

NATURAL  
PRODUCTS  
Related to  
PHENANTHRENE

by  
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THIRD EDITION

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*By L. F. Fieser*

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## GENERAL INTRODUCTION

### American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the

search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

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## PREFACE

Since the publication of the first and second editions of this book in 1936 and 1937, vast strides have been made in the development of the chemistry of naturally occurring phenanthrene derivatives, particularly the steroids. By 1937 most of the important physiologically active steroid hormones and vitamins had been isolated and their structures established, but very little was known of the stereochemical configurations. Extensive studies of the stereochemistry of the steroids have culminated only in recent years and months in the complete solution of all the major problems concerned. This, therefore, is a particularly appropriate time to present a revision in which we hope we have accurately interpreted a highly confused and voluminous literature in the light of present-day stereochemical evidence that seems secure. We are greatly indebted to Dr. Richard B. Turner for contributing a chapter devoted to a critical survey of the stereochemical evidence.

The advances of the past decade have been so generally extensive that the present edition represents a complete overhauling of the original book, with retention merely of a few of the sections describing events in the history of the science that have become classic. There is so much new material that some of the earlier chapters and sections have been omitted: chemistry of phenanthrene (not pertinent to the chemistry of hydrophenanthrene derivatives), carcinogenic hydrocarbons (not now indicated to be of probable natural occurrence), triterpenoid sapogenins (related to picene rather than to phenanthrene, problem of structure still unsettled). Even so, the book is twice as long as before.

Achievements in partial and total synthesis have been prominent in recent researches in the field, and we have endeavored to review all synthetic work that has afforded actual natural products or close relatives. In accordance with a further trend, considerable prominence has been given to the use of spectrographic and optical rotational data in the determination of structure or configuration. Unfortunately the empirical importance and possible future theoretical significance of accurately determined optical constants are only now gaining general recognition, and some of the current reports of constants are regrettably incomplete. It is now apparent that determination of the specific rotations of a parent compound and several of its derivatives under comparable conditions should be as obligatory as determination of the melting points, and that absorption characteristics should be reported in terms of the numerical values of the maxima and

extinction coefficients rather than in a graph that cannot be interpreted with ease or accuracy. Failure to state the solvent used in the determination is a source of confusion, since a change from one common solvent to another may shift the absorption maximum of an  $\alpha,\beta$ -unsaturated ketone by as much as 11  $m\mu$ . The effect of solvent on the absorption characteristics of steroid polyenes awaits investigation.

The preparation of this book has involved consideration of the merits and general applicability of various alternate schemes of steroid nomenclature. In making a choice of names, not only for use in this book but for presentation as a studied recommendation for general adoption, we have followed the principle of seeking maximum simplicity and systematization with minimum departure from current usage. Our proposals are as follows:

(1) Configurations at nuclear centers of asymmetry relative to the molecule as a whole are designated  $\beta$  if the orientation of the hydrogen atom or a substituent corresponds to that of the two angular methyl groups and the side chain (written above the plane of the ring system; full line),  $\alpha$  if the reverse (below the plane; dotted line). The Greek letters are written without parentheses. A purely arbitrary trivial index is written with quotation marks.

(2) The configuration at  $C_{20}$  relative to that at  $C_{17}$  and the whole ring system is designated  $\alpha$  or  $\beta$  according to the convention given on page 412.

(3) Arbitrary, non-relative configurations in the side chain are designated a and b. Cholesterol and the bile acids are described as compounds of 20b-orientation and ergosterol and stigmasterol as 20b,24b-compounds. Campesterol can be described as 24a-methylcholesterol. The substance arbitrarily named pregnane-3 $\alpha$ ,20 $\alpha$ -diol by Marker is called pregnane-3 $\alpha$ ,20 $\alpha$ -diol. The arbitrary, non-relative designations provisionally applied in one series imply no correspondence to those in another.

(4) Where a substance can be regarded as derived from either of two natural or typical compounds, the choice should be guided by the consideration of practical chemical relationship.

Examples. The products of the Oppenauer oxidation of cholesterol and of the dehydrohalogenation of cholestene hydrochloride are called cholestenone and  $\Delta^4$ -cholestene, not coprostenone and coprostene as suggested by Rosenheim and King. The two oxides of cholesterol are described adequately by their trivial names; thus cholesterol  $\beta$ -oxide is preferred to 5 $\beta$ ,6 $\beta$ -oxidocoprostanol-3 $\beta$ . The classical name coprosterol violates the spirit of the principle and can be replaced by coprostanol.

(5) A substance differing from a natural or typical steroid in the configuration at an asymmetric center other than  $C_5$  but similarly involving the orientation of a carbon-carbon or carbon-hydrogen linkage is ordinarily described as an iso compound.

