

Guanqun Chen · Randall J. Weselake
Stacy D. Singer *Editors*

Plant Bioproducts

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Preface

As a society on a global level, we have become increasingly dependent on energy, industrial products and consumer goods derived from petroleum. Unfortunately, such heavy use of petroleum results in the production of more carbon than can be offset by its capture and sequestration by living or recently living organisms, most often in the form of plants that are not used for food or feed. One possible way to reduce carbon emissions is through the increased use of sustainable, bio-based alternatives to petrochemicals. Bioproducts are materials, chemicals, fuels and energy derived from various renewable biological sources including plants, animals and microorganisms. In the strictest sense, bioproducts do not include food and feed. They may, however, have applications such as materials used in automobiles, adhesives, packaging, coatings for food products, components of pharmaceuticals, materials used in medical products and industrial enzymes. In terms of plant bioproducts, the major components used for their production include storage lipids, complex carbohydrates and proteins. Increasing our use of plant components for the generation of fuel and other bioproducts will contribute to a more sustainable and environmentally acceptable approach than a system which is heavily reliant on fossil fuels.

Plant Bioproducts presents an overview of how various plant-derived components can be used to generate bioproducts. The impetus for this book stems from our involvement in delivering third-year courses in plant bioproducts at the University of Alberta and University of Manitoba. We anticipate that this book will be particularly useful to the senior undergraduate student in plant sciences who may have a limited understanding of chemistry, biochemistry and molecular biology. It could also be valuable to those from the general public who are interested in learning about plant bioproducts, non-biological engineers who are interested in moving into the realm of biological engineering, and agricultural industrialists and other stakeholders who wish to increase their understanding of biology in relation to the generation of bioproducts.

Plant Bioproducts begins with a brief discussion of environmental problems associated with increasing carbon emissions and how plant bioproducts can contribute to help close the carbon cycle (Chap. 1). Chapter 2 presents a brief and

simplified review of how atoms can be united to form biomolecules of increasing complexity in plants and insight into the chemical diversity of plants as it relates to providing starting material for bioproducts. Depending on the reader's background knowledge, this chapter may serve as a minimal prerequisite for appreciating the ensuing discussions concerning the production of plant bioproducts from various plant components. Chapter 3 provides insight into how bioproduct production can benefit from the integration of various disciplines. Indeed, the area of plant bioproducts is based on several interdependent and allied disciplines including chemistry, plant biochemistry and physiology, plant breeding, agronomy, microbiology, molecular biology, chemical and biochemical engineering, biotechnology and the social sciences. Chapters 4, 5, 6, 7, 8 and 9 introduce plant lipids, carbohydrates and proteins, and demonstrate how these plant components can be used to produce various bioproducts. Chapters 4 and 5, in particular, place a strong emphasis on the potential of genetic engineering as a means of altering the lipid components of plants so as to provide a starting material that is more amenable to bioproduct production. To make plant bioproducts commercially attractive, it is important to integrate the production of bioproducts into existing well-developed chemical industries. The chemical industry is currently based on relatively small building block chemicals derived from petroleum; however, these molecules can also be produced from plant biomass. With the help of the background information provided in previous chapters, Chap. 10 introduces these molecules and describes how they can be used to produce a wide range of intermediates or end-products, with an emphasis on the production and use of these building block molecules from plants. Moreover, the full and effective use of all plant parts is important, in which the biorefinery plays a crucial role. Therefore, in Chap. 11, the biorefinery process of plant-based products is described, along with current research and development in this field. Although the production of bioproducts from plants is attractive, there have been concerns regarding the increasing use of plants for biofuel production instead of food. In the final chapter (Chap. 12), a background to biofuel policies in the leading biofuel producing nations and a contextual overview of what has occurred regarding commodity prices are presented. Subsequently, a discourse of the price spike assessments is offered, providing insight into just how complicated an issue this has turned out to be.

We thank our various colleagues who contributed critical chapters to making this book possible. We would also like to acknowledge Dr. Xiao Qiu of the University of Saskatchewan for stimulating discussions on plant bioproducts. In addition, we express our gratitude to Crystal Snyder for her outstanding contributions in the early stages of this project and to Lucas Falarz and Trinh Nguyen for their contributions to figures, tables and editorial aspects related to overall development of the book. We are deeply grateful to Susan Safren and Sabina Ashbough of Springer. Susan was incredibly patient and provided solid support from the early stages of this book's development. Finally, we acknowledge the support of the University of Alberta, Agriculture and Agri-Food Canada, Alberta Innovates

