discussing monosaccharides, with the D series assumed.

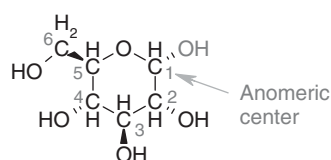
Enantiomers are mirror images of one another



Recall that the carbonyl group of aldehydes and ketones can react reversibly with the hydroxyl group of alcohols to form hemiacetals and hemiketals, respectively. Furthermore, if the carbonyl group and the hydroxyl groups occur in the same compound, they can react to form cyclic structures known as cyclic hemiacetals and cyclic hemiketals. Monosaccharides contain both carbonyl groups and hydroxyl groups and, thus, readily form cyclic structures. Indeed, hemiacetal forms of aldohexoses and aldopentoses predominate over open chain five-carbon and six-carbon aldoses, while hemiketal forms of ketohexoses and ketopentoses predominate over open chain five-carbon and six-carbon ketoses. Cyclic hemiacetals and cyclic hemiketals of carbohydrates that form five-membered rings are called furanoses; those that form six-membered rings are called pyranoses. The carbon atoms are numbered starting with the carbon atom nearest to the carbon atom at the anomeric center.

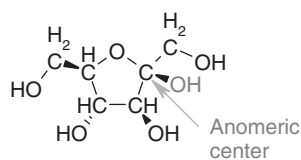


Perspective structural
formula of a furanose
(α -D-Fructofuranose)

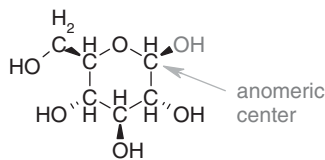


Perspective structural
formula of a pyranose
(α -D-Glucopyranose)

The carbon atom around which the hemiacetal or hemiketal structure forms is called the anomeric carbon atom or anomeric center. Note that it is the only carbon atom in the monomer attached to two oxygen atoms. Also note that the hydroxyl groups attached to the anomeric centers of the furanose and pyranose molecules illustrated above are directed below the plane of the cyclic structure (as indicated by the dashed wedge used to represent the C–OH bond). This isomeric form is designated by the prefix α -; thus, the hemiketal form of D-fructose with a downward projecting hydroxyl group attached to the anomeric center is called α -D-fructofuranose, while the hemiacetal form of D-glucose with a downward projecting hydroxyl group attached to the anomeric center is called α -D-glucopyranose. The epimers of these monosaccharides have the hydroxyl group associated with the anomeric center projecting upward and are designated with a prefix β -.

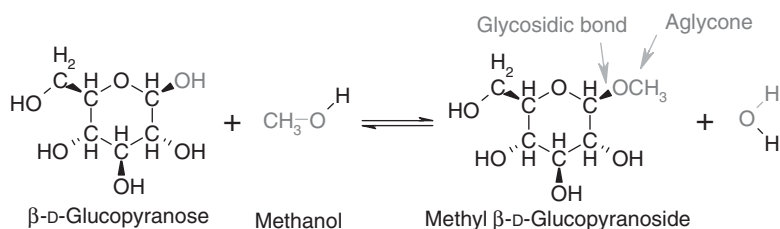


β -D-Fructofuranose

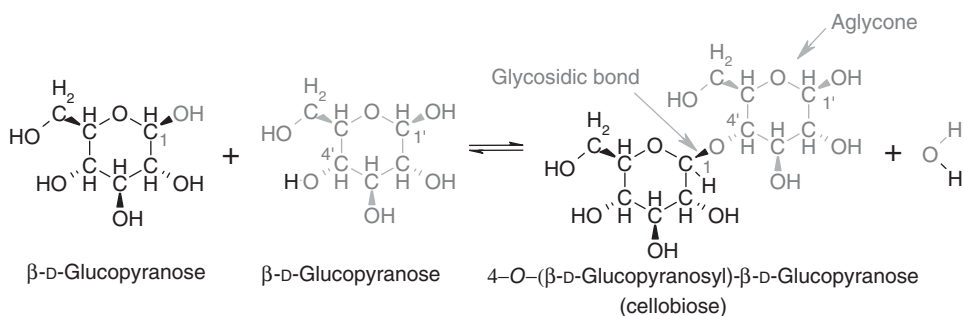


β -D-Glucopyranose

Recall that the hemiacetal and hemiketals can react with alcohols to form acetals and ketals. The acetals and ketals produced from the cyclic hemiacetal and hemiketal forms of monosaccharides are called glycosides, and the C–O bond thus formed is called the glycosidic bond. The group bonded to the anomeric carbon atom of a glycoside is an aglycone.



