ORGANIC CHEMISTRY
Miracles from Plants

JEFFREY J. DEAKIN

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Organic Chemistry

Human benefit from the organic chemistry of plants is incalculable in terms of health, food, comfort and security. Indeed, the future well-being of humanity rests in significant measure upon a responsible relationship with the plant kingdom in order to re-establish balance in the Earth's natural environmental systems.

In a highly readable volume, *Organic Chemistry: Miracles from Plants* presents many fascinating points of entry to the organic chemistry of a wide range of crucially-important, naturally-occurring, chemical substances which are derived from plants.

Features:

1. Presents in a readable and accessible manner many fascinating points of entry to the organic chemistry of a wide range of crucially-important, naturally-occurring, chemical substances which are derived from plants.
2. Key concepts in and knowledge of organic chemistry are reinforced.
3. Highly-relevant and contemporary context stimulates learning in organic chemistry.
4. Searching exercises and extension materials are provided at the end of every chapter each of which is amply illustrated.
5. In a single source, this volume provides knowledge, challenge and valuable learning opportunity in chemistry, medicine, nutrition and the environmental sciences.

Organic Chemistry

Miracles from Plants

By

Jeffrey J. Deakin

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Preface

This book concerns the study of organic chemistry in the context of diverse substances from plants that are of huge significance in the contemporary world.

Organic Chemistry: Miracles from Plants provides ample extension material to enrich knowledge, deepen understanding, strengthen appreciation of organic chemistry and provide inspiration for further study. The chemical compounds from plants that are described are associated with important drugs, foods, beverages, perfumes, cosmetics, pigments, materials and contemporary issues facing society.

This book will be of particular value to students who are in the upper age groups of high school or at early university level. Reinforcement of the relevance and importance of organic chemistry in the modern world offers powerful stimulus to motivate students and will enhance learning.

When used in the broader sphere of general studies classes, extracts selected by tutors from a wealth of cross-curriculum material may stimulate informed debate about the relationship between scientific development and commercial exploitation of the products of plant biochemistry fostering exploration of related business, ethical and social issues.

Furthermore, the material is also intended to excite the interest of scientifically literate people who wish to broaden their horizons on the basis of personal or professional motivation.

Author Biography

Dr Jeffrey J. Deakin earned a BSc degree in chemistry with first class honors from the University of London followed by a PhD degree in physical chemistry from the University of Cambridge.

As a teacher of science, Jeff headed chemistry and physics departments in grammar and comprehensive schools in the UK. He has written books and numerous articles aimed at demystifying chemistry and broadening interest in the subject.

Jeff is a Fellow of The Royal Society of Chemistry in London. He was a member of the Curriculum and Assessment Working Group at the Royal Society of Chemistry, which recently reviewed the national curriculum in chemistry in each of the four home nations of the United Kingdom of Great Britain and Northern Ireland.

Part I

Introduction

ORGANIC CHEMISTRY

In 1807, the Swedish chemist, Berzelius, considered organic compounds to be chemical substances derived from living organisms and inorganic compounds to be those obtained from inanimate matter. It was believed that organic compounds could only be produced through a' vital force' inherent in living cells and therefore could not be synthesized artificially.

However, in 1828, Woehler, a German chemist, showed that heating a compound hitherto regarded as inorganic, ammonium cyanate, produced a compound hitherto regarded as organic, urea:

$$NH_4NCO = CO(NH_2)_2$$

The 'vital force' theory was undermined and was finally disproved by Kolbe shortly thereafter who made acetic acid (ethanoic acid) directly from its constituent elements: carbon, hydrogen and oxygen.

Organic compounds are now defined as carbon compounds without reference to their source or to how they were produced.

Organic chemistry is essentially the study of the chemistry of life—illustrated in this book by products of and extracts from plants that are of significance to man.

Although metallic elements considerably outnumber non-metallic elements in the Periodic Table (Figure 1.1), the versatility of carbon ensures, through its ability to bond repeatedly to itself, that organic chemistry dominates the field of chemistry.

Organic chemistry is extensive because a carbon atom, having a valency of four, may be bound covalently to another carbon atom through a single bond, a double bond or a triple bond. Significantly, carbon atoms can bond together to form different structures, such as chains and rings. Carbon can also combine covalently with other elements, typically hydrogen, oxygen, nitrogen, sulfur and phosphorus. As a result, infinite combinations and permutations are possible, which lead to an apparently bewildering array of naturally produced organic molecules: some simple and others complex although all of them are fascinating.