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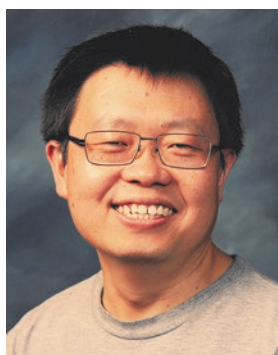
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Randall J. Weselake is Professor Emeritus with the Department of Agricultural, Food and Nutritional Science at the University of Alberta. Randall has over 30 years of experience in the biochemistry and molecular biology of storage lipid metabolism in oil crops and other oleaginous plant species. In addition, he has conducted research on lipid metabolism in yeast and livestock. Randall held a Tier I Canada Research Chair in Agricultural Lipid Biotechnology at the University of Alberta from 2005 to 2016. During his tenure there, Randall developed and taught a senior level course

dealing with plant bioproducts. From 2010 to 2016, Randall served as Scientific Director of the Alberta Innovates Phytola Centre which specialized in oilseed innovations, including research and development of industrial oil crops. In addition, Randall was leader (2007–2013) of the “Bioactive Oils Program”, funded by AVAC Ltd., and co-leader (2006–2011) of the large-scale Genome Canada/Genome Alberta project “Designing Oilseeds for Tomorrow’s Markets”. From 1989 to 2004, Randall was with the Department of Chemistry and Biochemistry at the University of Lethbridge (Alberta, Canada) where he served as Chair from 1996 to 1999. His doctoral research in plant biochemistry was conducted at the University of Manitoba and Grain Research Laboratory of the Canadian Grain Commission (Winnipeg, Manitoba, Canada). Randall previously served as Joint Editor-in-Chief of the *American Oil Chemists’ Society (AOCS) Lipid Library*, Associate Editor for *Lipids* and Editor for *Biocatalysis and Agricultural Biotechnology*. He has published extensively in refereed journals and books and is editor of the book *Teaching Innovations in Lipid Science* which was published in 2007 by the Taylor & Francis Group of the CRC Press and the AOCS Press. He is also one of the co-editors of the book *Industrial Oil Crops* which was published by Elsevier/AOCS in 2016. Randall is a Fellow of both the AOCS and the *International Society of Biocatalysis and Agricultural Biotechnology*.



Stacy D. Singer is a lead scientist with Agriculture and Agri-Food Canada at the Lethbridge Research and Development Centre (Lethbridge, Alberta, Canada) where her research focuses on the biotechnological improvement of forage crops using advanced molecular technologies. She received her bachelor’s and PhD degrees from the University of Regina, Canada. She was a postdoctoral research in plant-related research in the USDA, Cornell University, and the University of Alberta. She has published dozens of peer-reviewed research articles in such high impact journals as *Plant Physiology*; *Plant Journal*; *Plant, Cell & Environment*; and *Journal of Experimental Botany*. She has rich experience in plant molecular biology and crop improvement, and her research has contributed significantly to various areas of plant molecular biotechnology.

Chapter 1

Building a Case for Plant Bioproducts



Randall J. Weselake, Guanqun Chen, and Stacy D. Singer

Chapter Highlights

- Global carbon emissions associated with fossil fuel dependence are increasing steadily and are a major root cause of climate change.
- In order to reduce our reliance on fossil fuels, there is an imminent need to find sustainable alternatives to petrochemicals.
- Bioproducts are produced from renewable biomass and include biochemicals, bioenergy, biofuels and biomaterials.
- Increased use of bioproducts will assist in curtailing our dependence on fossil fuels and reduce greenhouse gas emissions.
- Ultimately, our goal should be for all carbon dioxide produced to be recaptured into renewable biomass, thus closing the carbon cycle.

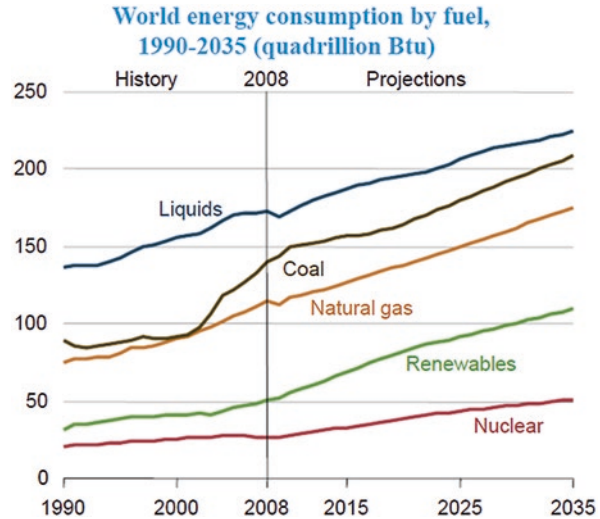
1.1 Introduction

Until about 200 years ago, humans relied almost exclusively on bioproducts to fulfil their material and energy needs (Primer on Bioproducts 2004). Since the Industrial Revolution, however, the global community has become increasingly dependent on energy derived from petroleum for heat, generation of electricity, transportation fuel and the manufacture of industrial products and consumer goods (Fig. 1.1). Indeed,

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Fig. 1.1 World energy consumption by energy source, 1990–2040 (quadrillion Btu). (From: International Energy Outlook (2017))



today's petroleum provides about 85% of the world's energy requirements. Although there is currently a glut of oil on the market, fossil fuels are still a finite resource. Experts debate on when fossil fuels will run out; however, a supply crisis is sure to eventually occur given our insatiable appetite for fossil fuel-derived energy. Furthermore, political instability and war in some oil-producing areas can also impact supply. In March 2002, a white paper prepared by the Colorado River Commission of Nevada (2002) indicated world petroleum, natural gas and coal reserves were estimated to last 98, 166 and 230 years, respectively. The recent identification of new fossil fuel deposits, along with improved extraction procedures, however, will likely increase the amount of time we have left before reserves run out (Kerr 2010, 2011).

