

proved over that reported previously³ by the addition of hydrogen peroxide following decomposition of the ozonide and by treatment of the residual neutral fraction with periodic acid. The keto acid melted at 154–154.5° and was smoothly converted to an enol-lactone (III), m. p. 94–94.5°, by heating with acetic anhydride and acetyl chloride. *Anal.* Calcd. for C₂₆H₄₂O₂: C, 80.77; H, 10.95. Found: C, 81.00; H, 10.89.

Condensation of III with phenyl acetate in the presence of sodium hydride gave an oily mixture which was simultaneously hydrolyzed, decarboxylated and cyclized by the action of acid or base. Chromatography furnished a pure product, m. p. 80–80.6°, which was identified as cholestenone by mixed m. p. determination and measurements of specific rotation (+80.1 ± 2°) and ultraviolet absorption (λ max 241.5 mμ, log ε 4.18).

It is evident that intermediates IV and V can both lead to cholestenone, and that in either case the methyl-carbon of phenyl acetate will occupy the 4-position in the reformed ring. The carbonyl group of phenyl acetate, however, will be

(3) Bolt, *Rec. trav. chim.*, **57**, 906 (1938).

incorporated only by the reaction of phenyl acetate with the enol-lactone anion to give IV. The use of carboxyl-labeled phenyl acetate thus provides a method for determining the relative amounts of the two intermediates.

This reagent was prepared from sodium acetate containing C¹⁴ in the carboxyl group⁴ and had a specific activity of 4.20 × 10⁴ counts/min./mmole.⁵ Condensation with III yielded cholestenone with a specific activity of 3.79 × 10⁴ counts/min./mmole.⁵ These results indicate that about 90% of the cholestenone obtained is derived from intermediate IV.

Details of the above observations will be published shortly. The use of methyl-labeled phenyl acetate and extension of the method to other steroids has been undertaken.

(4) Ruben, Allen and Nahinsky, *THIS JOURNAL*, **64**, 3050 (1942).

(5) The author is indebted to Dr. Warren W. Miller of the Radioactivity Center, M. I. T., for activity measurements. For a description of the counting method see Miller, *Science*, **105**, 123 (1947).

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NEW BOOKS

Modern Developments of Chemotherapy. By E. HAVINGA, H. W. JULIUS, H. VELDSTRA and K. C. WINKLER. (Monographs on the Progress of Research in Holland.) Elsevier Publishing Co., Inc., 215 Fourth Ave., New York 3, N. Y., 1946. xi + 175 pp. Illustrated. 14.5 × 21 cm. Price, \$3.50.

This monograph presents in lucid and concise form the results of research in Holland during the last war on sulfanilamide derivatives and other therapeutic agents. Many of the products synthesized were similar to those obtained in other countries and the data bearing on these and the foreign literature relating to similar products are presented as a critical study in an interesting and readable form. The critical analysis of these results is provocative even if the conclusions are not always convincing.

Considerable attention is given to the mechanism of the action of the sulfanilamide compounds, evidence being presented from both bacteriological and physical chemical investigations. Much of this evidence is similar to that obtained by other investigators but in certain instances novel conclusions are reached. Stress is laid on the importance of adsorption in determining the relative activities of the several sulfa drugs. The validity of this evidence cannot be assessed without having further information concerning the methods employed in obtaining the data. From the data one cannot say with certainty that activity is entirely dependent upon adsorption for sulfanilamide, the parent substance, is listed as showing no adsorption on the organisms used in the experiment within the experimental error of the method. Again, other investigators have shown that organisms grown on media containing metanilamide or orthanilamide retain more of these drugs than the same organisms grown on sulfanilamide

under similar conditions, yet the former are inactive in inhibiting the growth of the organisms in comparison with sulfanilamide.

The chapter on physico-chemical investigations in particular is well written and deserves careful consideration.

In the chapter on chemical investigations the sulfanilamide compounds studied are given in Table 3 beginning on page 120 and should follow paragraph 3 on page 119.