It is important reassure the reader at this point that he/she does not need to acquire detailed knowledge of every single organic compound for they can be divided into various classes, each containing a characteristic group of atoms that have particular chemical properties.

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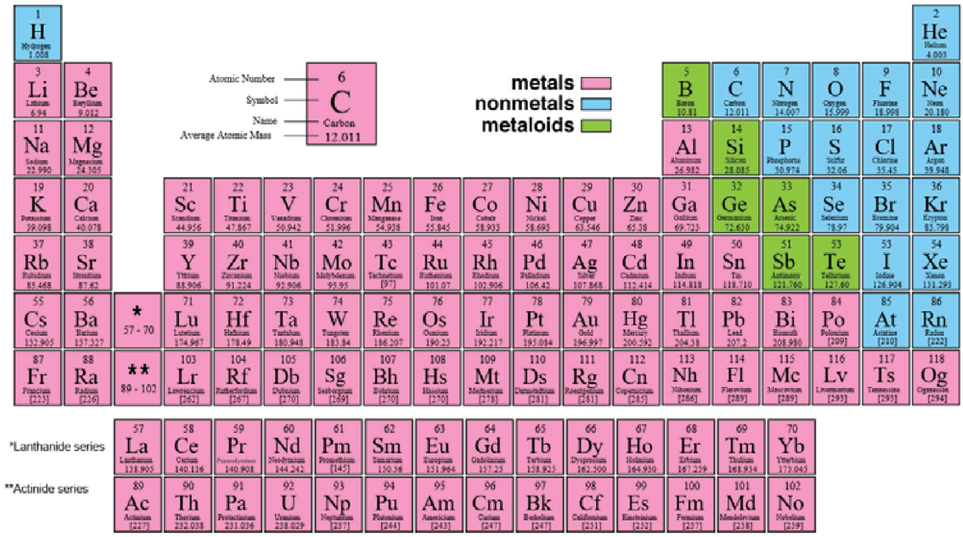

FIGURE 1.1 Periodic table of elements, metals and non-metals.

Source: https://commons.wikimedia.org/wiki/File:Periodic_Table_Of_Elements.svg

The naturally produced chemical substances illustrated are described in relation to the basis of the organic chemistry curricula for high school and early university courses in the United States of America and for sixth form and early university courses in the United Kingdom. The aims are to inspire, to inform and to extend the understanding of students while helping them to gain an appreciation of the organic chemistry involved.

Although the scope of the book is comprehensive, it has not been the intention to cover the curriculum systematically as an instructional textbook might do. Nonetheless, study of an extensive range of concepts and functional groups is interwoven in the text:

- covalent bonding
- alkanes, linear and branched
- halo alkanes
- cycloalkanes
- compounds containing the carbonyl group
- alcohols
- esters
- nitriles
- alkenes
- alkynes
- aromatic chemistry (arenes)
- amines and amides
- amino acids (including the peptide link and proteins)
- phenols
- heterocyclic compounds
- polymers
- isomerism
- optical isomerism
- chirality.

The chemistry of functional groups is drawn upon extensively to show how they influence the chemical behavior of the building blocks that make up large and complex molecules. A building block is a term used in organic chemistry to describe a part of the structure of a large molecule that has one or more active functional groups. Examples of building blocks from later in the book are isoprene, phenol, amino acids and sugars.

Different building blocks may be assembled, through reactions involving the functional groups, to form much bigger or more complex molecules. Organic chemists then divide compounds with large molecular structures into categories that have a common chemical background. Examples of these categories are carbohydrates, terpenoids, steroids, proteins, polyphenols, saponins, lipids (fats and waxes), carotenoids, sugars (polysaccharides) and fibers. These categories are examined.

The roles of isomers and polymers are fully explained since stereo-chemistry subtly and profoundly influences the interactions of large, complex molecules found in nature and hence their physical and chemical properties.

There is an introduction to techniques that are used to investigate the structure of large molecules and to the application of chromatography in purification and analysis.

For the instructor, the text supplements the core curriculum and offers inspiration and materials to inform and support project work by students working individually or in groups. Teachers and tutors may lead by choosing materials that will extend and illuminate the curriculum tailored both to the specific requirements of the syllabus and to the level and interest of their students.

CONTEXT: MIRACULOUS CHEMICALS FROM PLANTS

Plants have changed the world influencing civilizations, trade and conquest.

Important examples of the discovery of valuable medicinal plants are presented in **Part II** that were of inestimable benefit to mankind. It might be said that many people in the world only know of indigenous medicines based upon ancient tradition, yet we in the West are recipients of these wonderful gifts without perhaps ever appreciating their origins.