Carbon emissions associated with fossil fuel dependence are a main driver of global **climate change** and are thus a major concern, especially given the rate at which their production has been escalating in the past few decades. These emissions contain **greenhouse gases** (GHGs), which are gases that absorb and emit radiation within the thermal infrared range and result in atmospheric warming. Indeed, escalating fossil fuel emissions have been linked to rising global temperatures, increasing sea level and reduced snow cover and glacial thickness (Intergovernment Panel on Climate Change [IPCC] 2007). As an example of this, in early August 2016, arctic conditions allowed the 280-metre-long cruise ship, *Crystal Serenity*, to travel through the Northwest Passage and stop at the hamlet of Cambridge Bay, Nunavut (Canadian Broadcasting Corporation [CBC] News 2016). Climate change has also been implicated in an increase in severe weather and flooding (Smith and Katz 2013; Estrada et al. 2015), with other well-known environmental costs including the destruction of wildlife habitat and accidental exposure to chemicals. The BP oil spill in the Gulf of Mexico, which commenced on April 20, 2010, and continued until July 15, 2010, spilling an estimated 650 million litres of oil (CBC News 2015) is one example of this. This was one of the largest oil spills in history, affecting up to 400 animal species.

Table 1.1 Greenhouse gas emissions based on type of gas from 2010

Type of gas	Global contribution (%)
Carbon dioxide from fossil fuel and industrial processes	65
Methane	16
Carbon dioxide from forestry and land use	11
Nitrous oxide	6
Fluorinated gases	2

Source: IPCC (2014)

Table 1.2 Contributions of various countries to carbon dioxide emissions from fossil fuel consumption and some industrial processes

Country	Global contribution for carbon dioxide emission (%)
China	30
USA	15
India	7
Russian Federation	5
Japan	4
Other countries	39

Source: Data of 2014, from Boden et al. (2015)

GHG emissions come in many forms having different contributions (Table 1.1). Interestingly, while water is actually the most abundant GHG, it is not as sensitive to the impact of human activities as other gases and, as such, does not have much of an effect on the environment. Conversely, carbon dioxide is the worst offender in terms of GHGs, followed by methane and nitrous oxide (IPCC 2014). Global contributors to carbon dioxide emissions stemming from fossil fuel combustion and some industrial processes are shown in Table 1.2 (Boden et al. 2015), with China and the USA being the leading contributors.

GHG emissions come from various sources (IPCC 2014; Table 1.3), with fossil fuels and industrial processes being the greatest contributors to carbon dioxide emissions. GHG emissions from agricultural activity account for about 24–26% of total global **anthropogenic emissions** (Sejian et al. 2011; Natural Environment Research Council [NERC] 2016), which refers to pollutants originating from human activity. Similarly, livestock account for about 18% of the world’s anthropogenic GHG emissions, which includes the effect of deforestation to generate grazing land along with methane gas emissions (Gill et al. 2010; NERC 2016). Since plants actively take up carbon dioxide during photosynthesis, deforestation removes critical “carbon sinks” from the environment, which causes changes in the amount of solar radiation reflected back into the atmosphere and is referred to as **albedo**.

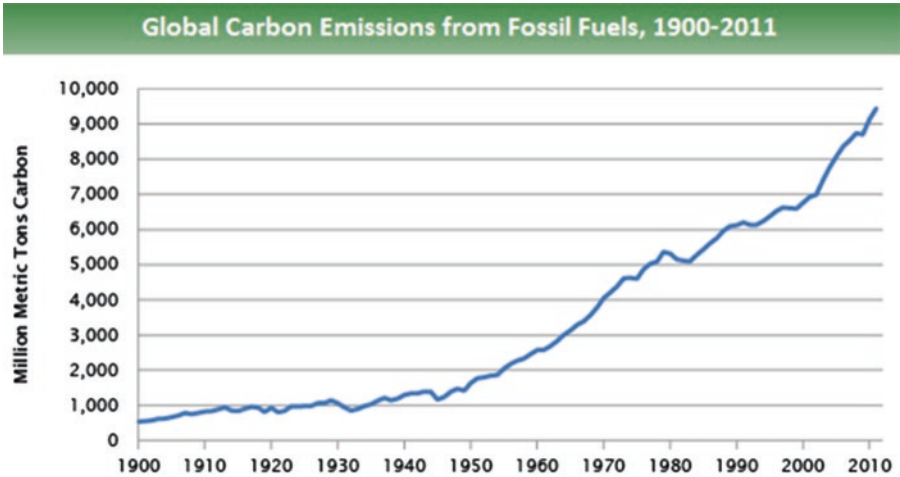
Furthermore, the “concrete jungles” of the world are dependent on enormous amounts of cement, which also contributes to GHG emissions. Cement production

Table 1.3 Global greenhouse gas (GHG) emissions by economic sector

Economic sector	Contribution to GHG emissions (%)
Electricity and heat production	25
Agriculture, forestry and other land uses	24
Industry	21
Transportation	14
Buildings	6.4
Other energy	9.6

Source: IPCC (2014)

GHG greenhouse gas

**Fig. 1.2** Carbon emissions over time. (From: Boden et al. (2015))

accounts for about 5% of anthropogenic carbon dioxide emissions (Hendricks et al. 2004; NERC 2016), with about half arising from the chemical process itself since cement is mostly made of calcium carbonate. Another 40% of carbon dioxide emissions related to cement production come from burning fuel associated with the process. Indeed, approximately 900 kg of carbon dioxide is emitted for every 1000 kg of cement produced.