Examples. 17-Isoallopregnane, 17-iso-R diacetate, 5-isoandrosterone (instead of the cumbersome  $3\alpha$ -hydroxyetiocholanone-17), 8-isoestradiol (not 8-epiestradiol), 8-isoestrone (not 8-epiestrone), *d*-14-isoequilenin (*d*-isoequilenin), 17-isoetioallocholanolic acid, 14-iso-17-isoetioallocholanolic acid.

Exceptions. Where convenient descriptive trivial names are available, these are preferred: lumisterol, lumiestrone.

(6) The configuration at  $C_5$  in most instances is indicated by classical names: cholestane, allocholanolic acid, allopregnane, androstane; coprostane, cholanic acid, pregnane, etiocholane or 5-isoandrostane. The prefix allo is reserved for indication of the configuration at  $C_5$ . The name allocholesterol is discarded and replaced by  $\Delta^4$ -cholestenol- $3\beta$ .

(7) The configuration of the carbon skeleton should be indicated by the basic name and not merely implied by the orientation of hydroxyl groups.

Example. The compound listed in the literature as allopregnanetriol- $3\beta, 17\beta, 20\beta$  is actually a 17-isoallopregnanetriol and should, we think, be so named.

(8) A substance differing from a natural or typical steroid with respect to the steric orientation of a hydroxyl group is ordinarily described as an epi compound.

Examples. Epicholestanol, epitestosterone, 11-epicorticosterone, epiestradiol (the natural hormone can now be called estradiol- $17\beta$ ), 16-epiestriol (not isoestriol-A), 17-epiestriol (third isomer), 12-epietiodesoxycholic acid, epiandrosterone (for isoandrosterone), dehydroepiandrosterone (for dehydroisoandrosterone).

(9) Where the basic name indicates the orientation of one of two groups at  $C_{17}$ , an index defining the orientation of the other group is unnecessary. However, the inclusion of the second index may be desirable in instances where an index has recently been reversed, for emphasis, or in order to avoid the implication that the orientation of one of several hydroxyl groups is unknown.

Examples.  $17\alpha$ -Hydroxyprogesterone (natural),  $17\beta$ -hydroxy-17-isoprogestosterone (synthetic series),  $17\alpha$ -ethinyltestosterone (OH in testosterone is  $\beta$ -oriented),  $17\alpha$ -vinyltestosterone (the trivial name is both more convenient and more informative than 17-iso- $\Delta^{4,20}$ -pregnandiene- $17\beta$ -ol-3-one), estradiol- $17\beta$ , cholestane- $3\beta, 5\alpha, 6\beta$ -triol.

(10) The position of a double bond, or of a pair of formerly unsaturated carbon atoms, is indicated by a number that locates the first atom of the pair. The number of the second atom is also given if it is not the next higher number. Alternate methods of writing the numbers are given in the examples.

Examples.  $\Delta^{7,14}$ -Cholestadiene, or cholestadiene-(7,14);  $\Delta^{7,9(11)}$ -cholestadiene, or cholestadiene-(7,9:11);  $\Delta^{8(14)}$ -cholestenol- $3\beta$ , or cholestene-

(8:14)-ol-3 $\beta$ ; 22-dihydroergosterol; 5-dihydroergosterol (" $\alpha$ "-dihydroergosterol); 7-dehydrocholesterol; 6-dehydroestrone ( $\Delta^6$ -isoequilin); 9-anhydrocorticosterone; 9-dehydroprogesterone.

We have aimed to present in this book reasonably complete topical discussions of a selection of the main points of interest in the chemistry of the phenanthrene derivatives, and to survey more briefly the biochemistry and pharmacology of the compounds. A few papers, even recent ones, have been omitted because the material does not fall within the framework of the present arrangement of topics. The literature coverage extends to journals received to November 1, 1948, and some later ones. In view of the current congestion of some of the chemical journals, we are particularly grateful to several colleagues in this country and in England and Switzerland for their courtesy in sending us advance copies of manuscripts, some of which are still in press.

We are greatly indebted to several American colleagues for critical comments on parts of the book, and we wish to acknowledge the very full and helpful cooperation in this respect extended by Dr. C. W. Shoppee and Dr. D. H. R. Barton in England. Dr. Turner, in addition to his own contribution, has given us constant guidance in the interpretation of the literature. Our collaborators Dr. Minlon-Huang and Dr. S. Rajagopalan kindly read and checked the entire manuscript. We are indebted to Eleanore Blaisdell for the drawing of our Siamese cat Georgie and to Dr. Frederic C. Chang for the Chinese seals.

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MARY FIESER

Cambridge, Massachusetts  
November 17, 1948





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