Chemical analysis of plant extracts has led to the identification of many natural products of considerable value in modern foods and beverages. These are described in **Part III** and in **Part IV.** A powerful example was the use of lime fruits by the British navy, which overcame scurvy even though it took another 200 years to discover the reason was the presence of vitamin C in the citrus plant.

In the 19th century, chemical compounds were identified as poisons or capable of affecting mood. Some of these are described in detail in **Parts V** and **VI**. Two powerful chemicals, morphine and strychnine, were isolated from different plants in 1815 and 1819, respectively, although their actual chemical structures were not defined for another 100 years! Numerous examples of pharmaceutical and over-the-counter drugs were derived directly from compounds found in nature or indirectly through chemical modification of the basic chemical structure.

We appreciate the beauty of color in the natural environment which inevitably influences art and science through the exploitation of natural pigments. Therefore, **Part VII** highlights the colorful chemistry of natural products. Have you ever wondered what makes the world of plants so colorful? Why are the leaves green and then turn to wonderful hues of yellow and red in the autumn? The explanation is due to the presence of natural pigments in the plants. Indeed, historically, many pigments from plants were used as dyes and these were revered also for possessing 'magical properties' with the power to heal and to keep evil spirits at bay. Mystery and superstition surrounded the extraction of the essence. An example of this is provided in the use of *Woad*. This is a plant*, Isatis tinctoria*, which yields the purple-blue color, indigo, scarce in the natural world. The desire and need for different colored dyes stimulated much research by chemists in the 19th century that contributed to transformation of society from its historic agrarian foundation to the modern industrial era.

In **Part VIII**, the vital importance of all the plants of the natural world is reinforced. Directly and indirectly, humankind and other members of the Animal Kingdom are wholly dependent upon plants. The Plant Kingdom is dominated by green plants converting carbon dioxide and water into a vast and diverse array of organic compounds, not only providing vital resources in food but also for clothing and shelter and releasing indispensable oxygen into the atmosphere for respiration.

Attention is drawn to plants as providers of a wide variety of materials, instances being paper products, fabrics used in clothing and those of high strength offering tools and shelter.

In the concluding **Part IX**, we consider the inestimable value and highly significant influence of plants upon the well-being of the natural chemical cycles and inter-dependent systems of planet Earth.

REFERENCES

Selected reading material is included for those wishing to delve further into the background. Primary references are cited which support key points.

Nomenclature

Many natural chemical products are given trivial names and these are used throughout. However, where appropriate, the IUPAC system is adopted to describe chemical formulae.

Botanical names

Every plant belongs to a botanical family, which is further classified into its genus and its species. The taxonomy of the plant is given a Latin name expressing both the genus and species and is italicized.

Scope of chemistry

For ease of reference, the scope of the organic chemistry presented in this book has been tabulated at the beginning of each section and chapter.

Part II

Medical Marvels

INTRODUCTION

Medicines derived from plants are widely used in traditional cultures all over the world. People who use traditional remedies may not understand the scientific rationale for why they work but know from personal experience that some plants can be highly effective.

Traditional medicine often aims to restore balance to the body. Western allopathic medicine, in contrast, often uses a well-defined, single chemical entity with specific medicinal properties. Nevertheless, many of our so-called modern day drugs have origins in ancient medicine.

The vast array of medicinal plants available from all parts of the world has stimulated much scientific and clinical interest which, in some instances, has provided significant commercial returns and modern medications of inestimable value to humankind.

A summary of the chemistry in Part II follows.

Chapter	Organic Chemistry	Context
Humble potato	Alkanes, cycloalkanes	Steroids
	Benzene and aromaticity	Hormones
	Industrial fractional distillation	
Willow Bark	Carboxylic acids	Salicylic acid and aspirin
	Phenol	
	Acetylation	
	Substituted aromatic compounds	
Cinchona and Artemisia	Carbon–oxygen bonds	Quinine
	Oxygen–oxygen bonds	Artemisinin
	Peroxides	
Foxglove	Alcohols, Acids, Esters	Glycoside lactones (cyclic esters)
Periwinkle	Functional groups	Alkaloids
	Fractional distillation	Indole alkaloids
	Acid—Base extraction	Vincristine and vinblastine

(*Continued*)

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(Continued)

Chapter	Organic Chemistry	Context
Pacific Yew	Isomers	Terpenes
	Elimination reactions	
	Stereo-chemistry	
	Chirality	
	NMR spectroscopy	
Vaccines	Alkenes	Saponins
Adjuvants	Carbohydrates	Chilean Soapbark Tree
	Proteins	RNA and DNA
	Glycosides	
	Isomers	

CENTRAL AMERICA'S HUMBLE POTATO!