Between 1950 and 2010, our global carbon emissions have increased by about sixfold (Boden et al. 2015; Fig. 1.2). If this rate of GHG emissions continues, it has been estimated that we could exceed the 2 °C global warming threshold set by the IPCC as early as 2036 (Mann 2014). Global warming above this threshold value has been predicted to have serious, and potentially irreversible, consequences to both the environment and human livelihood. In order to limit global warming to 2 °C or less between now and the year 2100, we will need to reduce our GHG emissions by 40–70% by 2050 and reach a point of zero GHG emissions by the end of the century (IPCC 2014). Given that our global demand for energy, fuel and industrial chemi-

cal is projected to grow at a very fast rate over the next few decades, it is essential that we reduce our reliance on fossil fuels and switch to cleaner and more sustainable forms of energy.

1.2 Towards Closing the Carbon Cycle

In order to reduce our reliance on fossil fuels and reduce GHG emissions, there is a need to use them more efficiently and to diversify our energy usage to include hydroelectric, hydrogen fuel cell, nuclear, wave action, wind, solar, geothermal and **biofuel**-derived power. Currently, the burning of fossil fuels results in the production of more carbon than can be offset by **biomass** (Fig. 1.3a), which can be generally defined as biological material from living or recently living organisms and most often refers to plants or plant-based materials that are not used for food or feed (<https://en.wikipedia.org/wiki/Biomass>). If our fossil fuel dependence is eliminated, however, we will then have a situation where the carbon dioxide produced from burning biomass is recaptured into renewable biomass, thus closing the carbon cycle (Fig. 1.3b).

In 2005, 192 countries signed the Kyoto Protocol, which was aimed at “stabilizing GHG concentrations in the atmosphere to a level that would prevent dangerous anthropogenic interference in the climate system” (United Nations Framework Convention on Climate Change). This document established legally binding commitments to reduce major GHGs. The USA, however, did not end up ratifying and Canada withdrew in 2011 (CBC News 2011). That being said, Canada remains a member of the Copenhagen Accord (2009), which represents a nonbinding agree-

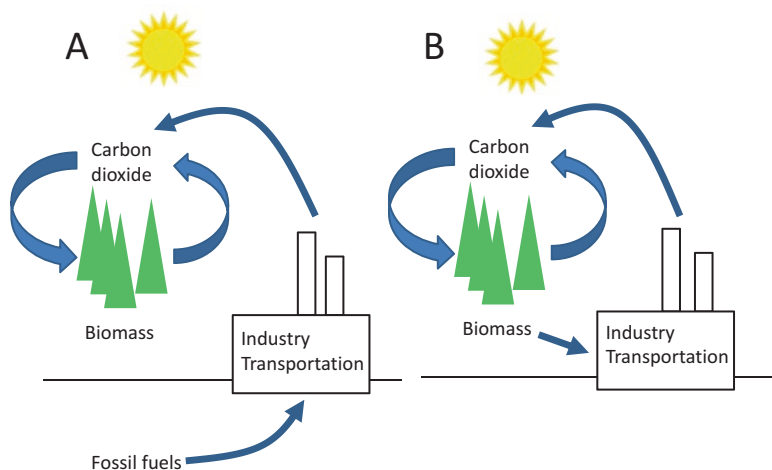


Fig. 1.3 Using biomass for energy can close the carbon cycle. (a) Burning fossil fuels results in the release of more carbon than can be utilized. (b) Using only biomass for energy closes the cycle. (Adapted from Primer on Bioproducts (2004))

ment involving a subset of Kyoto signatories. As such, Canada is still committed to reducing emission levels, but the target is more realistic, with updated commitments reflected in the Paris Agreement (World Economic Forum 2016).

There is a lot that we can do as citizens of the globe to reduce our own carbon footprint. Strategies to conserve energy include the use of energy-efficient appliances and vehicles, improved building practices, increased use of public transport and carpooling and purchasing carbon offsets. In this regard, it can be an interesting exercise to calculate one's own carbon footprint (see www.carbonfootprint.com/calculator.aspx).

There has also been recent interest in generating large-scale carbon sinks for capturing carbon dioxide from the atmosphere. For example, in the case of **carbon capture and storage**, carbon dioxide is captured, compressed into a liquid and injected into deep reservoirs for permanent storage (Haszeldine 2009; Alberta Energy 2016). Intriguingly, Mayumi et al. (2013) have shown that captured and stored carbon dioxide can lead to methane production via the action of microbial methanogens. These investigators suggested that this represented a new opportunity for the production of energy from methane derived from the stored carbon dioxide. Unfortunately, carbon capture and storage also has some potential disadvantages. This includes the fact that the separation of carbon dioxide from other gases is energy intensive and there are technical challenges associated with large-scale capture that still need to be overcome.

The potential use of microalgae to capture carbon dioxide derived from industrial processes is also under extensive investigation (Sayre 2010). Some types of microalgae produce very high levels of vegetable oil, which accounts for as much as 60% of its dry weight. Since carbon makes up about 75% of this oil, it can be extracted from the microalgae and injected into geological formations to store the carbon. Alternatively, microalgae can be converted into **biochar** by **pyrolysis** under oxygen-free conditions in the presence of catalysts (Hielmann et al. 2010). Biochar contains more than 90% carbon and can remain unaltered in the soil for millions of years.

