

of proteins after cleavage of their dithio bonds also might be caused by transformation of a random coil form of their peptide chains into an  $\alpha$ -helix. Since L-cystine differs from all the other natural  $\alpha$ -amino acids by its extremely high levorotation, we investigated the optical rotation of some typical proteins in the native state and after oxidation of the dithio bonds.

Crystalline bovine serum albumin was obtained from Armour Laboratories, edestin from the Nutritional Biochemicals Corporation. Ovalbumin was prepared from hens' eggs.<sup>5</sup> The protein samples were oxidized by performic acid.<sup>6</sup> The excess of performic acid was reduced by ethanol and the oxidized protein precipitated with 5 *M* sodium chloride solution. The protein suspension was dialyzed and lyophilized. The optical rotation of both the native and the oxidized proteins was measured after redissolving them in 88% formic acid. The results are presented in Table I.

TABLE I

	Bovine serum albumin	Ovalbumin	Edestin
$[\alpha]^{25}_D$ native	-81.7 $\pm$ 0.8	-53.7 $\pm$ 0.5	-66.9 $\pm$ 0.6
$[\alpha]^{25}_D$ oxidized	-59.2 $\pm$ 0.9	-48.8 $\pm$ 0.9	-60.5 $\pm$ 0.2
Mol. wt. <sup>7</sup>	69,000	46,000	50,000
Cystine residues per molecule <sup>1</sup>	17	1	2
Change in rotation after oxidation			
$\Delta[\alpha]_D$			
Obsd.	+22.5 $\pm$ 1.2	+4.9 $\pm$ 1.0	+6.4 $\pm$ 0.6
Calcd.	17.3	1.5	2.8

(5) R. A. Kekwick and R. K. Cannan, *Biochem. J.*, **30**, 227 (1936).

(6) M. E. Reichmann and J. R. Colvin, *Can. J. Chem.*, **33**, 163 (1955).

(7) G. R. Tristram in Neurath-Bailey (eds.), "The Proteins," Vol. 1, p. 181 (1953).

The specific rotation of L-cystine in 88% formic acid was found to be  $-285.0^\circ$ , that of L-cysteic acid  $+5.5^\circ$ . Since one mole (240 g.) of cystine gives 2 moles of cysteic acid (338 g.), the increase in dextrorotation for a 1% solution of cystine is  $(285.0/100) + (5.5 \times 338)/(100 \times 240) = +2.928$ . If *n* is the number of cystine residues per protein molecule and *M* the molecular weight of the protein, the calculated increase in dextrorotation is  $(240 \times 100 \times 2.928 \times n)/M = 70,272n/M$ . It can be seen from Table I that the change in rotation increases with the cystine content of the proteins and that the calculated value of  $\Delta[\alpha]_D$  is of the same order as the observed value. A similar result was obtained with lysozyme where  $\Delta[\alpha]_D$  was  $+15.6^\circ$ , and the calculated value  $+19.1^\circ$ . We conclude that the large change in  $[\alpha]_D$  following performic acid oxidation of the dithio bridges in those proteins which are rich in dithio bonds is caused chiefly by destruction of the strained, hydrogen-bonded, structure of the cystinyl residues which has been described by Fieser,<sup>8,9</sup> and that other conformational changes of the peptide chains cause only minor changes in  $[\alpha]_D$ .

**Acknowledgments.**—Support of this work by grants of the U. S. Public Health Service (#1852) and the National Science Foundation (#G 1296) to F. H. and by contracts of Indiana University with the U. S. Atomic Energy Commission (At-11-1-209) and the Office of Naval Research (NR 120-035) is gratefully acknowledged.

(8) L. F. Fieser, *Rec. trav. chim.*, **69**, 410 (1950).

(9) We are grateful to Drs. E. Campaigne and M. Carmack for discussion of these problems.

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RECEIVED MAY 15, 1958

## BOOK REVIEWS

**The Pentaerythritols.** ACS Monograph No. 136. By EVELYN BERLOW, ROBERT H. BARTH and JOHN E. SNOW. Research Department, Heyden Newport Chemical Corporation, Garfield, New Jersey. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1958. vii + 317 pp. 16  $\times$  23.5 cm. Price, \$10.00.

The publication of this excellent, short monograph upon the pentaerythritols is an indication of the interest which has developed in the manufacture and uses of the pentaerythritols.