Biochemical investigations beginning in the middle of page 119 are continued on page 134.

Chapter 4 deals with pharmacological, immunological and clinical investigations, while Chapter 5 covers the researches on antibiotic substances and related mycotherapy.

The monograph is a valuable contribution to the literature of chemotherapy.

M. L. CROSSLEY

Medical Biochemistry. By MARK R. EVERETT, Ph.D., Professor of Biochemistry, University of Oklahoma School of Medicine. Second edition, completely revised. Paul B. Hoeber, Inc., Medical Book Department of Harper and Brothers, 49 East 33rd Street, New York 16, N. Y., 1946. xii + 767 pp. 106 tables. 16.5 × 24 cm. Price, \$7.00.

"Medical Biochemistry" is intended to serve as "a modern, concise and correlated survey of biochemical knowledge" primarily for students of medicine, and as a convenient reference volume for more general use. The subject matter is divided into ten chapters dealing successively with acid-base relations, colloids, enzymes and oxidation, digestion, lipides, carbohydrates, proteins, prosthetic radicals of nucleoproteins and chromoproteins,

inorganic substances, vitamins and avitaminoses, hormones and endocrines. The large text is compactly organized and well indexed. There are 106 tables for succinct reference and many diagrams to simplify the teaching of metabolic pathways and similar topics. Each chapter is followed by a bibliography of general references which are well selected, on the whole, though not up-to-date in some instances.

This second edition, appearing four years after the first, has been revised to include such subjects of current interest as adaptive enzymes, amino acid therapy, antibiotics, cephalin fractions, dicumarol, gangliosides, phosphorylation, Rh factor, thiouracil. Other topics have been expanded, notably anoxia, carboxylation and decarboxylation, the chemistry of development, hypertensive factors, ketogenesis, the metabolism of bile acids, oxidation-reduction enzyme systems, peptidases, phosphatases, plasma proteins, renal function, spreading factor, steride hormones, sulfonamides, transamination, transmethylation, vitamins A and K and vitamins of the B complex.

An effort has been made throughout to integrate the basic facts of biochemistry and physiology with their application to clinical medicine; there are extensive sections dealing with pathology, disease patterns and even treatment of disease. Granting that such integration is in keeping with a prevailing philosophy of medical pedagogy, and is to be desired, many sections of the book reveal the strain placed upon one author attempting to cover so wide a range. This is most evident in the discussions of disease patterns and treatment of disease.

A peculiarity of the book is the indiscriminate scattering of quotations, many of which are incongruously placed, throughout the text.

ALEXANDER B. GUTMAN

The Chemical Aspects of Light. By E. J. BOWEN, F.R.S., Fellow of University College, Oxford. Second edition, revised. Oxford University Press, 114 Fifth Avenue, New York 11, N. Y., 1946. 300 pp. Illustrated. 14.5 × 23 cm. Price, \$5.00..

The first edition of the book was reviewed in *THIS JOURNAL*, 65, 998 (1943). The second edition covers essentially the same material as the first, but more of the physical and chemical principles are explained and illustrated. Chapter III on "The Absorption and Emission of Light" and Chapter IV on "The Transformation of Absorbed Radiation" are especially well done. The book is a concise treatment of important chemical aspects of light.

LAWRENCE J. HEIDT

Quantitative Organic Microanalysis. Based on the Methods of Fritz Pregl. Fourth English Edition Completely revised and edited by JULIUS GRANT, M.Sc., Ph.D., F.R.I.C., London; Editor of Hack-Grant's Chemical Dictionary, etc. The Blakiston Company, 1012 Walnut Street, Philadelphia 5, Penna., and Toronto, Canada, 1946. vii + 238 pp. 94 figs. 15 × 23.5 cm. Price, \$5.00.

The new book follows quite closely in all essentials the previous translations of F. Pregl's original editions, particularly E. Beryl Daw's translation of the 4th German edition (1937) and to a lesser extent E. Fyleman's older translations of the 3rd (1930) and 2nd German editions (1924).