1.3 Why Plant Bioproducts?

Another way in which we can reduce GHG emissions is through increased usage of sustainable, bio-based alternatives to petrochemicals. **Bioproducts** are industrial and consumer goods manufactured wholly or in part from renewable biomass and may be derived from crops, trees, marine plants, microorganisms and some animals (Spellman 2014). In terms of plant bioproducts, the major plant components used for their production include storage lipids, complex carbohydrates and proteins.

In the strictest sense, bioproducts have more to do with industrial applications than representing a source of human food or animal feed and may include biochemicals, bioenergy, biofuels and biomaterials. For example, many fatty acids produced by certain plants are highly valued for their use in the generation of various industrial products that are currently derived mainly from petroleum, such as lubricants and solvents. In addition, various other biochemical components of plants have also

been found to be useful in the development of a plethora of bioproducts such as natural rubber and bioplastics.

The use of bioproducts as renewable replacements for petrochemical-based materials has far-reaching benefits. This includes not only a decreased dependence on fossil fuels, along with an associated reduction in GHG emissions and enhancement in environmental safety, but also the generation of additional markets for commodities and by-products that were considered waste materials in the past for growers and food processors.

1.4 Closing Comments

Increased use of plant bioproducts, combined with the use of energy derived from hydroelectric, hydrogen fuel cell, nuclear, wave action, wind, solar and geothermal sources, can collectively contribute to decreasing our reliance on petroleum and subsequently lead to environmental benefits such as reduced GHG emissions. Interestingly, **biodiesel**, which can be produced from seed oil, is often considered to be carbon neutral because burned biodiesel ends up as carbon dioxide that plants can take up from the atmosphere and reconvert into new biomass. Unfortunately, this is not entirely true, since growing certain oilseeds, such as canola (mainly *Brassica napus*), requires the application of nitrogen fertilizer, which represents a substantial cost input in crop production (Karmakar et al. 2010). In addition, the production of nitrogen fertilizer generates nitrous oxide, which we have already identified as powerful GHG. In contrast, soybean (*Glycine max*) can be produced with little or no nitrogen, which highlights the fact that crop choice can be extremely important in terms of achieving carbon neutrality.

Although the use of plant-derived products as feedstocks for the generation of biodiesel and biofuel has garnered the majority of interest in terms of non-food applications for crops, a host of additional uses also exist. Indeed, plant bioproducts have the potential to provide a sustainable, renewable, environmentally friendly alternative to many fossil fuel-derived chemicals. Therefore, while the actual closing of the carbon cycle may be considered somewhat of a fantasy by some, it is of the utmost importance that we work towards trying to achieve it, and plant-derived bioproducts will certainly play a role in this endeavour.

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Chapter 2

Introduction to Plant Biomolecules and Cellular Metabolism



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Chapter Highlights

- Lipids, carbohydrates, and proteins represent the major starting materials for the production of various bioproducts in plants.
- These organic compounds contain carbon atoms that share electrons with hydrogen and other elements.
- Lipids comprise fatty acids and their derivatives and tend to be either hydrophobic or amphipathic in nature.
- Carbohydrates include sugars and sugar polymers and are made up of carbon, hydrogen, and oxygen atoms.
- Proteins are made up of 20 different amino acids and include enzymes, which act as biological catalysts to speed up the chemical reactions that constitute metabolism.
- Plant metabolites offer an abundance of structural diversity and thus offer enormous potential in terms of bioproduct production.

2.1 Introduction

Some knowledge of elementary chemistry and biochemistry is required to appreciate why certain components of plant biomass are used for producing specific bioproducts with desired functionality. In order to reach a broader audience of readers interested in plant bioproducts, this book only relies on a basic knowledge such as that

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provided by a junior undergraduate course in biology. This chapter begins with a brief and simplified review of how atoms can be united to form biomolecules of increasing complexity. Most of the discussion in this chapter will focus on lipids, carbohydrates, and proteins, which represent the major components of plants used as starting materials for production of various bioproducts. The goal is to develop an appreciation of the complexity and chemical diversity of plants as it relates to providing starting material for bioproducts rather than becoming overly obsessed with developing an in-depth structural understanding of these biomolecules. The chapter is mainly based on information found in introductory chemistry (e.g., Silberberg and Amateis 2015), biology (e.g., Purves et al. 2001), and biochemistry (e.g., Buchanan et al. 2015; Moran et al. 2012; Nelson and Cox 2005) textbooks.