Abstract: *How a humble potato led to the genesis of the birth control pill. Few chemical extracts have had a greater impact on modern society. The potato is indigenous to Central America and was originally used as a staple food. The tuber of the potato contains chemical compounds that led to the transformation of the world through the development of the modern birth control pill, bringing about the profound social, cultural and economic impacts of oral contraception.*

Organic Chemistry

- *hydrocarbons*
- *alkanes and cycloalkanes*
- *benzene and aromatic compounds*

Context

- *steroids*
- *hormones, estrogen and progestogen.*
- *the profound social, cultural and economic impacts of oral contraception.*

Steroids

A steroid contains a characteristic arrangement of four cycloalkane rings that are joined to each other. The main way in which steroids vary from one another is through the functional groups attached to the four-ring core (**Figure 2.1).**

Hundreds of distinct steroids are found in plants, animals and fungi. Examples of steroids include the dietary fat, cholesterol and the sex hormones, testosterone and progesterone **(Figure 2.2).**

The Search for the Modern Birth Control Pill

The modern, oral contraceptive pill, often referred to as the birth-control pill or colloquially as 'the pill', is a birth control method that involves a combination of hormones, an estrogen and a progestogen. When taken orally every day, these pills inhibit female fertility. They were first approved for contraceptive use in the United States in 1960 and have become a very popular form of birth control used by many millions of women worldwide.

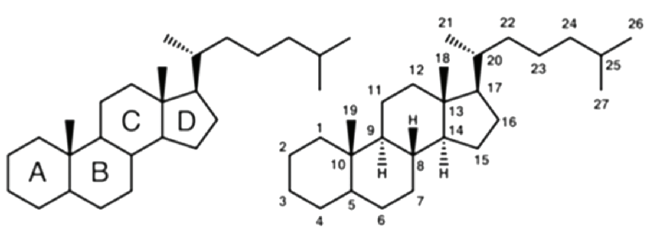

FIGURE 2.1 The carbon skeleton and ring structure of steroids together with the numbering system for steroids.

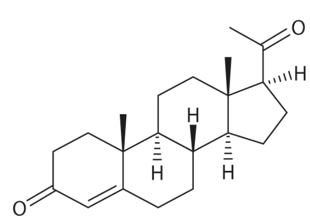

FIGURE 2.2 Chemical structure of progesterone.

The Mexican potato (*Dioscarea villosa or Dioscarea barbasco*) was a key and early commercial source of important chemical compounds known as steroid saponins. The wild potato itself has no contraceptive value. Essentially, it provides the starting material from which the steroidal hormones are manufactured by modern technology through a combination of synthetic methods and also microbial transformation. However, in the 1930s, before the discovery of the usefulness of this potato, two important discoveries were made.

Firstly, scientists isolated and determined the structure of small amounts of steroid hormones. They then found that high doses of these hormones, in the form estrogens or progesterone, inhibited mammalian ovulation. The isolation of these natural hormones was achieved by research on animal sources and carried out by the major European pharmaceutical companies. Since only small amounts were recovered they were extraordinarily expensive. However, it became immediately apparent that an urgent need for an abundant, reliable and cheap supply of steroids was needed.

Isolation of Natural Diosgenin from the Mexican Potato

In 1939, Professor Russell Marker, at Pennsylvania State University, developed a method of synthesizing progesterone from plant steroids, which are known as sapogenins.

This led to the investigation of a variety of Mexican potato, including *Dioscorea mexicana* and *barbasco*, which are found in the rain forests of Veracruz, for the tuber (root) of the potato contains the natural chemical called diosgenin **(Figure. 2.3).** This abundant compound could be used as the starting material in the synthesis of hormones on an industrial scale. Diosgenin can be easily converted chemically by opening the rings containing C21 to C27 as shown in **Figure. 2.1**. This is then followed by further degradation of the molecule to reach the structure shown in **Figure. 2.2.**

Although by midway through the 20th century the stage appeared set for the development of an oral hormonal contraceptive, pharmaceutical companies, universities and governments showed little interest in pursuing further research. At this time in 1944, having developed a synthesis of progesterone from diosgenin from the Mexican potato, Professor Marker left Pennsylvania State University to found a new company, Syntex, in Mexico City. At Syntex, Marker continued to perfect the extraction of the saponins from *Dioscorea mexicana* and then the manufacture of the key hormones. Importantly, due to this achievement, the monopoly of the European pharmaceutical companies was broken, which had until that time controlled production of steroid hormones. As a consequence, the price of progesterone fell dramatically by almost 200-fold over the next 8 years.

