found when the values of log log (I_0/I) were plotted against the frequency or reciprocal wave length. Separate isomerization experiments indicated that the "flavoxanthin-like carotene," which apparently is not identical with a similar carotene of yellow corn,[6] contains the stable or *trans* form of the polyene chromophoric group.

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[6] White, Zschelle and Brunson, THIS JOURNAL, **64**, 2603 (1942).

STANFORD UNIVERSITY, CALIF. RECEIVED MAY 10, 1943

COMMUNICATIONS TO THE EDITOR

α,β,γ,δ-TETRAPHENYLCHLORIN

Sir:

In 1939 Rothemund[1] described the preparation of tetraphenylporphin from pyrrole and benzaldehyde and claimed the separation of two isomers which he believed to be due to the two possible positions of the pyrrole acid hydrogen atoms. This work was continued by Aronoff and Calvin[2] in which a more complete separation was achieved by chromatographic adsorption. It was also shown that not only two but probably six different porphyrin-like substances were formed in the reaction.

Recently an examination of their spectra and a comparison with the spectra of naturally and synthetically derived porphyrins and chlorins[3] indicated that the spectra of the first two most abundant materials obtained in the tetraphenylporphin synthesis, called A (most abundant) and B (next most abundant) might be related as porphyrin to chlorin, respectively. If this be so it should be possible to convert B into A by oxidation and A into B by reduction. This we have succeeded in doing in the following manner. The spectrum of the Cu salt was used as identification since the difference there is greater and easier to observe than in the free base.

1. A sample A (several mg.) is dissolved in about 15 cc. of *n*-hexanol. Several crystals of cupric acetate are added and the solution is brought to a boil, cooled, and washed thoroughly with 6 *N* hydrochloric acid and then with water. The hexanol solution (after drying with sodium sulfate) then shows only the spectrum of the Cu salt of A, *i. e.*, a single intense band at 538 m.

2. Another sample (several mg.) of A is dissolved in 15 cc. of *n*-hexanol and several crystals (*ca.* ten-fold excess) of zinc acetate added and the solution brought to a boil. After cooling, the solution is washed with dilute acetic acid and with water and dried with sodium sulfate. This solution now shows the spectrum of the Zn salt of A which seems to consist of three bands in the following order of intensity: 555 mμ, 596 mμ and 518 mμ.

3. The solution of the A Zn salt is now boiled for two minutes and a piece of metallic sodium (5 mm.) dropped in and the boiling continued until all the sodium is dissolved or more sodium is added until the A Zn salt spectrum is completely replaced by a new one consisting of three bands 620 mμ, 600 mμ and 559 mμ. This solution shows a very powerful red fluorescence.

4. The solution from 3 is washed with water, then with 6 *N* hydrochloric acid which removes the Zn and converts the free base into the deep green hydrochloride (in the *n*-hexanol). This is then washed with water until all the hydrochloric acid is removed, leaving a solution of the free base (B) in the *n*-hexanol.

5. The solution from 4 is converted into Cu salt as described in 1 and shows two approximately equally intense bands 536 mμ and 615 mμ which is the spectrum of the B Cu salt. Operations 4 and 5 must be done as nearly in the absence of oxygen as possible.

6. Upon blowing oxygen through the solution obtained in 5 for several minutes and warming, the 615 mμ band disappears and, after a washing with water, the spectrum is that of the pure A Cu salt. The Cu salt of B obtained by chromatographing the original porphyrin preparation has also been oxidized by oxygen to give the A Cu salt.

Thus we have shown that A and B are related by oxidation and reduction and suggest that B is tetraphenylchlorin.

The work is being repeated quantitatively and will be so reported later, together with observations on the intermediate products in the oxidation and reduction.

CHEMISTRY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA
M. CALVIN
R. H. BALL
S. ARONOFF

RECEIVED OCTOBER 13, 1943

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[1] Rothemund, THIS JOURNAL, **61**, 2912 (1939).

[2] Aronoff and Calvin, *J. Org. Chem.*, **8**, 205 (1943).

[3] Fischer-Orth, "Die Chemie des Pyrrols," Vol. 2, Part 2, 1940, Akademische Verlagsgesellschaft, Leipzig.

ROTENONE IN THE YAM BEAN (*PACHYRRHIZUS EROSUS*)

Sir:

The question of the possible occurrence of rotenone in the yam bean is of particular interest because this plant has recently been suggested[1] as a source of insecticidal material to supplement the usual rotenone-bearing insecticides. The seeds have long been known to be toxic to insects and fish, and Hwang[2] has reported the occurrence of

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[1] Hansberry and Lee, *J. Econ. Entomol.*, **36**, 351 (1943).