Thus in orderly fashion Pregl's standard micromethods of organic elementary analysis (95 pages) and chemical structure analytical procedures (71 pages) are taken up as before. This is preceded by descriptions of various microchemical balances (Kuhlmann, Oertling and Bunge) (15 pages) and a chapter on general microanalytical technique (16 pages). It is followed by chapters dealing with the determination of principal physical constants (29 pages) and short sketches of physical structure analytical methods

(13 pages). While unessential matters have been shortened by about one fifth and literature references have been enlarged, the book unfortunately still leaves uncorrected many of the glaring errors of its previous translations, *i. e.* on p. 14, last paragraph, lines 2 and 3.

With the exception of a more thorough discussion of methods of isolation and purification (6 pages) and a few short paragraphs on certain physical and electrometric methods (5 pages) no new organic microchemical method or improvements thereof and not contained in the previous translations, could be found. Compared with the standard works in microchemistry at the present available in America and which are largely unquoted, the present edition offers nothing of any importance and consequently the high sounding pronouncements of the author in the preface of the book remain largely unsubstantiated in the text.

JOSEPH B. NIEDERL

A New Notation and Enumeration System for Organic Compounds. By G. MALCOLM DYSON, M.A. (Oxon.), Ph.D. (Lond.), F.R.I.C., Technical Director, Genatosan Ltd., Loughborough. Longmans, Green and Co., 55 Fifth Ave., New York 3, N. Y., 1947. iv + 63 pp. 15.5 × 24.5 cm. Price, \$1.75 (paper).

This is an explanation of a new system which has already attracted attention in England. It was introduced to the public last October in a lecture delivered by Dr. Dyson under the joint auspices of the Chemical Society, the Royal Institute of Chemistry, the Society of Chemical Industry and the Bureau of Abstracts.

Employing the capital alphabet, Arabic numerals and a few other characters the method reduces the structural formula of each organic compound to a linear "cipher" which, it is claimed, is unique for a given structure, determines the numbering with certainty and can be applied to a punched card. Examples of the ciphers: methane, C; decane, C10; neopentane, C3.2,2C; cyclohexane, AC6; *p*-xylene, B.1,4C; ethyl acetate, C2.X[C2]; maltose, [G6.1-5AQ.3L]θ1;4 (θ has the effect of doubling all that precedes it); progesterone, HJ8.17C.2,13C.8E.-7,18EQ. Each cipher carries with it a numbering for the entire skeletal structure.

Since the ciphers are so constructed that an important feature of the structure is expressed first, then others in order, the ciphers may be used as the basis for a logical classification or, if some other basis is used, for a cipher index.

Details of the application of the system to punched cards are not given in the book; these will be the subject of a separate article by Dr. Dyson. A scheme of multiple punches has been devised for the standard Hollerith card of 80 columns by which, for example, the cipher for ψ -strophanthidin is recorded as 71 punches in 24 columns. The average number of columns required for a cipher is 14-20, and even a complex structure like that of ergotoxine (56 columns) does not use up all the space, so that room is left for the tabulation of properties or references. Experiments are being conducted on sensing and sorting with machines of the electromatic type. An interesting feature of the ciphers is that the machines can calculate from them the empirical formulas.

Since the ciphers are independent of language (and therefore international) it is difficult to foresee what effect such a system may have on ordinary nomenclature. It would be desirable if a system of ciphers and an interpretation of them in words (and numbers) could run parallel; but in this case present numberings might have to be changed considerably, with risk of much confusion. One also wonders what bearing the punched-card code by the cipher system may have on similar codes now being developed in this country. Perhaps two or more kinds of code for organic compounds will be needed for differing conditions.

The Dyson ciphers constitute a radical departure and, like any new and untried system, will require study and experience to determine their range of usefulness. They

offer the promise, however, of a valuable additional tool for classification, indexing, sorting and communication.