These glycosidic bonds are the basis for constructing oligosaccharides and polysaccharides from monosaccharides because they allow linkage between the anomeric center of one monosaccharide with a hydroxyl oxygen atom of a second monosaccharide. Consider the bonding of two D-glucose monosaccharides in their cyclic forms of β-D-glucopyranose: a glycosidic bond is formed between the anomeric center of the first monosaccharide (designated the C-1 carbon atom) and one of the hydroxyl carbon atoms of the second monosaccharide. If the fourth carbon atom of the second monosaccharide is involved (called the C-4' carbon atom), the resulting disaccharide is called cellobiose, the structural unit of cellulose. The IUPAC name is 4-O-(β-D-glucopyranosyl)-β-D-glucopyranose. The -syl suffix on the first monosaccharide parent name indicates that this unit is linked to the second unit by a glycosidic bond. The prefix 4-O refers to the position of the oxygen atom of the aglycone unit.

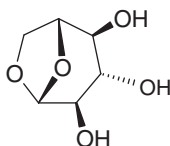


Note that the reverse of this disaccharide-building reaction is hydrolysis of an oligosaccharide to release monosaccharides.

Other common disaccharides are maltose, a combination of α-D-glucopyranose and β-D-glucopyranose by a α-1,4'-glycosidic bond; lactose, a combination of β-D-galactopyranose and β-D-glucopyranose by a β-1,4'-glycosidic bond; and

sucrose, a combination of α -D-glucopyranose and β -D-fructofuranose linked by their anomeric centers by both a α -glycosidic bond on the glucose and a β -glycosidic bond on the fructose.

Dehydrated sugars play a prominent role in thermochemical conversion of polysaccharides. Whereas depolymerization of polysaccharides in an aqueous environment produces monosaccharides through the action of hydrolysis, the scarcity of water during thermal depolymerization of polysaccharides in a gaseous environment results in monosaccharides that are missing the water molecule inserted during aqueous-phase hydrolysis. These singly dehydrated sugars are called anhydrosugars. The dehydrated analogs of sugars with six-member rings are called anhydrofuranoses, while the dehydrated analogs of sugars with five-member rings are called anhydrofuranoses. For example, cellulose, a polymer of glucose monomers ($C_6H_{12}O_6$), can thermally depolymerize to 1,6-anhydro- β -D-glucopyranose ($C_6H_{10}O_5$), commonly known as levoglucosan.



1,6-Anhydro- β -D-Glucopyranose (levoglucosan)

Multiple dehydration products of monosaccharides can also occur including five-member aromatic ethers known as furans; five-member saturated ring ethers known as tetrahydrofurans; six-member unsaturated ring ethers known as pyrans; and six-member saturated ring ethers known as tetrahydropyrans. These ring ethers typically include multiple functional group substitutions.



Furan



Tetrahydrofuran



Pyran



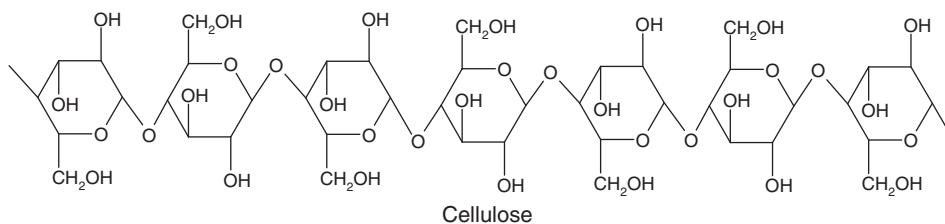
Tetrahydropyran

Among the most important polysaccharides in nature are starch, cellulose, and hemicellulose. Starch is a polymer of α -1,4-linked glucose molecules consisting of the disaccharide maltose as the basic structural unit. Starch, an important energy source in nature, accumulates as granules in the cells of many kinds of plants. Starch occurs as both linear molecules, known as amylose, and branched molecules, known as amylopectin. Different plants accumulate various proportions of amylose and amylopectin. Cellulose and hemicellulose are discussed in the next section.

3.5.2 Lignocellulose

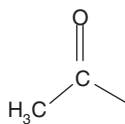
Lignocellulose is the term used to describe the three-dimensional polymeric composites formed by plants as structural material. It consists of variable amounts of cellulose, hemicellulose, and lignin. Hardwoods (from deciduous trees), softwoods (from coniferous trees), and herbaceous material (from grasses and agricultural crops) have distinct compositions from one another, as detailed in Chapter 4.

Cellulose, a homopolysaccharide of glucose, is an important constituent of most plants.