[2] Hwang, *Kwangsi Agr.*, **2**, 269 (1941) (in Chinese), summary in *Rev. Applied Entomol.*, **30A**, 418 (1942).

rotenone, but only on the basis of a color test not specific for rotenone itself. Camson[3] has obtained a crystalline substance resembling rotenone from a carbon tetrachloride solution of the oil-free resin from the seeds.

Two kg. of ground yam bean seeds from Mexico were extracted with ether, the ether removed, and the insecticidally active resin (1.4%) separated from the large amount of fatty oil (26.7%) by partition between 90% acetic acid and petroleum ether. The oil-free resin in benzene solution was fractionated by chromatographic adsorption on alumina. The fraction giving a strong Goodhue[4] red color test deposited from benzene solution several crops of crystalline material giving little or no color test. The benzene was removed from the remaining solution, and the residue taken up in hot carbon tetrachloride. A heterogeneous brownish deposit formed after cooling overnight, and was removed. On scratching the flask walls or seeding with rotenone–carbon tetrachloride solvate, a mass of white needles was deposited, similar in appearance to the rotenone solvate. When warmed with alcohol, these needles were converted rapidly to thin plates like those of rotenone.

The compound was identified as rotenone by a m. p. of 164–165° (cor.) both alone and in admixture with known rotenone; the formation of a dehydro compound of m. p. 222°; optical rotation in 1% benzene solution $[\alpha]^{25}\text{D}$ −236°; quantitative Goodhue and Meyer and qualitative Durham color tests; and a high toxicity to insects; all in satisfactory agreement with the corresponding properties of authentic rotenone.

The isolated rotenone amounted to about 0.1% of the original beans. The total material giving the red color test in this sample was 0.15%, calculated as rotenone. It is therefore probable that rotenone itself accounts for a substantial proportion of the color tests reported by previous workers. Some samples have been reported to have a much higher content of color-producing material than the sample used in this work.

Rotenone does not account fully for either the toxicity or the red color test of the yam bean. A number of other compounds of yet unknown constitution also have been isolated, some giving the color test, and some showing definite toxicity to insects. Investigation of these compounds is now in progress.

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[3] E. J. Camson, Orbis Products Corp., Newark, N. J., personal communication.

[4] Goodhue, *J. Assoc. Off. Agr. Chem.*, **19**, 118 (1936).

CHEMISTRY DIVISION
NEW YORK STATE AGRICULTURAL EXPERIMENT STATION
GENEVA, NEW YORK L. B. NORTON

RECEIVED OCTOBER 11, 1943

SYNTHESIS OF 1,4-EPOXYCYCLOHEXANE

Sir:

It was to be expected that refluxing 1,4-cyclohexanediol in the presence of activated alumina would yield cyclohexadienes and cyclohexanol.[1] It has now been found, however, that 1,4-epoxycyclohexane is predominantly formed. It has also been observed that by passing a solution of *trans*-1,4-cyclohexanediol over activated alumina at 275°, 73% of 1,4-epoxycyclohexane is formed, while the *cis* isomer under similar conditions gives only 28% of the epoxide. The type of solvent, contact agent, and temperature used exert a strong influence upon the yield of the epoxide.

1,4-Epoxycyclohexane boils at 120.1° (760 mm.), d^{20}_4 0.9707, $n^{20}\text{D}$ 1.4477, $M^{20}\text{D}$ 27.05. *Anal.* Calcd. for $C_6H_{10}O$: C, 73.47; H, 19.20. Found: C, 74.19; H, 10.14. It is soluble in the usual organic solvents and is partially soluble in water, with which it forms an azeotropic mixture boiling at 90°. It is soluble in 40-60% sulfuric acid from which it may be recovered by dilution with water. On heating with 48% aqueous hydrogen bromide *trans*-1,4-dibromocyclohexane is formed.

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[1] V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The MacMillan Company, New York, 1936, p. 106.

CHEMISTRY DEPARTMENT R. C. OLBERG
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS, AND HERMAN PINES
UNIVERSAL OIL PRODUCTS COMPANY
RIVERSIDE, ILLINOIS V. N. IPATIEFF

RECEIVED SEPTEMBER 20, 1943

A NEW POTENTIOMETRIC METHOD TO DETERMINE CATIONS AND ANIONS WITH COLLODION AND PROTAMINE-COLLODION "MEMBRANE ELECTRODES"

Sir:

I should like to point out that collodion membranes of high ionic selectivity as described recently[1] may be used successfully for the potentiometric determination of K^+, Na^+, Li^+, NH_4^+, Mg^{++}, and probably some other cations. The nature of the anion seems to have no specific influence. As yet, however, the collodion membranes are inferior to Marshall's[2] clay membranes in that the presence of other cations seriously interferes in all instances.