2.2 Atoms and Molecules

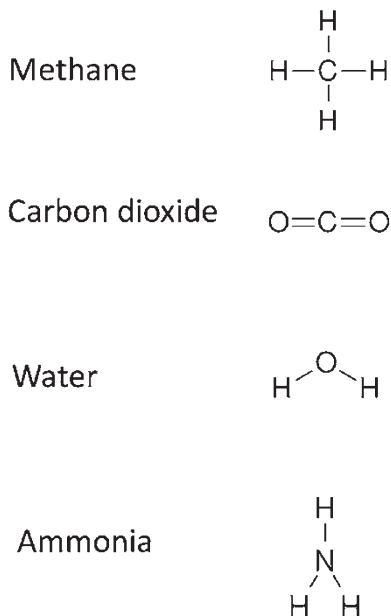
Living organisms are composed of a small number of elements which appear as part of the periodic table. The proportions of elements in plants, animals, and bacteria are depicted in Table 2.1. Oxygen (O) is the most abundant element followed by carbon (C), hydrogen (H), and nitrogen (N). Among the remaining elements, phosphorous (P) and sulfur (S) are also found in living organisms. In their simplest form, elements exist as atoms. An atom consists of a nucleus surrounded by electrons. The outer electrons of an atom tend to be unstable because they are unpaired. Stability can be achieved, however, when electrons from different atoms participate in electron sharing to form molecules. When electrons are shared between two atoms, this is often referred to as a **covalent bond**. Four examples of two-dimensional representations of abundant simple molecules are shown in Fig. 2.1. An **organic molecule** (or compound) contains carbon atoms which share electrons (or form covalent bonds) with hydrogen and possibly other elements. Methane, which is an example of a greenhouse gas, is categorized as an organic molecule. The chemical formula for methane is CH_4 . In essence, carbon “shakes hands” four times to form methane. Carbon can also share electrons with oxygen to form carbon dioxide (CO_2), and oxygen can share electrons with two hydrogen atoms to form water (H_2O) (Fig. 2.1). Ammonia (NH_3), which is the result of nitrogen sharing electrons with three

Table 2.1 Proportions of elements found in plants, animals, and bacteria

Element	Composition by weight (%)
Oxygen (O)	65
Carbon (C)	18
Hydrogen (H)	10
Nitrogen (N)	3
Other elements	4

Other elements include phosphorous (P) and sulfur (S)

Fig. 2.1 Four examples of two-dimensional representations of simple molecules



hydrogen atoms, is also shown in Fig. 2.1. Unlike methane, carbon dioxide, water, and ammonia are not organic molecules because none of these represent a situation where carbon shares electrons with hydrogen.

2.3 Lipids

Lipids are described as “fatty acids and their derivatives, and substances related biosynthetically or functionally to these compounds” (<http://lipidlibrary.aocs.org/>). Many lipids tend to have **hydrophobic** attributes which are “water-fearing.” Hydrophobic groups can associate in a watery environment through hydrophobic interactions. Just imagine two droplets of oil coalescing in a glass of water. The increased disorderliness of water as a result of lipid droplets coming together can be thought of as the driving force for hydrophobic interactions. Other lipids have both hydrophobic and polar (“water-loving”) components as part of the same molecule and can be thought of as “schizophrenic” molecules. These types of lipids are often referred to as **amphipathic** molecules. Lipids can serve as an energy store, are critical component of membranes, and can have biological activity within cellular signaling pathways. Compared to other organic molecules, lipids are the most highly reduced yielding a maximum amount of energy when burned (Durrett et al. 2008).

Palmitic acid is an example of a fatty acid. Two different ways of depicting palmitic acid are shown in Fig. 2.2. From Fig. 2.2a, it can be seen that all the bonding requirements are fulfilled (i.e., carbon forms four covalent bonds, hydrogen forms

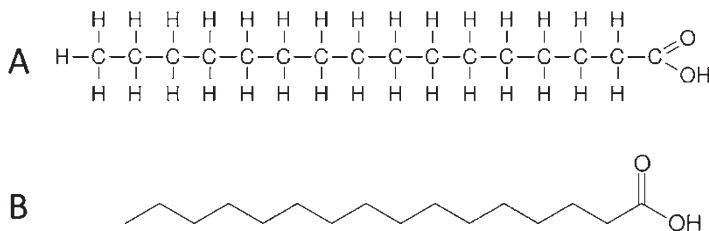


Fig. 2.2 Two representations of palmitic acid (16:0) which is a saturated fatty acid. (a) All atoms are shown; (b) a more concise representation

one covalent bond, and oxygen forms two covalent bonds). The CH_3 - end of palmitic acid is known as the methyl end, whereas the opposite end, containing oxygen, is known as the carboxyl end. The jagged line in Fig. 2.2b implies the tetrahedral nature of the carbon center, and all the H atoms are assumed to be in place. In a watery environment, the carboxyl group can ionize to release a proton (H^+) and become $-\text{COO}^-$. This is an attribute of a weak acid, which explains the term fatty acid. Palmitic acid is known as a **saturated fatty acid** because all of the carbons, other than the carbon in the carboxyl group, are saturated with hydrogens. Palmitic acid can be described in shorthand form as 16:0 where “16” means 16 carbon atoms and “:0” refers to the absence of unsaturation or a double bond in the interior of the fatty acid chain.

