(IX) is identical with that of a known sample of 17α-hydroxycorticosterone acetate. 1,3-Propanediol may be substituted for ethylene glycol in the over-all process with success. Compound F acetate was prepared by this method in approximately 15% over-all yield from 11α-hydroxyprogesterone, the synthesis of which by the bio-oxygenation of progesterone was recently described in a communication from these laboratories.[4] Similarly treatment of VI as given for VIII above, gave the hitherto unreported 11β,17α-dihydroxy-4-pregnene-3,20-dione (21-desoxy Compound F), m.p. 225–228°, $[\alpha]^{24}\text{D}$ +136° (acetone); $\lambda_{\text{max.}}^{\text{EtOH}}$ 241 mμ, E = 15,500. (*Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.72; H, 8.70). Further details of this work will be published shortly.

The authors are indebted to V. R. Shellman, A. Koning, and G. Beyer for technical assistance; to L. M. Reineke and group for papergram analyses; to Dr. J. L. Johnson, J. E. Stafford, and Mrs. G. S. Fonken for infrared and ultraviolet absorption studies; and to W. A. Struck and group for microanalyses.

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[4] D. H. Peterson and H. C. Murray, THIS JOURNAL, **74**, 1871 (1952); D. H. Peterson, H. C. Murray, S. H. Eppstein, L. M. Reineke, A. Weintraub, P. D. Meister and H. M. Leigh, *ibid.*, **74**, 5933 (1952); U. S. Patent 2,602,769, July 8, 1952.

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RECEIVED DECEMBER 12, 1952

ELECTRON DISTRIBUTION IN TRIPHENYLMETHYL:[1] HYPERFINE STRUCTURE OF THE PARAMAGNETIC RESONANCE ABSORPTION OF $(C_6H_5)_3C^{13*}$

Sir:

Hyperfine structure in the paramagnetic resonance absorption of free radicals is associated with interactions between electronic and nuclear magnetic moments.[2] From the magnitudes of the hyperfine splittings, deductions concerning the electronic distribution may be made.

The abundant isotope of carbon, C^{12}, has zero magnetic moment and leads to no hyperfine splittings. C^{13}, on the other hand, possesses spin $^1/_2$ and a magnetic moment of 0.7021 nuclear magneton. One C^{13} nucleus in a free radical molecule should split the paramagnetic resonance absorption spectrum into two components. The magnitude of the splitting is dependent on the average magnetic field at the nucleus contributed by the spin and orbital motion of the electron.[3] This field is determined in part by the average of the reciprocal of the cube of the distance between electron and nucleus.

We have examined the paramagnetic resonance absorption of triphenylmethyl containing C^{13} in the methyl position. The sample contained 53 atom per cent. of C^{13} in this position. The spectrum in dilute solution (10^{-3} M in hexaphenylethane) consists of three lines, equally spaced.[4] The interval between the low field line and the high field line is 22 ± 5 oersteds. The central line arises from molecules containing C^{12} in the methyl position. The intensities are consistent with the isotopic abundance of the original sample. Triphenylmethyl prepared from materials of normal isotopic abundance by a procedure identical with the one used for the C^{13} containing compound gave a single line.

The splitting which we have observed arises from an average field at the C^{13} nucleus of about 3×10^4 oersteds.[5] This field corresponds to a separation of 0.7 ångström units between the unpaired electron and the nucleus of the methyl carbon atom. This interpretation must be viewed with caution. Further work, now being pursued, on the anisotropies in the spectra of single crystals dilute in the free radical constituent, is essential for a more quantitative description of the electronic distribution.

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[1] Assisted by the joint program of O.N.R. and A.E.C.

[2] G. E. Pake, J. Townsend and S. I. Weissman, *Phys. Rev.*, **85**, 682 (1952); C. A. Hutchison, Jr., R. C. Pastor and A. G. Kowalsky, *J. Chem. Phys.*, **20**, 534 (1952).

[3] In the case here considered the orbital contribution is unimportant.

[4] The measurements were made at 9000 mc. in fields close to 3200 oersteds.

[5] This number may be compared with a field of 6×10^4 oersteds at the nitrogen nucleus in nitric oxide.

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STUDIES ON ADRENOCORTICOTROPIN. V. THE ISOLATION OF CORTICOTROPIN-A

Sirs:

By means of a 200-plate counter-current distribution of a fraction derived from unhydrolyzed hog pituitary extract by means of an ion exchange column[1] we have obtained a product which appears to be pure.

In this work we have started with the slow-moving fraction from Amberlite XE-97 columns, referred to as ID in a previous publication.[1] The system *s*-butyl alcohol/0.2% trichloroacetic acid has been used for all the distribution studies reported here.

A preliminary 24-plate run showed that fraction ID gave a single peak with a distribution coefficient of about 1.7. Comparison with the theoretical curve suggested a purity of 80–85% with most of the impurities running slower than the main peak and imperfectly separated from it. On the basis of this information, a 200-plate run was made on a large batch of material. Because of the tendency of ACTH to give broad peaks in concentrated solution, the 300-mg. sample was scattered over six tubes. As before, a single peak was obtained, broader than theoretical and with a distribution coefficient of about 1.75. Material from the center of this peak, falling well within the limits of the theoretical curve for k = 1.75 was recovered as the trichloracetate and used for the remainder of this study.