Collodion membranes impregnated with protamine[3] are electropositive, and show an analogous selectivity with regard to anions as do clay or collodion membranes with regard to cations. Such protamine collodion membranes may be used for the determination of Cl^-, Br^-, I^-, F^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_3^-, NO_3^-, acetate$^-$, etc. For some of these ions no other potentiometric method is available.

The determinations may be made in various ways. The potential difference which arises between a known solution on the one side of the membrane and the solution of unknown concen-

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[1] K. Sollner, I. Abrams and C. W. Carr, *J. Gen. Physiol.*, **25**, 7 (1941); C. W. Carr, Ph.D. Thesis, University of Minnesota, 1942.

[2] C. E. Marshall and W. E. Bergman, THIS JOURNAL, **63**, 1911 (1941), *J. Phys. Chem.*, **46**, 52, 325 (1942); C. E. Marshall and C. A. Krinbill, THIS JOURNAL, **64**, 1814 (1942).

[3] I. Abrams, and K. Sollner, *J. Gen. Physiol.*, **26**, 369 (1943).

tration on the other side of the membrane may be evaluated on the basis of some semi-theoretical standard curve. Or, these potential values may be compared to an empirical curve, determined for a specific membrane in advance. A third method consists of an electrometric titration: the membrane separates the solution of unknown concentration from water, to which electrolyte solution of known (higher) concentration is added stepwise, whereby the potential difference is diminished stepwise and finally is reversed. Zero potential difference indicates that the activity of the critical ion is the same on both sides of the membrane. The preliminary results listed below were obtained using the third method.

TABLE I

THE DETERMINATION OF CATIONS WITH COLLODION MEMBRANES

Electrolyte (0.01000 mole/liter)	Concentration, found, mole/liter
KCl	0.00998
$KClO_3$	.00988
$KClO_4$	.01008
KNO_3	01022
K_2SO_4	.01012
NaCl	.01014
LiCl	.01012
NH_4Cl	.01000
$MgCl_2$	.01018

TABLE II

THE DETERMINATION OF ANIONS WITH PROTAMINE COLLODION MEMBRANES

Electrolyte (0.01000 mole/liter)	Concentration found mole/liter
KCl	0.01016
NaCl	.00980
$MgCl_2$	.01008
NaF	.01012
KNO_3	.01016
$NaNO_3$	.00980
NaAc	.01012
$KClO_3$	.01018
$KClO_4$	.00988
KIO_3	.01018

This method should be useful in studies of the activity of the counter-ions in colloidal systems, for the determination of the anion and cation binding capacity of proteins, and similar problems.

A detailed description and evaluation of this method will be published shortly. In how far "oil-chains" can be employed in a similar way for organic ions in general will also be discussed at a later date.

DEPARTMENT OF PHYSIOLOGY
THE MEDICAL SCHOOL
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINN. KARL SOLLNER

RECEIVED OCTOBER 14, 1943

X-RAY FIBER PATTERN FROM AMYLOSE WITH A GLYCEROL PLASTICIZER

Sir:

Reports from this Laboratory[1] have been made of films and fibers of amylose,[2] and a structure for the "B" modification of starch has been proposed on the basis of amylose film and fiber diagrams.[3] In the course of attempting to produce amylose fibers, plasticizers were employed to aid in the stretching of the amylose films. The X-ray fiber diagrams obtained from fibers containing plasticizers were by no means identical with those produced by fibers containing no plasticizer.[3]

In Fig. 1, a fiber diagram is reproduced of amylose with a glycerol plasticizer. The diagram was taken with Cu K α radiation and a sample to flat film distance of 3 cm. The fiber spacing is 7.5 Å. This is very different from the 10.6 Å. spacing found for the "B" modification of starch, and indicates a flexibility of the starch chain not found in the cellulose chain.

