1.1 Introduction

Phytochemicals, as the word implies, are the individual chemicals from which plants are made. In this chapter, we will look at these materials, specifically, the organic components of higher plants. Numerous journals, individual books, and encyclopedic series of books have been written on this subject. The goal here is to review this area in a concise format that is easily understandable. The reader not familiar with chemistry may be somewhat intimidated by the material presented here. However, we believe that understanding the chemical composition of plants is a prerequisite to understanding many of the remaining topics of this book. This is especially true for material covered in Chapters 2 and 3. For those interested in reviewing a specific area in greater detail, the references section includes numerous citations for each organic group covered.

During the course of this survey, several themes will be emphasized. These include (1) the rich diversity of chemical structures known to be synthesized by plants through an amazingly diverse network of metabolic pathways (see Figure 2.1 in Chapter 2); (2) basic differences in the chemical properties of the compounds; (3) adaptive functions of these compounds for plants; (4) uses of the compounds by humans (see essays below); and (5) examples of typical plants (listed by common name and scientific binomial name) that contain the respective types of compounds. Often, these will be derived from common plants with which most of us are familiar. Some marine algal plants are also included, because they contain many truly unique bioactive molecules.

The general categories of plant natural products are organized very broadly in terms of increasing **oxidation state**. This begins with the lipids, including the simple and functionalized hydrocarbons, as well as the terpenes, which are treated separately. Following this are the unsaturated natural products, including the polyacetylene and aromatic compounds. We then cross over into the realm of the primarily hydrophilic molecules, including the sugars, and continue with those that can form salts, including the alkaloids, the amino acids, and the nucleosides. Overall, this scheme provides a simple organizational pattern for discussing the phytochemicals. It is consistent with the way that chemists often categorize organic chemicals in general and is roughly equivalent to a **normal-phase chromatographic analysis** of a given plant species. Like any organizational scheme for this subject, be it taxonomic, phylogenetic, or biochemical, it should only serve as a rough guide.

Essay on Phytochemicals of Medicinal Value in Plants

In common usage today, many phytochemicals are associated with health benefits. They have a long history, which continues today, as medicines (Rouhi, 2003b). Many, though not all, of these materials are classified as **secondary metabolites**. This terminology suggests, often incorrectly, that they are not essential for the normal growth, development, or reproduction of the plant. Numerous journals, individual books (Robinson, 1991; Bruneton, 1999; Duke, 1992), dictionaries (Buckingham, 2005), and databases (Duke, 2005) were dedicated to plant natural products. Journals in natural products chemistry recognized by the **American Society of Pharmacognosy** include *Chemistry of Natural Compounds* (Russian), *Economic Botany*, *Fitoterapia*, *Journal of Antibiotics*, *Journal of Asian Natural Products Research*, *Journal of Essential Oil Research*, *Journal of Ethnopharmacology*, *Journal of Natural Products*, *Journal of Natural Remedies*, *Natural Products Letters*, *Natural Products Reports*, *Natural Toxins*, *Nigerian Journal of Natural Products and Medicines*, *Pharmaceutical Biology* (note name change from *International Journal of Pharmacognosy*), *Phytochemical Analysis*, *Phytochemistry*, *Phytochemistry Reviews*, *Phytomedicine*, *Phytotherapy*

Research, *Planta Medica*, *Toxicon*, and *Zeitschrift für Naturforschung*. Professional societies dedicated to research on phytochemistry include the American Society of Pharmacognosy (www.phcog.org), the Phytochemical Society of Europe (www.dmu.ac.uk/ln/pse/psetoday.htm), AFERP (Association Francaise pour l'Enseignement et al Recerche en Pharmacognosie; www.aferp.univ-rennes1.fr/aferpnouveau/index.htm), the Phytochemical Society of North America (www.ucalgary.ca/~dabird/psna), and the Society of Medicinal Plant Research (www.ga-online.org), among others.

Essay on Natural Products and Commercial Medicines (Rouhi, 2003a)

Natural products have, until recently, been the primary source of commercial medicines and drug leads. A recent survey revealed that 61% of the 877 drugs introduced worldwide can be traced to or were inspired by natural products. However, beginning in the 1990s, natural product drug discovery was virtually eliminated in most big pharmaceutical companies. This was primarily due to the promise of the then-emerging field of combinatorial chemistry (Cseke et al., 2004), whereby huge libraries of man-made small molecules could be rapidly synthesized and evaluated as drug candidates.

Thus far, this approach has led to lukewarm results at best. From 1981 to 2002, no combinatorial compounds became approved drugs, although several are currently in late-stage clinical trials. At the same time, the number of new drugs entering the market has dropped by half, a figure of which the large pharmaceutical corporations are painfully aware. The haystack is larger, but the needle within it is more elusive. This has led only recently to a newfound respect for the privileged structures inherent within natural products (DeSimone et al., 2004).

Of the roughly 350,000 species of plants believed to exist, one-third of those have yet to be discovered. Of the quarter million that have been reported, only a fraction of them have been chemically investigated. Many countries have become aware of the value of the biodiversity within their borders and have developed systems for exploration as well as preservation. At the same time, habitat loss is the greatest immediate threat to biodiversity (Frankel et al., 1995; see also Chapter 14).

1.2 Lipids and Derivatives

Lipids are often defined as water-insoluble biomolecules that are soluble in nonpolar solvents (Bruice, 2004). This is a convenient definition because it encompasses a large area of chemical space, including many types of compounds that are otherwise hard to classify. There are two problems with this definition. First, given a large enough hydrocarbon (**hydrophobic**) component, most organic compounds could fall within this scope. Second, many of the classical lipids (for example, the fatty acids) have significant solubility in water.

A more constricted definition of lipids is to simply classify them as fatty acids and their derivatives, and to treat other hydrocarbon-based natural products separately. **Fatty acids** are carboxylic acids that contain a long, hydrocarbon chain. The derivatives of fatty acids may be acyglycerol esters, wax esters, or alcohols such as sterols. Additional acid derivatives include phosphates (glycerophospholipids) or carbohydrates (glycoglycerolipids).

1.2.1 Hydrocarbons

Comprising a relatively small group of compounds, the least polar organic natural products are the **hydrocarbons** (see plant examples illustrated in Figure 1.1). Hydrocarbons are simply molecules that contain only hydrogen and carbon atoms. The aliphatic hydrocarbons are straight chain hydrocarbons,