The pentaerythritols have been manufactured, commercially, for over twenty years, and have reached an annual U. S. peacetime production of close to 60,000,000 pounds. Practically all of the production is being used in the coatings industry.

The pentaerythritol industry has reached the stage where a monograph, such as this, serves a very useful purpose in that it provides a ready reference work for the executive, marketing, engineering, operating, research and patent personnel.

The work is divided into seventeen chapters, an author index and a subject index.

Chapter 1 is the Introduction. It is short, but gives an easy-to-read account of the discovery of pentaerythritol, its manufacturing growth and the manufacturers in the United States responsible for this growth.

Chapter 2 on the Preparation brings together about 194 references having a bearing upon the processes available for the manufacture of the pentaerythritols. It does not attempt to evaluate the substance of these references from standpoints of utility or theoretical soundness. It is, however, a very useful and thought-provoking chapter.

Chapter 3, which deals with the Physical Properties of the pentaerythritols, contains appreciable new material, particularly data relating to the solubility of pentaerythritols in a long list of solvents, and data relating to the infrared spectrum of pentaerythritol, of dipentaerythritol and of tri-pentaerythritol.

Chapter 4, dealing with the Physiological Properties is very short and lists only eight references. However, since it appears that the pentaerythritols are non-toxic, this chapter serves as an assurance of the safety involved in working with these products.

Chapter 5 pertains to Methods of Analysis. The methods described are very practical. However, no critical analysis

of the relative merits of available methods is given. It is to be hoped that, if a second edition of this work is made, that more emphasis will be placed upon methods of analysis.

Chapter 6 on the Reactions of the Pentaerythritols, is short, but, since there are later chapters dealing specifically with nitrates, amines, halides, ethers, etc., this chapter may be viewed upon as a collector of difficultly classifiable compounds. It lists 61 references covering products of oxidation, reduction, pyrolysis and reactions with alkalies and acids, with phosphorus compounds and with metals.

Chapter 7, on the Nitrates of the Pentaerythritols gives a very compact compilation of the processes available for the manufacture of pentaerythritol tetranitrate, lists the physical and explosive properties of PETN and its mixtures with other agents, and refers to its use in medicine. It also refers to nitrates closely related to PETN, such as dipentaerythritol hexanitrate and the higher pentaerythritol nitrates as well as substituted pentaerythritol nitrates. It lists 332 references closely related to PETN.

Chapter 8, covering Amines; Chapter 9, dealing with Halides; Chapter 10, pertaining to Ethers; Chapter 11, on Acetals; Chapter 12, relating to Sulfur-containing Derivatives; and Chapter 13, on Esters, are excellent reviews of the literature related to the subject matter of each chapter. These six chapters discuss more than 600 references and have been very carefully prepared.

Chapter 14, on the Drying Oils, is rather short and attempts to cover a large subject. It serves as a practical guide for processing the pentaerythritols into drying oils and lists 217 pertinent references.

Chapter 15, covering the Rosin Esters, lists 170 references and interprets these in a clear and concise manner.

Chapter 16, on the Polyesters, Alkyd Resins and other Resins, includes 221 references pertaining to alkyds, etc., and, taken in conjunction with the chapters on drying oils and rosin esters, is well worth the price of the book.

The final chapter on Miscellaneous Uses gives unusual uses for the pentaerythritols, such as stabilizers for vinyl chloride and chlorinated paraffin wax; as constituents of fire-retardant coatings as well as a number of surprising applications.

This rather small and attractive volume attempts to cover a large subject. The text has been prepared with great care and discrimination. The style is easy to read and the data have been well documented. It provides a quick review which points out where, if not what, the comprehensive literature contains.

The Author and Subject Indexes appear to be adequate, and the make-up and editing are excellent.

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**Fortschritte der Chemie organischer Naturstoffe (Progress in the Chemistry of Organic Natural Products). Volume XIV.** Edited by L. ZECHMEISTER, California Institute of Technology, Pasadena. Springer-Verlag, Mölkerbastei 5, Wien I, Austria. 1957. viii + 377 pp. 16 × 23.5 cm. Price, \$16.90, Ganzleinen, \$17.85.

The distinctive features of Zechmeister's "Fortschritte" series are well known to organic chemists, and have been discussed in reviews of previous volumes.