The basic building block of this linear polymer is cellobiose, a compound of two glucose molecules. The number of glucose units in a cellulose chain is known as the degree of polymerization (DP). The average DP for native cellulose is on the order of 10 000, although chemical pulping reduces this to the range of 500–2000. Cellulose molecules are randomly oriented with a tendency to form intra- and intermolecular hydrogen bonds. The strong tendency for intra- and intermolecular hydrogen bonding in cellulose results in molecular aggregation to form microfibrils. High packing densities result in highly ordered microfibrils known as crystalline cellulose. Low packing densities result in less ordered microfibrils known as amorphous cellulose. Crystalline cellulose is relatively inert to chemical treatment and insoluble in most solvents.

Hemicellulose is a large number of heteropolysaccharides built from hexoses (D-glucose, D-mannose, and D-galactose), pentoses (D-xylose, L-arabinose, and D-arabinose), and deoxyhexoses (L-rhamnose or 6-deoxy-L-mannose and rare L-fucose or 6-deoxy-L-galactose). Xylan is a general term to describe the predominant hemicellulose in most plants, which is built of a backbone of β -(1 \rightarrow 4)-D-xylopyranose with a variety of side chains. The composition and linkages of the side chains vary among types of plants. Because the side chains of grasses and annuals are mainly arabinofuranoses and acetyl groups, these xylans are referred to as arabinoxylans. The ester-linked acetyl groups are attached to C2 or C3 hydroxyl groups.



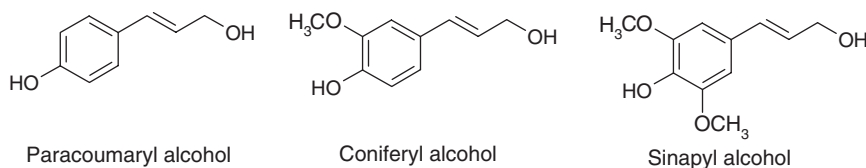
Acetyl functionality

Hardwood xylans are termed glucuronoxylans because they are highly substituted with acetyl and 4-*O*-methyl glucuronic acid (a carboxylic acid with a ring structure similar to glucose). 4-*O*-methylglucuronic acid is linked to the xylan backbone by α -(1 \rightarrow 2) glycosidic bonds, while the acetic acid is esterified at the two- and/or three-carbon hydroxyl groups. The molar ratio of xylose/glucuronic acid/acetyl residues is about 10:1:7.

In contrast, softwood hemicellulose is dominated by galactose and mannose units (known as galactoglucomannan) (15–20% dry biomass weight), with xylans comprising only 7–10% of the biomass dry weight. The galactoglucomannans are divided into two subtypes of low and high galactose content with galactose/glucose/mannose ratios of 0.1:1:4 and 1:1:3, respectively. Softwood xylans are not acetylated but are more highly substituted with 4-*O*-methyl glucuronic acid than are hardwood xylans.

The monosaccharides released upon hydrolysis of hemicellulose include a large fraction of pentoses as opposed to hexose from cellulose. The chemical and thermal stability of hemicelluloses is lower than that of cellulose, presumably due to their lack of crystallinity and lower DP, which is only 100–200.

Lignin, illustrated in Figure 3.1, is a phenylpropane-based polymer and the largest non-carbohydrate fraction of lignocellulose. It is constructed of three monomers—paracoumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, each of which has an aromatic ring with different substituents.



The functional groups associated with lignin, including phenolic and alcoholic hydroxyl groups, and aldehyde (CHO–) and methoxy (CH₃O–) groups result in highly reactive molecules. The number of various functional groups per 100 phenylpropane (C₆H₃) units is given in Table 3.4 for hardwoods and softwoods. Lignin can be depolymerized by heat or laccase or peroxidase enzymes although not necessarily back to its original building block monomers. Lignin and hemicellulose form a sheath that surrounds the cellulosic portion of the biomass. Lignin protects lignocellulose against pests.

Natural lignins are roughly classified according to plant source: softwood, hardwood, and grasses. Attempts to chemically liberate lignin from lignocellulose almost always produce a modified product distinct from the natural form with different physical and chemical properties. Thus, it is common to distinguish lignin by the process that liberated it: kraft or sulfate lignin from kraft pulping; alkali or soda lignin from soda processing; lignosulfonates from sulfite pulping; organosolv lignin from treating wood with alcohol solvents; acid hydrolysis and enzymatic hydrolysis lignins from these respective processes to “saccharify” lignocellulose;