AUSTIN M. PATTERSON

An Introduction to the Chemistry of the Silicones. By EUGENE G. ROCHOW, Research Laboratory, General Electric Company, John Wiley and Sons, Inc., 440 Fourth Ave., New York 16, N. Y., 1946. x + 137 pp. 15 × 24.5 cm. Price, \$2.75.

This monograph contains a comprehensive account of organosilicon chemistry, dealing not only with monomeric substances, but also the various types of polymers, with a chapter on the properties of specific silicone polymers, especially the alkyl silicones.

The fundamental chemistry of the simple covalent compounds of silicon, including hydrides, halides and esters, serves as an introduction to those aspects of silicon chemistry which are responsible for the formation of the silicon polymers which have grown to have commercial importance, including silicone oils, resins, and silicone rubber. Tables containing some of the physical properties of representative compounds will be found useful to the reader or investigator in this field and at the end of the book a glossary of terms pertaining to the subject matter is another helpful feature.

The methods of large-scale production of organosilicon compounds is discussed in a chapter on the technical aspects of the silicones, in which the course that future developments in this field are likely to take is pointed out. The state of the art is considered still to be crude and elementary, roughly equivalent to that of organic chemistry in the year 1860. A start has been made and it is reasonable to predict that "with an expanding literature, a more standardized nomenclature and a greater variety of synthetic methods available to today's worker, progress should be ever faster."

The book is nearly free from typographical errors, is interestingly written and logically presented, and may be heartily endorsed as the first comprehensive survey of the subject, and as such it will prove to be indispensable to any reader desirous of acquiring a working knowledge of silicone chemistry.

WALTER C. SCHUMB

Contribution to the Physics of Cellulose Fibers; A Study in Sorption, Density, Refractive Power, and Orientation. By P. H. HERMANS. Communication No. 21 from the Institute for Cellulose Research of the A. K. V. and Affiliated Companies, Utrecht. Elsevier Publishing Company, Inc., Amsterdam, Brussels; London and New York, N. Y., 1946. 221 pages, in English. Price, \$4.00.

This book covers a series of original physical measurements and theoretical deductions on native cellulose, rayon and various synthetic "model fibers" aimed at increasing our understanding of the crystalline and amorphous nature of cellulose, the penetrability of both types of structure by liquid media and the nature of their binding of water.

The present accepted hypothesis that cellulose is made up of crystallites and amorphous regions with the primary cellulose chains extending through several crystallites and amorphous regions in series, with cellulose chains from different crystallites entering adjacent crystallites, is used as the basis for further theoretical deductions.

The native fibers used were ramie and "standard cotton." The hydrate celluloses were viscose, Lillienfeld and Benberg rayons spun with different degrees of stretch to give different degrees of orientation. Hydrate "model filaments" were made by slowly extruding cellulose xanthate (8 per cent. cellulose) through one-millimeter internal diameter glass capillaries. These highly swollen practically isotropic filaments, after dextranation, were swollen to six to seven times their dry volume. "Aniso-

tropic model filaments" were made by stretching isotropic model filaments by 100 per cent. before dextranation.

Sorption measurements, using these materials together with data from the literature, show that all hydrate celluloses, practically regardless of orientation, show about double the sorption of native celluloses at relative vapor pressure between 0.05 and 0.65. Mercerized celluloses show intermediate constant sorption ratios.

Isotropic model fibers shrink about equally in the length and thickness directions down to 65 per cent. relative humidity. Below this the length decreases faster than the thickness with a loss in isotropic properties. Dry model fibers immersed in water show an advancing wet line toward the center. Longitudinal swelling is negligible until the wet line reaches the center and then it occurs rapidly. The rate of take-up of water in both the liquid and vapor phase is a slow process and is apparently controlled by the laws of diffusion. In a two-liquid system (water-glycerol), water diffuses into the fiber first, followed by the glycerol as is indicated by two advancing boundary lines. Apparently, glycerol does not penetrate into dry cellulose gels unless a pathway has been made by a certain amount of water. Studies of the rate of diffusion at different temperatures indicate a temperature coefficient per 10° of about 2.4 which is a normal chemical reaction temperature coefficient.

