THE PORPHYRINS

Volume VI

Biochemistry, Part A

Edited by

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General Preface

> Man cannot give a true reason for the grass under his feet why it should be green rather than red or any other color.
>
> Sir Walter Raleigh
> *History of the World: Preface (1614)*

Just over two centuries after these words of Raleigh, Verdeil in 1844 converted chlorophyll to a red pigment which prompted him to suggest a structural relationship between chlorophyll and heme. Shortly thereafter, Hoppe-Seyler, in 1880, strengthened this hypothesis by showing the spectral resemblances between hematoporphyrin and an acid degradation product of chlorophyll. The final steps in these structural elucidations were initiated by Willstätter and culminated in the heroic work of Hans Fischer who showed that but for two hydrogen atoms grass would indeed be red and that only two more hydrogen atoms would have ensured that Raleigh and his countrymen would indeed have been blue-blooded Englishmen.

The close structural similarity between the porphyrins and chlorins gives little measure of the relationships among and the diversity of their numerous and important biochemical functions. All life on this planet relies directly on the central role of the chlorophylls and cytochromes in photosynthesis by means of which photonic energy is converted and stored as chemical energy. It is likely that long before oxygen was abundant in the Earth's atmosphere the cytochromes were responsible for respiration. With the advent of photosynthesis the oxygen produced is the terminal electron acceptor for all aerobic respiration. For many organisms the means by which oxygen is transported, stored, reduced, and activated are frequently mediated by heme proteins. In mammals, oxygen is transported by the cooperative tetrameric protein hemoglobin and stored by monomeric myoglobin. When oxygen is reduced to water, in the terminal step of respiration, four electrons are transported via a series of cytochromes to cytochrome oxidase. Cytochrome oxidase contains two iron porphyrins and two copper atoms. In addition, nature also brings about one- and two-electron reductions to superoxide and peroxide. Both the decomposition and further activation of hydrogen peroxide are mediated by the heme proteins catalase and peroxidase. Furthermore, heme proteins function as both mono- and dioxygenases, and recently cytochrome *P*-450, which functions as a monooxygenase by combining properties of both oxygen binding and electron transport, has been shown to be important in a wide variety of biological hydroxylations.

This brief insight into a few of the many central roles played by metalloporphyrins in nature plus the challenges that porphyrins present to the inorganic, organic, physical, and biological chemist suggest the wealth of knowledge that is documented in these areas. It is the objective of "The Porphyrins" to present a full and critical coverage of all the major fields relating to porphyrins, their precursors, catabolic derivatives, and related systems in a manner that we trust will be useful to those in physics, chemistry, biochemistry, and medicine.

The treatise consists of seven volumes. Volumes I and II (Structure and Synthesis, Parts A and B) cover nomenclature, history, geochemistry, synthesis, purification, and structural determination of porphyrins, metalloporphyrins, and mono- and polypyrrolic compounds and related systems. Volumes III, IV, and V (Physical Chemistry, Parts A, B, and C) cover electronic structure and spectroscopy including uv-vis, ORD, CD, MCD, mass, ir, resonance Raman, Mössbauer, Zeeman, nmr (diamagnetic, paramagnetic), esr, and X-ray crystallography. In addition, redox chemistry, electron transfer, aggregation, oxygenation, and solid state phenomena are included. Volumes VI and VII (Biochemistry, Parts A and B) cover the biosynthesis and enzymatic synthesis of porphyrins, chlorophylls and their precursors, and the chemistry and biochemistry of the bile pigments and the roles of porphyrins and bile pigments in clinical chemistry. The structure and function of the major hemoproteins are also covered.

It remains for me to thank my colleagues and co-workers for their support and assistance. A special debt of gratitude goes to my mentors: Alan Johnson who introduced me to these areas and who taught me why chlorophyll is green, and Bob Woodward who showed the world how to make chlorophyll and taught me why.

DAVID DOLPHIN

Preface

Volume VI (Biochemistry, Part A) contains chapters on the biosynthesis of prophyrins and chlorophylls. The formation and metabolism of bile pigments in animals and plants as well as the synthesis, characterization, and chemistry of the bile pigments and their derivatives are covered. In addition, the historical and clinical aspects of porphyrins and bile pigments are included.

This volume complements Volume VII (Biochemistry, Part B) which contains chapters on the structure and functions of the major heme proteins as well as on their reconstitution and metal substitution.

I wish to take this opportunity to thank the contributors to this volume. For those who completed their chapters on time, I give my thanks for their patience during the period between submission of their manuscript and the publication of this book. Of those who were not so prompt, I ask that they understand my impatience.

DAVID DOLPHIN

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