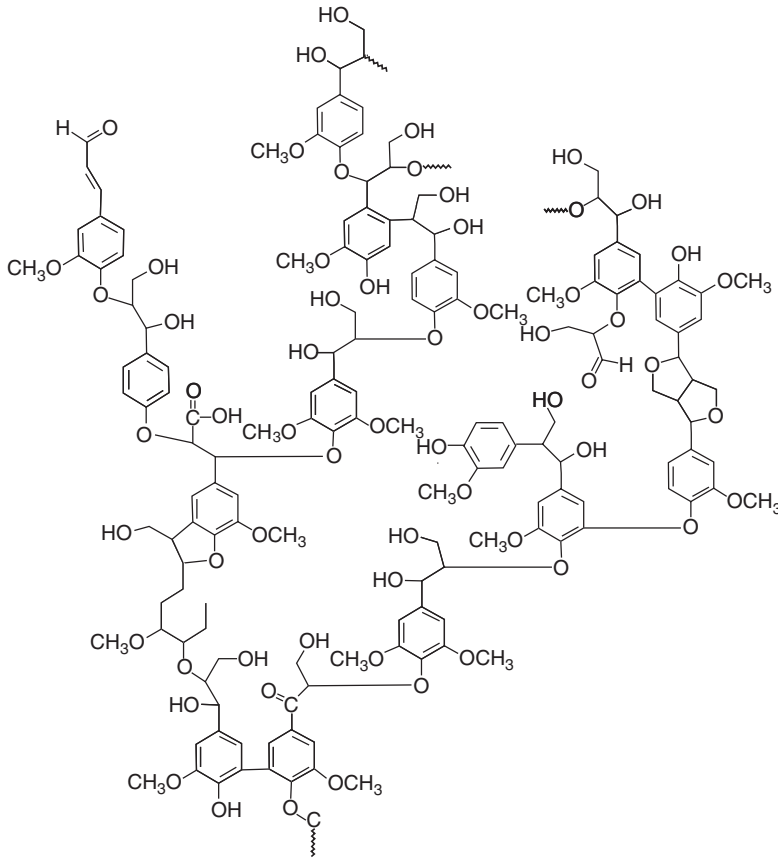


FIG. 3.1 Polymeric structure of softwood lignin. Adapted from Adler, E. (1977) Lignin chemistry—past, present and future. *Wood Science Technology*, 11, 169–218.

and pyrolytic lignin from the pyrolysis of lignocellulose. The lignin is condensed to different degrees by these processes. Very fine mechanical milling of wood can liberate “milled wood” lignin, which is thought to be very close to natural lignin in composition and chemistry.

Plant materials also contain thousands of other chemical compounds known as “extractives.” These include resins, fats and fatty acids, phenolics, phytosterols,

Table 3.4 Number of functional groups in natural lignin (per 100 C₆H₃ units)

Functional Group	Softwood Lignin	Hardwood Lignin
Phenolic hydroxyl (Ar–OH)	20–30	10–20
Aliphatic hydroxyl (R–OH)	115–120	110–115
Methoxyl (CH ₃ O–)	90–95	140–160
Aldehyde (CHO–)	20	15

and other compounds, the content of which is extremely dependent on the plant species. These are often classified as either hydrophilic or lipophilic depending on whether they are soluble in water or organic solvents, respectively. Resin is often used to describe the lipophilic extractives with the exception of phenolic substances. Extractives impart color, odor, and taste to wood. Although some extractives (lipids) are an energy source for the plant, the functions of most appear to protect the plant against microbiological damage or insect attacks. They are a valuable byproduct of many manufacturing processes, especially in the pulp and paper industry. For example, southern pines, favored in pulp making, have particularly high content of extractives, which are recovered as crude turpentine and raw tall oil.

The cell walls of both woody and herbaceous biomass consist of lignocellulose. These cells can be classified into two broad categories: prosenchyma cells, which are long, thin cells, with flattened or tapered closed ends, and parenchyma cells, which are short, rectangular cells. Prosenchyma cells are on the order of 1–6 mm in length with widths of 20–50 μm . Parenchyma cells are shorter than 0.2 mm with widths of 2–50 μm .

Softwoods consist primarily of prosenchyma cells, about 90% of the total, referred to as tracheids, which both transport fluids through the plant and support the plant. These are long, strong fibers ideal for pulp and paper applications. Parenchyma cells provide storage of nutrients in softwoods.

Hardwoods consist of a much smaller fraction of prosenchyma cells, about 55% of the total, along with a significant fraction of parenchyma cells, about 20%, and cells intermediate in size to prosenchyma and parenchyma cells known as vessel cells. In hardwoods, prosenchyma cells provide structural support, parenchyma cells provide both transport of fluids and nutrient storage, and vessel cells serve primarily for transport. Herbaceous plant material more closely resembles hardwoods than softwoods.

Further Reading

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Kole, C. Joshi, C.P., and Shonnard, D.R. (eds.) (2012) *Handbook of Bioenergy Crop Plants*. Boca Raton, FL: CRC Press.

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