The integral heat of sorption, like the total sorption, varies about twofold between native and hydrate celluloses. The initial differential heat of sorption, however, is practically identical for the different forms of cellulose, indicating that the intensity factor of sorption is the same in all cases. From this it is concluded that hydrate celluloses have about double the percentage of sorbing matter compared to native cellulose. From thermal data taken from the literature it is concluded that the first 6 per cent. of water taken up by native cellulose is bonded by true chemical forces, and presumably about double this amount is bonded by chemical forces in hydrate cellulose.

X-Ray evidence shows no change in the unit cell dimensions of native cellulose due to sorption of water, whereas the dimensions of the unit cell of hydrate cellulose expands on sorption of water. The dimension changes correspond to the formation of a supposedly definite hydrate having either the composition $C_6H_{10}O_5 \cdot 1/3 H_2O$ or $C_6H_{10}O_5 \cdot 1/2 H_2O$. The former is considered the most probable (3.7 per cent. bound water).

From the foregoing it is concluded that all the sorption by native cellulose occurs in the amorphous regions. Correcting for the sorption of 3.7 per cent. water by the crystallites of hydrate cellulose and assuming equal sorptive power per unit weight of the amorphous part of both native and hydrate cellulose, it is calculated that there is 1.9 times as much amorphous cellulose in hydrate cellulose as in native cellulose. This is in agreement with optical findings that native cellulose is 40 per cent. amorphous and hydrate cellulose 75 per cent. amorphous.

The determination of the density of cellulose in different media is discussed and new data presented. The generally accepted theory that water gives higher values than helium gas because of the adsorption compression of water is discounted in favor of the explanation that water more completely penetrates the structure, in spite of the fact that measurements in helium agree most closely with the theoretical densities calculated from X-ray measurements. Hermans believes that the density determined in nonswelling organic liquids is most nearly the true density of the cellulose (fiber but not necessarily the fiber substance). Data are presented that show a slightly higher density for native cellulose than for hydrate cellulose when determined in nonswelling organic liquids and the reverse when determined in water. The former is explained on the basis of a higher crystallite than amorphous density and higher proportion of crystallites in native than in hydrate cellulose. The latter is explained on the basis of more penetration into hydrate cellulose because of the greater proportion of penetrable amorphous cellulose. The apparent density of regenerated fibers determined in water decreases on steaming the fiber, drying at high tem-

peratures and transformation to cellulose IV. The quantity of bound water is estimated from apparent density measurements in aqueous sodium chloride solutions.

Refractive power and double refraction of cellulose are discussed and new data presented. The refraction of all cellulose fibers, according to the empirical relationship of Gladstone and Dale, are equal on a unit density basis. The influence of moisture on the refractive index of cellulose fibers was quantitatively accounted for applying the rule of additivity of refraction according to Gladstone and Dale.

The relationship between optical constants and orientation is considered and mathematical expressions derived which are simpler than those deduced by others, but give the same numerical results. The case of ideal orientation is considered for both native and mercerized ramie. An optimum double refraction value of 0.055 is obtained.

The evaluation of the orientation of cellulose fibers from X-ray diagrams is discussed and data for a number of fibers presented. Orientation factors obtained in this way are compared with those obtained from optical anisotropy studies. It is concluded that the double refraction of regenerated fibers at ideal orientation must lie between 0.050 and 0.055. From these values the optimum percentage of regenerated fibers made up of crystallites is estimated to be 25 per cent. This is in agreement with values estimated from sorption and density considerations.

An appendix is included in which the methods of making the various measurements are described.

This highly theoretical booklet is worthy of study by all those interested in the physical structure of cellulose. It is felt that it contains no final answers, but it discloses a number of highly commendable coordinated approaches to solve a problem that will require further efforts by many to attain a complete solution.

