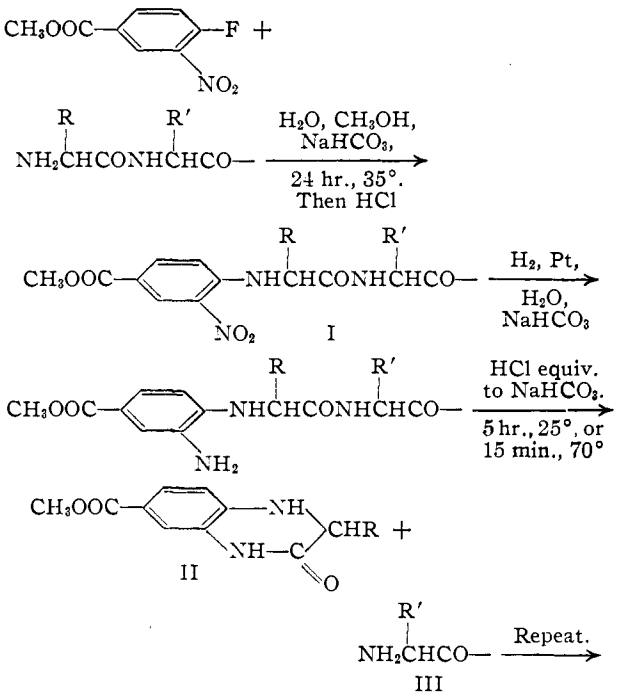

O_3: C, 58.24; H, 4.89; N, 13.59. Found: C, 58.44; H, 4.73; N, 13.31.) From L-alanine, R = CH_3, m.p. 216.5–218°, $[\alpha]^{24}D$ +17° (*c*, 1.1; methanol). (*Anal.* Calcd. for $C_{11}H_{12}N_2O_3$: N, 12.7. Found: N, 13.1). From L-leucine, R = $(CH_3)_2CHCH_2$, m.p. 212–215°, $[\alpha]^{26}D$ +20° (*c*, 1.1; methanol). (*Anal.* Calcd. for $C_{14}H_{18}N_2O_3$: N, 10.7. Found: N, 10.5.) From L-phenylalanine, R = $C_6H_5CH_2$, m.p. 197–201° (transition 190–192°), $[\alpha]^{22}D$ −99° (*c*, 0.5; methanol). (*Anal.* Calcd. for $C_{17}H_{16}N_2O_3$: N, 9.46. Found: N, 9.79). The extension of this degradation to more complex peptides, such as those containing cystine and lysine, may require modification of the present procedure. This is now under investigation.

Using the reaction shown in equation (2), the *o*-nitrophenoxyacetyl group can be removed from N-*o*-nitrophenoxyacetylpeptides by catalytic reduction of the nitro group followed by lactam formation, which is complete in 30 to 120 minutes at 100° in aqueous solution. Similarly, the chloroacetyl group can be removed from N-chloroacetylpeptides by reaction with *o*-phenylenediamine in aqueous solution for 30 to 120 minutes at 100°, the reaction presumably proceeding by way of equation (1). The yields of once-recrystallized peptides prepared from their *o*-nitrophenoxyacetyl and chloroacetyl derivatives, respectively, and identical with authentic samples, were: glycylglycine 73%, 76%; glycylglycylglycine 76%, 68%; glycyl-L-alanyl-L-leucine 65%, 59%; and L-phenylalanyl-L-leucine 70%, 31%. These reactions suggest the use of the *o*-nitrophenoxyacetyl and chloroacetyl groups as protecting groups during peptide synthesis. In preliminary experiments, using the *o*-nitrophenoxyacetyl group and the Curtius azide procedure,[5] L-phenylalanyl-L-leucine ($[\alpha]^{22}D$ −21° (*c*, 1; 1% sodium bicarbonate solution)), identical with material prepared by the carbobenzoxy method, was synthesized in 31% yield[6] (from L-phenylalanine ethyl ester hydrochloride). With the chloroacetyl as the protecting group, glycylglycylglycine was synthesized from glycylglycine in 18% yield using the method of Boissonnas.[7]

(5) T. Curtius, *Ber.*, **35**, 3226 (1902).

(6) C. S. Smith and A. E. Brown, THIS JOURNAL, **63**, 2605 (1941), synthesized D-phenylalanyl-D-leucine from D-phenylalanine in 12% yield by the carbobenzoxy method. B. F. Erlanger and E. Brand, THIS JOURNAL, **73**, 3508 (1951), report yields of 30 to 35% for six dipeptides, which is more representative of the method.

(7) R. A. Boissonnas, *Helv. Chim. Acta*, **34**, 874 (1951).

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RECEIVED DECEMBER 19, 1951

ON A PHOSPHO-TRI-ANHYDRIDE FORMULA FOR THE NUCLEIC ACIDS

Sir:

In a recent issue of this Journal[1] a hypothetical structure for desoxyribonucleic acid is proposed, having as its core a polymer chain of phosphorus atoms held together by oxygen atoms. In formulating a hypothetical structure for a substance one must take care that the structural elements of which use is made are reasonable ones, for which some precedent exists, or one must show that there is an overwhelming necessity for a radical proposal. In the proposed structure for the nucleic acids each phosphorus atom has five oxygen atoms attached to it, three of which bind it to adjacent phosphorus atoms, and two of which are in a hydroxyl group and a sugar ester group, respectively. There is, however, no precedent for a structure in which phosphorus is bonded to five oxygen atoms. Of the scores of phosphorus compounds that have been subjected to complete structural investigation, the phosphorus atom is surrounded by four oxygen atoms in every compound in which it has oxidation number +5.

