

THE ALKALOIDS

Chemistry and Physiology

Edited by

R. H. F. MANSKE

R. G. A. RODRIGO

VOLUME XVII

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PREFACE

The first volume of "The Alkaloids" appeared in 1950 and since then sixteen volumes of this series of reviews have been favorably received. We record here with deep regret the untimely death of the series' founding editor, Dr. R. H. F. Manske, and pay a brief tribute to the man and his work. The reviews now offered in Volume XVII were commissioned by him and it is our hope that this and subsequent volumes will continue to maintain the rigorous standards of excellence set by the late Dr. Manske.

R. G. A. RODRIGO

RICHARD HELMUTH FREDERICK MANSKE

(1901-1977)

Richard H. F. Manske was born in Germany in 1901 and came with his parents to Canada in 1906. He died in Guelph, Ontario in September 1977 from injuries sustained in an automobile accident early in the same year.

Manske began his education in the public schools of Saskatchewan where his family had settled after arriving in Canada. He later journeyed east to Ontario to attend Queen's University in Kingston, Ontario, where he was awarded the bachelor of science degree in 1923 and the master of science degree during the following year. In his graduate studies at Queen's he held a bursary awarded by the National Research Council of Canada. At Queen's he met his first wife, Jean Gray, whom he married in 1924. There were two daughters from this marriage, Barbara and Cory. On completion of his master's degree he moved to Manchester, England as an 1851 Exhibition Scholar where he studied in the laboratories of Robert Robinson. It was there that he began his work on alkaloids for which he will always be remembered.

As a graduate student at Manchester, Manske determined the structures of harmine and harmaline and synthesized both alkaloids. He also synthesized rutaecarpine, as he liked to recall, by accident. Another fortuitous experiment was his discovery of the use of hydrazine in the hydrolysis of phthalimides. He also collaborated at this time with A. Lapworth in one of the pioneering studies of physical organic chemistry. He was awarded the Ph.D. by Manchester in 1926.

Upon his return to North America, Manske worked briefly with the General Motors Company in the United States as a research chemist and then for three years as a research fellow at Yale University. In collaboration with T. B. Johnson at Yale he developed a new synthesis of ephedrine and related compounds. In 1929 he returned to Canada to assume a post with the National Research Council.

In Ottawa he began a systematic investigation of Fumariaceae plants for their alkaloid content. By developing new methods of separation of the alkaloids he found many new bases of the aporphine, benzophenanthridine, phthalideisoquinoline, protopine, and protoberberine ring systems. Three new classes of isoquinoline alkaloids also owe their discovery to this work. In his examination of *Dicentra cucullaria* he found the alkaloid cularine, determined its structure, and thereby demonstrated that it belonged to a new ring system. In the same period he isolated many of the alkaloids that are now known as the spirobenzylisoquinolines. Some 25 years later he was

co-author of the paper announcing the structure of ochotensimine, the first representative of this ring system to yield its structural secrets. The cancentre alkaloids were the most complicated structurally of all the alkaloids that he isolated. They were obtained from *Dicentra canadensis* Walp. in 1932, and nearly 40 years elapsed before the structure of cancentre itself was finally resolved.

Many of the alkaloids that he isolated in the 1930's and 1940's were found in small amounts, insufficient for structural examination by the methods available at that time. He had the foresight to put them away, carefully labeled and purified, until a time should come when science would reach the stage where they might be profitably examined. With the advent of refined spectroscopic methods in the last several decades the samples were removed from storage, usually from small brown bottles, and their structures elucidated, often in collaboration with younger and grateful colleagues.

Besides his classic studies on the isoquinoline family of alkaloids, Manske also undertook, in collaboration with Leo Marion, an examination of the Lycopodiaceae native to Canada. From this work some thirty alkaloids were characterized, and though he did not himself participate in a major way in their structural elucidation, he always followed the work with interest and insight. Other alkaloids with which he was concerned were members of the Senecio and Lobelia families, and in the latter group he discovered lobinaline, the first dimeric member of this family to be isolated.

In 1943 while still a relatively young man he left the National Research Council to assume the directorship of the newly established Research Laboratories of the Dominion Rubber Co. Ltd., now Uniroyal Ltd. He remained in this position for 23 years and retired in 1966. Under his direction the laboratory soon became a leading center of industrial research in Canada. At Guelph, alkaloids, of necessity, were relegated to a secondary role, but they were not entirely neglected. During this period "The Alkaloids" was begun and whenever there was time available from his other duties Manske would be found at the bench. He also encouraged his younger colleagues in the laboratory to carry on alkaloid research on a part-time basis. In this way some of us who worked there as young chemists acquired a taste for pure research and after a few years of Manske's tutelage moved on to university positions.

Upon his retirement from Uniroyal in 1966 he assumed the position of Adjunct Professor at the University of Waterloo where he applied himself once again to alkaloid chemistry. There he continued to be actively involved in research and teaching until his untimely accident.

During his career Manske was the recipient of many honors and awards. Among other things he was made a Fellow of the Royal Society of Canada in 1935, received a D.Sc. from Manchester in 1937, was Centenary Lecturer of

the Chemical Society, London, in 1954, was awarded the Chemical Institute of Canada Medal in 1959 (the highest distinction of the Institute), was the recipient of several honorary degrees from Canadian universities, received the Morley Medal of the Cleveland Section of the American Chemical Society in 1972, and inaugurated the A. C. Neish lectures at the National Research Council of Canada, Halifax, Nova Scotia. He was active for many years in the Chemical Institute of Canada and served as its president from 1963 to 1964.

His other interests were many and varied and he approached them with the same enthusiasm and commitment as his chemistry. He loved music and was himself a violinist. Growing orchids was a passion with him. It began as a hobby, developed into a business, and in later years became a hobby once again. There was always an orchid blooming in his greenhouse which he was happy and pleased to show to visitors. On his extensive property in Guelph he had many varieties of trees, shrubs, and flowers, some of which were used by him and by others for scientific ends, but they were there mainly for his own enjoyment and that of others. Birds, stars, cooking, martinis, wines, politics, economics, and philosophy were all subjects about which he was knowledgeable and willing and eager to discourse upon.

One of his main concerns was the role of the scientist in modern society and he lectured extensively on this subject during his tenure as vice-president and president of the CIC. His views are succinctly expressed in the following passage taken from one of his lectures: "He who professes science is truly a scientist only if he strives to achieve an awareness of his place in society as a whole. If he buries himself in the confines of his discipline and neither knows nor cares about the broad vista of the world about him he has failed as a man; and if he does not apply the objective, that is scientific, method to matters other than to those of his narrow discipline he has failed as a man. Indeed the scientist has failed as a man if he does not make it a *sine qua non* of his life to question authority, be it of Mohamet or of Darwin."

He was a man with a tremendous appetite for life. He was always busy with his chemistry, his hobbies, or his family. He lived his life to the fullest, enjoyed it all, and transmitted his zest for living and learning to all who knew him well.

He is survived by his second wife, Doris, his two daughters, and five grandchildren. His death is mourned not only by his family but also by his many colleagues and friends.

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—CHAPTER 1—

THE STRUCTURE AND SYNTHESIS OF
C₁₉-DITERPENOID ALKALOIDS

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