In contrast, oleic acid has a double bond at the ninth carbon from the carboxyl group (Fig. 2.3). This bond results in a “kink” in the hydrocarbon chain. This introduced bend in the hydrocarbon chain results a compound that has a much lower melting point than palmitic acid or stearic acid (18:0), which is a commonly occurring saturated fatty acid which is two carbons longer than palmitic acid. Oleic acid is an example of a **monounsaturated fatty acid** because it has one point of unsaturation in the fatty acid chain outside of the carboxyl group. In shorthand form, oleic acid can be described as 18:1 Δ^9 *cis* where “18” means 18 carbon atoms with “:1” meaning one point of unsaturation in the interior of the fatty acid chain. “ Δ^9 ” indicates that the double bond occurs at position number 9 from the Δ (delta) end of the fatty acid chain, which is the carboxyl end. “*cis*” refers to the configuration of the two hydrogens participating in the double bond. In the *cis* configuration, both hydrogens are on the same side of the double bond as shown in Fig. 2.3. In the *trans* configuration, the hydrogens would be located diagonally from each other around the double bond. Another shorthand form, which tends to be used more by nutritionists, uses the ω (omega) end of the fatty acid chain as a reference point. The ω end is the methyl end of the fatty acid chain. Thus, oleic acid can also be described as 18:1 ω 9 or 18:1*n*-9. This type of nomenclature is useful in understanding metabolic relationships involving different fatty acids.

Linoleic acid is an example of a **polyunsaturated fatty acid** because it has more than one double bond, or point of unsaturation, in the interior of the fatty acid chain (Fig. 2.3). In shorthand form, linoleic acid can be described as

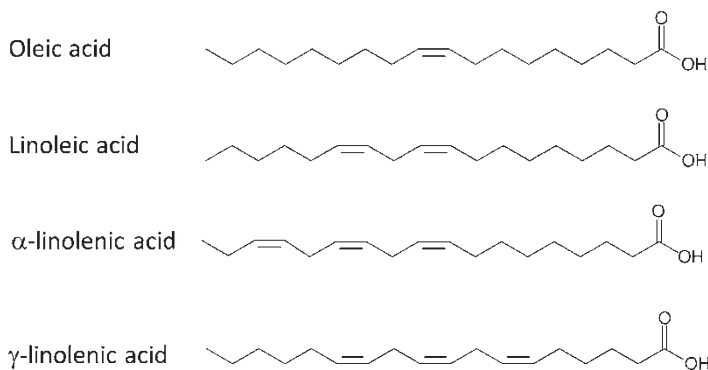


Fig. 2.3 Four examples of unsaturated fatty acids

18:2 $\Delta^{9cis,12cis}$ or 18:2 $n-6$ (18:2 $\omega 6$). Note that the omega system only tells you about the bond closest to the methyl end of the fatty acid chain. α -Linolenic acid is an example of a polyunsaturated fatty acid with three double bonds in the interior of the fatty acid chain (Fig. 2.3). In shorthand form, α -linolenic acid can be described as 18:3 $\Delta^{9cis,12cis,15cis}$ or 18:3 $n-3$ (18:3 $\omega 3$). γ -Linolenic acid (Fig. 2.3) is another “isomer” of linolenic acid (18:3) which can be described in shorthand form as 18:3 $\Delta^{6cis,9cis,12cis}$ or 18:3 $n-6$ (18:3 $\omega 6$).

Fatty acids are typically found as components of more complex lipids such as **triacylglycerol** and **phospholipid** (Fig. 2.4). In triacylglycerol, fatty acids are “esterified” to a three-carbon glycerol backbone. The result is a very hydrophobic molecule since esterification greatly diminishes the polar character of the carboxyl groups. Triacylglycerol is the major component found in plant seed oils and is the main lipid feedstock for producing biodiesel and other bioproducts. A **feedstock** is a starting material for the production of industrial products. Triacylglycerol occurs in micro droplets, known as oil bodies, in the cytoplasm of the oil-forming cells of developing seeds.

Phospholipids, such as phosphatidylcholine (Fig. 2.4), are involved in the formation of cellular membranes which usually consist of two layers of phospholipid molecules (Fig. 2.5).

Phosphatidylcholine is an amphipathic molecule with two fatty acid chains comprising the hydrophobic component and phosphocholine comprising a water-loving polar head group. The fatty acyl chains interact through hydrophobic interactions in the interior of the membrane, while the phosphocholine head group faces a watery environment. The polar head group of a phospholipid can participate in **hydrogen bonding** and ion-dipole interactions with water. In a hydrogen bond, a hydrogen atom with a partial positive charge is shared between two atoms which have tendency to attract a bonding pair of electrons (referred to as electronegative). In a water molecule, the electrons tend to spend more time around the oxygen atom than the hydrogen atoms. This results in a distribution of charge, known as **dipole**, such that one end of a water molecule is positive and the other end is negative.

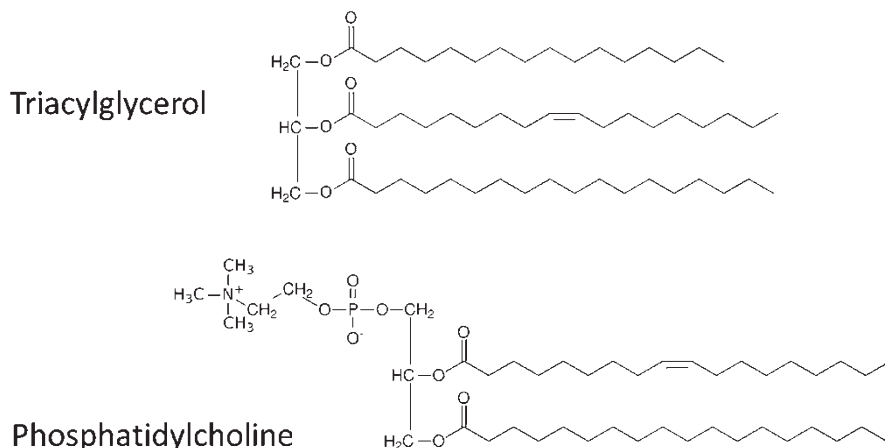


Fig. 2.4 Structures of triacylglycerol and phosphatidylcholine. In the triacylglycerol molecule shown, the glycerol backbone is esterified, from top to bottom, with palmitic acid, oleic acid, and stearic acid, respectively. The phosphatidylcholine molecule is esterified with oleic acid and stearic acid at the middle and bottom position of the glycerol backbone, respectively