The proposer of this extraordinary formula for the nucleic acids has not quoted any significant evidence in support of it. The ligation of five oxygen atoms about each phosphorus atom is such an unlikely structural feature that the proposed phospho-tri-anhydride formula for the nucleic acids deserves no serious consideration.

(1) E. Ronwin, THIS JOURNAL, **73**, 5141 (1951).

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RECEIVED JANUARY 24, 1952

THE MOLECULAR WEIGHT OF AMYLOPECTIN[1]

Sir:

Potter and Hassid[2] have reported measurements of the molecular weights of acetylated starch fractions by osmotic methods. We here report the results of light-scattering measurements of one of their acetylated amylopectins, Easter Lily sample L-3-B, in nitromethane solution at 25°. The apparatus and procedures used have previously been

(1) This work was supported by the Office of Naval Research.

(2) A. L. Potter and W. Z. Hassid, THIS JOURNAL, **70**, 3774 (1948).

described.[3] The molecular weight obtained was 420,000,000 ± 100,000,000 with R, the root-mean-square radius about the center of mass, equal to 14,000 ± 4000 Å. The extreme angular dependence of the scattering caused the precision of the results to be lower than usual. This result is not in real disagreement with Potter and Hassid's molecular weight of 6,000,000, the latter being actually a lower limit in view of the well-known lack of precision of the osmotic method for this molecular weight range.

A sample of acetylated amylose also was measured. The weight-average molecular weight was about ten times the number-average value reported by Potter and Hassid, but the angular dependence of the scattered light indicated the presence of a few per cent. of high molecular weight impurity (possibly amylopectin).

(3) B. H. Zimm, *J. Chem. Phys.*, **16**, 1099 (1948); P. Outer, C. I. Carr and B. H. Zimm, *ibid.*, **18**, 830 (1950).

The angular dependence of the amylopectin scattering was of the normal type for a chain polymer. There was no evidence that the material was heterogeneous. Moreover, the measurements were repeated at 70° with almost identical results, indicating that the solution was actually a molecular dispersion without temperature-dependent aggregates. This is the first time, to our knowledge, that a molecular weight of this magnitude has been reported for an amylopectin.

We are indebted to Professor Hassid for his kind coöperation with this work.

(4) General Electric Research Laboratory, The Knolls, Schenectady, New York.

(5) Bell Telephone Laboratories, Murray Hill, New Jersey.

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RECEIVED JANUARY 29, 1952

BOOK REVIEWS

Die biogenen Amine. 4th edition. By M. GUGGENHEIM, Dr. phil., Dr. med. h. c., Basel. Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y. (S. Karger, Holbeinstrasse 22, Basle, Switzerland.) 1951. xv + 619 pp. 17 × 23.5 cm. $19.50 (Swiss francs 75.-.).

The new edition of Guggenheim's now classical monograph on the biogenic amines represents an extensive revision of the previous one. It follows the general plan of the earlier editions, presenting detailed information on the chemical, biochemical and pharmacological properties of these materials, their isolation, identification, quantitative determination, probable biogenesis and biochemical reactions. Some material has been omitted to make way for the great mass of information which has been added to our knowledge of these substances in the past decade. This is reflected in the fact that there has been approximately a forty per cent. increase in the number of substances covered with only a ten per cent. increase in the number of pages or references, now approximately 4600. Certain changes in the pattern of the chapters reflect the trend of recent discoveries. In particular, the discussions on biogenesis have been expanded and an introductory general chapter on the subject added.

A blemish in the chemical formulations throughout the book is the retention of uncharged structures for the amino acids. More serious is the perpetuation of uncharged forms for the guanidinium bases. While the author recognizes on page 396 that the guanidinium cation exists in solution, his formulation of guanidine as CH_5N_3 helps to carry on the common misconception that non-resonating, anhydro-base forms of this and related materials are commonly isolated.

In the formulations of the reactions of biogenesis, it would have been desirable if the author had critically examined all equations proposing the assumption of formaldehyde as a biochemical intermediate. Some of these formulations should undoubtedly be replaced by transmethylation or formate ion reactions. Only those should be included in which investigators succeed in obtaining positive evidence that formaldehyde as such is utilized as an intermediate.

The new feature of this edition is the series of short but excellent reviews of enzymatic reactions, such as transmethylation, oxidative deamination and many others, in which biogenic amines participate as substrates, as coenzymes and as products. Such reactions help to bring the biochemical significance of these substances into clearer focus and to make their pharmacological manifestations more intelligible.

The work as a whole is a valuable and welcome review. The excellent quality of craftsmanship entering into the manufacture of the book is entirely in keeping with the high standards of scholarship displayed in the preparation of the manuscript.

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Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Volume 31. By R. S. SCHREIBER, Editor-in-Chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1951. vi + 122 pp. 15.5 × 23.5 cm. Price, $2.75.

Ever since Volume 1 in this series appeared, organic chemists have looked forward with keen anticipation to the appearance of the next volume. The standards of publications throughout have been exceptionally high and the present volume is no exception.

Detailed directions are given for the preparation of forty organic compounds which include not only aliphatics and aromatics but some phosphorus compounds which are rapidly becoming important.

As usual there is a great deal of variety in the types of reactions and a mere study of the reactions involved is a good lesson in organic chemistry. No student of the subject, and no worker in the field, can afford to be without these volumes.

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