Chemical Magic in the Laboratory—Synthesis of Norethindrone

In 1951, the combined brilliance of three extraordinary chemists at the Syntex company in the USA (Carl Djerassi, Luis Miramontes and George Rosenkranz) led to the synthesis of the first oral progestin, namely, norethindrone (**Figure 2.4).** This synthetic hormone is a variation of natural progesterone.

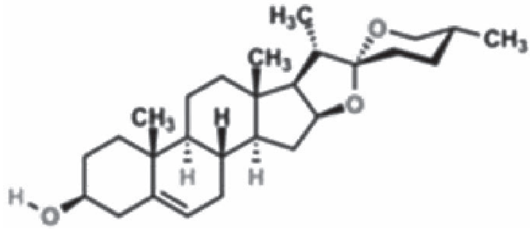

FIGURE 2.3 The chemical structure of diosgenin.

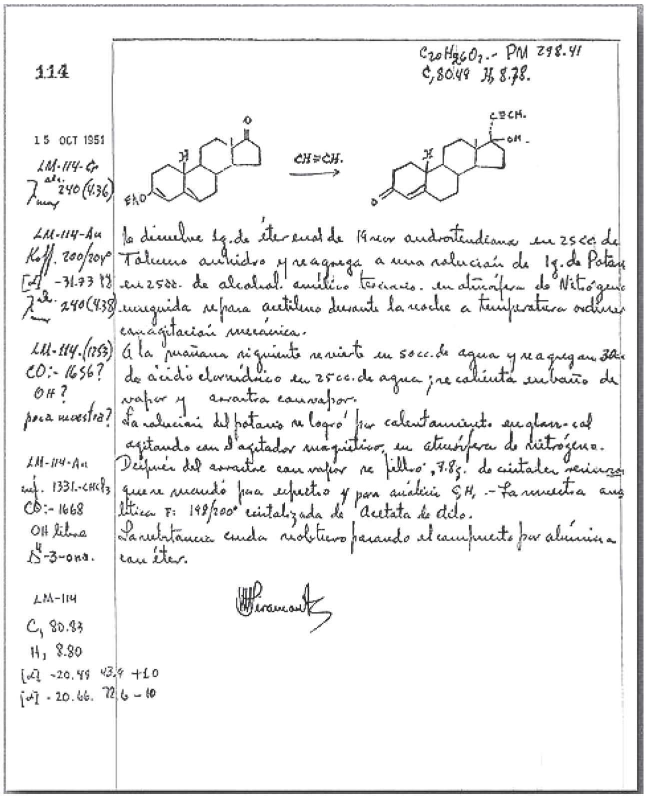

FIGURE 2.4 A copy of the original page from Luis E. Miramontes' laboratory notebook, signed October 15, 1951.

Biological Studies of Progesterone to Prevent Ovulation

Stimulated by a steady supply of research grade chemical compounds, important biological studies on the activity of progesterone in inhibiting ovulation progressed rapidly. In early 1951, the reproductive physiologist Dr. Gregory Pincus, who was at the time a leader in hormone research, met with Margaret Sanger, the founder of the American birth control movement (see historical note).

HISTORICAL NOTE: THE IMPACT OF MARGARET SANGER

The importance of Margaret Sanger, a nurse and a huge advocate of female contraception, cannot be overlooked. Her crusade to legalize birth control spurred the movement for women's liberation.

Margaret Sanger became acutely aware of the effects of unplanned and unwelcome pregnancy during her work with poor women on the Lower East Side in New York. Sanger had witnessed how her own mother's health had suffered as she bore eleven children. Sanger appreciated the importance to women's lives and health of the availability of birth control. In 1912, Sanger gave up her nursing work to dedicate herself full time to the distribution of birth control information. During World War I, Sanger set up the first birth control clinic in the United States, yet she was arrested and prosecuted many times. The resulting public outcry helped lead to changes in the law, which in turn empowered doctors to give birth control advice to their patients.

In 1927, Sanger helped to organize the first World Population Conference in Geneva.

In 1942, after several organizational mergers and name changes, The Planned Parenthood Federation (PPFA) came into being.