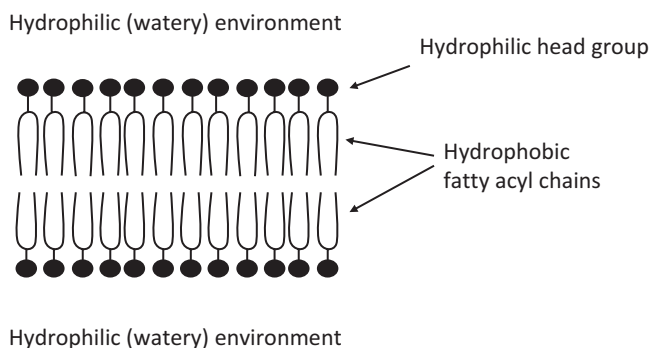


Fig. 2.5 Cross section of a segment of a lipid bilayer. Hydrophobic interactions occur between the fatty acyl chains in the inner region of the bilayer. The polar head groups of phospholipid can participate in hydrogen bonding and ion-dipole interactions with water

Therefore, the positive charge on the choline group can interact with the negative end of a water molecule.

A simplification of a plant cell is shown in Fig. 2.6. Plant cells have a **plasma membrane**, below a **cell wall**, which defines the outer boundary of the cell. In contrast, animal cells do not contain a cell wall. A plant cell contains a nucleus along with various subcellular organelles, which include **mitochondria**, **plastids**, **vacuoles**, and **peroxisomes**. All of these organelles have membranes. In addition, the plant cell contains an extensive network of membrane known as the endoplasmic reticulum. The nucleus houses the genetic material of the cell, which contains the

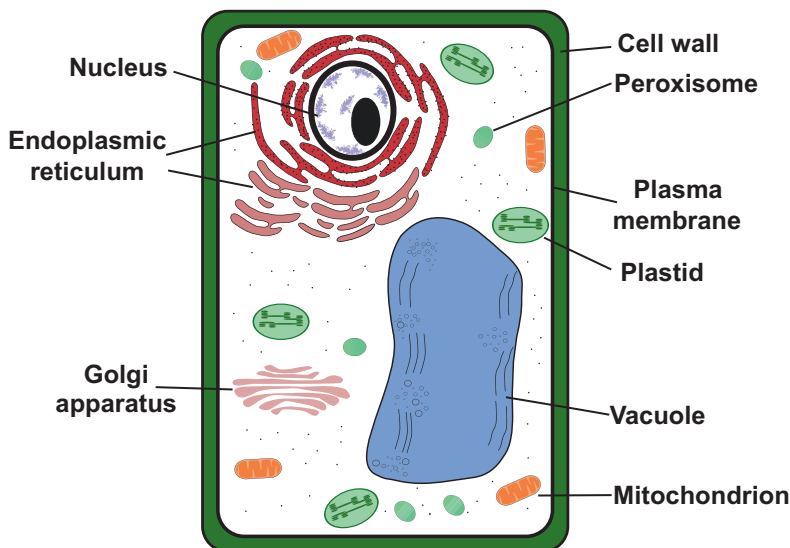


Fig. 2.6 Schematic representation of a plant cell. (Adapted from Alberts et al. 1994)

“blueprint” for the formation of components of the cell and its operation. Mitochondria are known as the “power houses” of the cell because of respiration and the formation of adenosine triphosphate (ATP), the universal energy currency. Fatty acid formation occurs in plastids. The plastids of leaves are known as **chloroplasts** because they contain chlorophyll and are involved in photosynthesis. Fatty acid degradation occurs in both mitochondria and peroxisomes. Vacuoles are multi-functional organelles. In seeds, vacuoles serve as storage sites for reserve proteins and soluble carbohydrates. These various subcellular structures characterize what are known as **eukaryotic cells**. These subcellular organelles are absent in **prokaryotic cells** such as bacteria. In a eukaryotic cell, the content of the cell, minus the nucleus, is known as the **cytoplasm**, whereas the soluble component of the cytoplasm (without subcellular organelles and internal membranes) is known as the **cytosol**.

Bioproducts produced from lipids are dealt with in Chaps. 4 and 5.

2.4 Carbohydrates

Carbohydrates can be thought of as sugars and sugar polymers. Carbohydrates consist of carbon, oxygen, and hydrogen and have the general formula $(\text{CH}_2\text{O})_n$. Most carbohydrates have cyclic monomers as fundamental structural components. Complex carbohydrates have roles in energy storage and cellular structure, such as contribution to the rigidity of the cell wall. Carbohydrates also serve as a source of