ALFRED J. STAMM

Chemistry of Food and Nutrition. By HENRY C. SHERMAN, Ph.D., Sc.D., Mitchell Professor of Chemistry, Columbia University. Seventh Edition. The Macmillan Company, 60 Fifth Avenue, New York, N. Y., 1946. viii + 675 pp. 15 × 22 cm. Price, \$3.75.

The seventh edition of this standard text in nutrition thoroughly fulfills the purpose of the author which is "to present the principles of food chemistry and nutrition with as many of the scientific facts as space permits, and as are deemed most important to an effective grasp of the subject." This most recent edition follows the general pattern of previous editions though every chapter has been revised, some completely rewritten, and new chapters have been added dealing with food groups and the variations in the nutritive values of food. The concept that food is a principal factor in the chemical control of the internal environment of the body is especially well presented. The first twenty-four chapters deal principally with the chemical and physiologic characteristics of nutrients. The reviewer would like to have had more material included on B-complex vitamins other than thiamine, riboflavin and niacin. The last eight chapters deal with applied nutrition. There are four useful appendices deal-

ing with food composition and one with the statistical treatment of the data of nutrition investigations.

FREDRICK J. STARE

BOOKS RECEIVED

January 10, 1947-February 10, 1947

ARTHUR K. ANDERSON. "Essentials of Physiological Chemistry." Third Edition. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 395 pp. \$3.50.

C. J. ENGELDER. "Fundamentals of Semi-Micro Qualitative Analysis." John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 385 pp. \$3.50.

FRANCISCO GIRAL. "Chemical and Pharmaceutical Products." (In the Spanish language.) Based on the work entitled "Preparation of Chemical and Chemical-Pharmaceutical Products" by C. A. Rojahn. Three Volumes. Editorial Atlante, S. A., Mexico, D. F. 2226 pp. \$26.00.

ROBERT S. HARRIS AND KENNETH V. THIMANN, Editors. "Vitamins and Hormones." Vol. IV. Academic Press, Inc., 125 East 23rd Street, New York, N. Y. 406 pp. \$6.80.

C. N. HINSHELWOOD. "The Chemical Kinetics of the Bacterial Cell." Oxford University Press, 114 Fifth Avenue, New York 11, N. Y. 284 pp. \$6.75.

W. NORTON JONES, JR. "Inorganic Chemistry." The Blakiston Company, 1012 Walnut Street, Philadelphia 5, Pa. 866 pp. \$4.25.

E. JOSEPHY AND F. RADT, Editors. "Elsevier's Encyclopedia of Organic Chemistry." Volume 14. "Tetra-cyclic and Higher-cyclic Compounds." Series III. "Carboisocyclic Condensed Compounds." Elsevier Publishing Company, Inc., 215 Fourth Avenue, New York 3, N. Y. 711 pp. (Cloth). Subscription price, \$45.00; serial price, \$52.50; single volume price, \$60.00.

WILLIAM KLYNE. "Practical Chemistry for Medical Students." The Williams and Wilkins Company, Baltimore, Md. 460 pp. \$6.00.

WOLFGANG PAULI. "Meson Theory of Nuclear Forces." Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y. 69 p. \$2.00.

CHARLES C. PRICE. "Mechanisms of Reactions at Carbon-Carbon Double Bonds." Interscience Publishers, Inc., 215 Fourth Avenue, New York 3, N. Y. 120 pp. \$2.50.

WALTER STILES. "Trace Elements in Plants and Animals." The Macmillan Company, 60 Fifth Avenue, New York 11, N. Y. 189 pp. \$2.75.

Y. K. SYRKIN AND M. E. GIETKINE. "The Chemical Bond and the Structure of Molecules." (In the Russian language.) State Scientific-Technical Publishing House of Chemical Literature, Moscow, Leningrad, Russia. 588 pp.