We find the current volume of particular interest because it contains, in addition to the usual authoritative reviews of organic structural problems, a number of chapters of broad significance to biology and even to geochemistry.

Bohlmann and Mannhardt discuss, in the first chapter, the chemistry of the considerable number of naturally occurring acetylenes. Ch. Tamm's chapter deals with the cardiac glycosides, with emphasis on their glycosidic character; the chemistry of the aglycones was discussed by the same author in volume 13 of the "Fortschritte." Brockmann contributes a good summary of the work on hypericin and related pigments. The chapter by Birch on the role of acetate as precursor for various classes of naturally occurring compounds is interesting and stimulating, although it would have benefited by a greater clarity of exposition in several spots. Sobotka, Barsel and Chanley discuss the chemistry of the "aminochromes," the orthoquinonoid dihydroindole oxidation products of adrenaline and related compounds. Morton and Pitt contribute an

extremely interesting account of the visual pigments, which gives an impressive picture of the advances in this field and of the formidable experimental difficulties which face the investigator. The chapter by Harrison Brown, on the carbon cycle, discusses "organic" chemistry on the cosmic scale.

There are undoubtedly a few misprints in the book, for those who enjoy finding them, and we would have enjoyed a chapter written in French. However, the book is an excellent production.

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**Purity Control by Thermal Analysis.** Proceedings of the International Symposium on Purity Control by Thermal Analysis, Amsterdam, 1957. Sponsored by the I. U. P. A. C. and organized by the Committee on Physico-Chemical Data and Standards. Edited by W. M. SMIT, Director of the Netherlands Central Institute for Physico-Chemical Constants, Utrecht, The Netherlands. D. Van Nostrand Company, Inc., 126 Alexander Street, Princeton, New Jersey. 1957. xii + 182 pp. 17 × 24.5 cm. Price, \$4.75.

This book brings into one place the current ideas of experts in the field of "purity control by thermal analysis." Reported in this book are the latest experimental apparatus and procedures being used in laboratories in different countries: Ubbelohde, University of London, England; Aston, Pennsylvania State University, U.S.A.; Herington, Handley, National Chemical Laboratory, England; Smit, Kate-man, University of Utrecht, The Netherlands; Saylor, Glasgow, Ross, Horton, Enagonio, Dixon, Furukawa, Reilly, Henning, National Bureau of Standards, U.S.A.; Keinitz, Badische Anilin and Sodafabrik A.G., Germany; Swietoslowski, Zieborak, University of Warsaw, Poland; McCullough, Waddington, U. S. Bureau of Mines, U.S.A.; Mazee, University of Amsterdam, The Netherlands; Skau, Magne, Mod, U. S. Department of Agriculture, U.S.A.; Barnard-Smith, White, British Petroleum Company, England; Stull, Dow Chemical Company, U.S.A.; Pilcher, Chemical and Petroleum Research Laboratory, Carnegie Institute of Technology, U.S.A.

The discussion covers all phases of the problem of the determination of freezing points and purity from calorimetric methods and from time-temperature freezing and melting experiments.

This book is a recommended reference for all scientists concerned with freezing points and purity of substances.

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**Vitamin A.** By THOMAS MOORE, Sc.D. (Cantab.) and D.Sc. (Belfast). Dunn Nutritional Laboratory, Cambridge, England. D. Van Nostrand Company, Inc., 126 Alexander Street, Princeton, N. J. 1957. xx + 645 pp. 16 × 23 cm. Price, \$14.00.

This monumental work comprehensively and critically surveys all aspects of vitamin A, including chemistry, physiology, biochemistry, pathology, medicine and spectroscopy. The historical development of our knowledge of vitamin A has been traced in all these diverse fields. In his preface Dr. Moore proposes that a book written by a single author rather than by a number of specialists might present a better balance between various disciplines. The author has succeeded admirably in preparing a book uniform in style, integrated, and exceptionally well-written.

The book begins with a five-page summary of units and nomenclature, a section vital for clear comprehension of the complex nature of vitamin A and the carotenoids. Dr. Moore then continues with an outstanding historical introduction based on his three decades of experience in the field. The next two chapters deal with the estimation and chemistry of vitamin A and the pro-vitamins A. In the opinion of this reviewer, these two chapters are relatively weak, probably because Professor Moore was largely dependent upon published data rather than upon personal ex-