Figure 1 shows a re-distribution of this material

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[1] W. F. White and W. L. Fierce, THIS JOURNAL, **75**, 245 (1953).

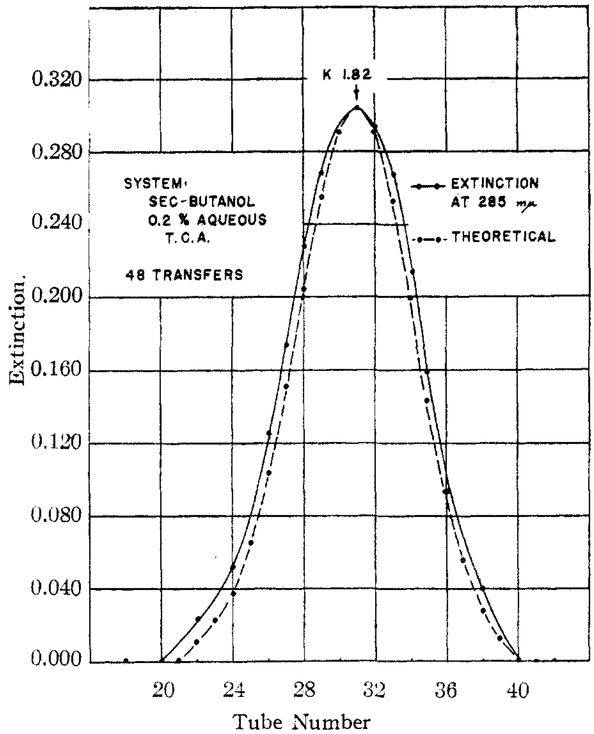

Fig. 1.

in the same system. In this case only 13 mg. of sample was used. A comparison of the actual and theoretical curves indicated a purity of about 93%. On the basis of the small (about 20%) purification effected in the distribution experiments, it would be expected that the product would be of the same order of activity (100–150 USP units/mg. of peptide) as the starting material. This has been the case only when hydrogen sulfide has been used in the distribution system. Without antioxidant considerable losses in activity have been suffered without any substantial change in distribution pattern.[2]

A preliminary amino acid determination has been made on the purified material using a paper-chromatographic technique.[3] Within the limits of error of the method (10%), the empirical formula appears to be: $Arg_2His_1Lys_3Phe_2Ser_1Leu_2Val_2Glu_4$-$Asp_1Gly_2Ala_2Pro_3$. Tryptophan has not yet been determined on the purified product, but values obtained on Fraction ID by the method of Spies and Chambers[4] correspond to one residue. On portions of the pure material which have been deionized by electrolytic means, the amino acid composition accounts for 88.5% of the dry weight. The identity of the remaining 11.5% is under investigation.

Since type ID material has been shown to be a parent of the hydrolyzed forms of ACTH,[1] we propose the term Corticotropin-A for our purified product. This is done in the realization that an adjustment in the nomenclature will be required in the event that a more complex naturally occurring form of porcine ACTH is isolated.

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(2) In many experiments with hydrogen sulfide and other antioxidants, we have never obtained significant increases in total activity. The effect has only been one of protection against loss.

(3) Details are to be published under the authorship of J. F. Roland and A. M. Gross of this Laboratory.

(4) J. R. Spies and D. C. Chambers, *Anal. Chem.*, **20**, 30 (1948).

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RECEIVED DECEMBER 22, 1952

BOOK REVIEWS

Biochemical Preparations. Volume 2. By ERIC G. BALL, Editor-in-Chief. John Wiley and Sons, Inc., 440 Fourth Avenue, New York 16, N. Y. 1952. vii + 109 pp. 15.5 × 23.5 cm. Price, $3.00.

Detailed directions are given for the preparation of twenty-three compounds, which are representative of a wide range of biochemical interests. The ultimate cost of some of these compounds, which can be readily obtained from supply houses, would probably approximate the purchase cost, unless large scale operations were introduced. Nevertheless, the information provided in this volume will be of great value for the further purification of commercial products. Moreover, since the directions are clear and detailed, the book should be of great value in courses in biochemistry in which preparative work is stressed. In criticism, it may be said that considerable space is given to compounds which will be of interest to a small group of workers only. Moreover, several preparations could have been published more appropriately in "Organic Syntheses." In view of the large number of publications in the current literature dealing with the purification of enzymes, it is surprising that only one enzyme is discussed in this volume.

On the whole, this volume, as well as Volume 1 of "Biochemical Preparations" will be a valuable asset to both the teachers and research workers in biochemistry.

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ANN ARBOR, MICHIGAN A. A. CHRISTMAN

Annual Review of Nuclear Science. Volume I. By COMMITTEE ON NUCLEAR SCIENCE, National Research Council Annual Reviews, Inc., Stanford, California. 1952. x + 645 pp. 16.5 × 22.5 cm. Price, $6.00.

This first volume of a projected series of annual reviews on nuclear science is an interesting account of researches published for the most part in 1950. It is really too bad that in a rapidly moving field a time lag of two years has to intervene between the time the material actually appeared in the literature and the appearance of the review volume. Although recognizing that a considerable time lag is inevitable, the reviewer feels that to include the date 1952 as a prominent part of the title, as done on the present volume, gives the prospective reader a misleading impression of timeliness. The lag is felt seriously in some fields, less so in others;