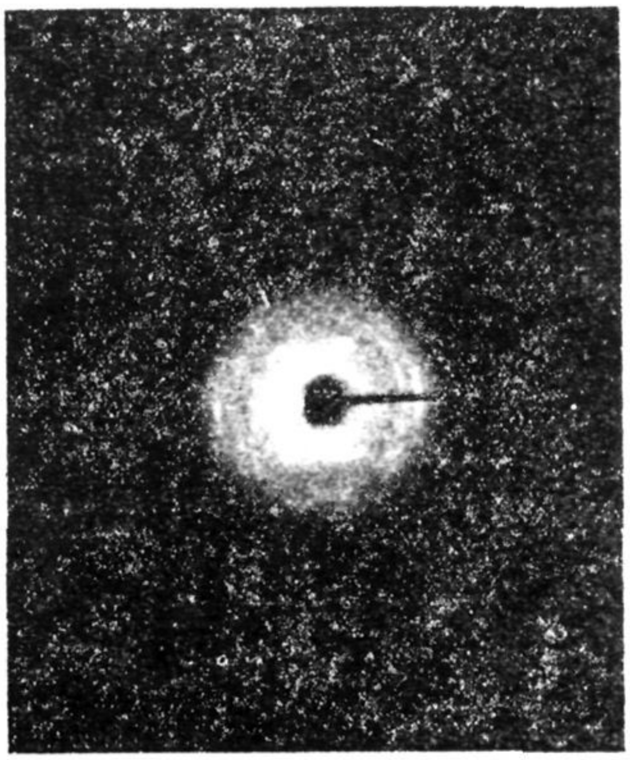

Fig. 1.—X-Ray fiber diagram of amylose with glycerol plasticizer. Fiber axis is vertical.

Alcohol-precipitated starch, the "V" modification, is found to have a helical structure and a periodicity along the helix of 8 Å.[4] The optical properties of this material indicate that the greatest polarizability is normal to the helix axis,[5,6] or normal to the long axis of the molecule. The greatest polarizability of the glycerol-amylose

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(1) R. Rundle and D. French, THIS JOURNAL, **65**, 558 (1943).

(2) The amylose used was prepared by T. Schoch's fractionation, *ibid.*, **64**, 2957 (1942). For a discussion of its purity and properties see L. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

(3) R. Rundle, L. Daasch and D. French, *ibid.*, in press.

(4) R. Rundle and D. French, *ibid.*, in press.

(5) R. Rundle and R. Baldwin, *ibid.*, **65**, 554 (1943).

fiber is parallel to the fiber axis.[1] The chains are probably extended linearly, rather than possessing the helical configuration of the "V" modification, but they must be folded, less extended than in the "B" modification, as indicated by the difference in the fiber spacings.

PLANT CHEMISTRY SUBSECTION R. E. RUNDLE
IOWA AGRICULTURAL EXPERIMENT STATION
AMES, IOWA LESTER W. DAASCH

RECEIVED JUNE 23, 1943

NEW BOOKS

Organic Syntheses. Collective Volume 2. A Revised Edition of Annual Volumes X–XIX. Edited by A. H. BLATT, Secretary to the Board, Queens College, Flushing, New York. John Wiley and Sons, Inc., 440 Fourth Avenue, New York, N. Y., 1943. ix + 654 pp. 15.5 × 23.5 cm. Price, $6.50.

The material in the annual Volumes 10 through 19 is here collected, edited, revised to date, and indexed in the same manner as in Collective Volume I which embraces the first nine annual volumes. This great contribution to the serviceability of "Organic Syntheses" has been made with all the care and accuracy of editing and printing which are generally associated with this series. Eleven new sets of directions are included as alternates to those previously given, and the literature is surveyed through the 1941 volume of *Chemical Abstracts* for reports of methods of preparation. The only obvious ways in which the usefulness of future collective volumes might be further increased are by making at least the general index cumulative for the entire series and, if the times permit, shortening the present interval of four years between the publication of the material in its annual and collected forms. The latter purpose might be promoted by substituting a collective volume entirely for Volume 29.

PAUL D. BARTLETT

Micromeritics, the Technology of Fine Particles. By J. M. DALLAVALLE. Pitman Publishing Corp., New York, N. Y., 1943. 376 pp. 100 figs. 15 × 25 cm., Price, $8.50.

Micromeritics, a new term in the vocabulary of the scientist and engineer, means, according to the author, the science of small particles.

In the introduction the author defines the size of the particles as those ranging from 10^{-1} to 10^5 microns. In other words, the text is for the most part limited to a discussion of particles ranging from the upper limits of the colloidal range to fairly large ones. The systems, therefore, are identical with those which O. Chwala termed cloudy systems or mechanical turbidities. That a better understanding of the properties of such systems, as well as a more comprehensive knowledge of the methods available for their study, is becoming of increasing importance, not only to the chemical engineer, but to the soil physicist, to geology, hydrology, etc., induced the author to write this text. For this alone he deserves lasting credit.

The book is divided into eighteen chapters which deal with the dynamics of small particles, their shape and size distribution, methods of particle size measurements, sifting and grading, packing characteristics, electrical, optical, sonic and chemical properties, thermodynamics, flow of fluids through packings, infiltration and moisture relationships, capillarity, determination of particle surface, a discussion of muds and slurries, the transport of particles, the theory of fine grinding, the separation from air, and finally a chapter on atmospheric and industrial dusts.

The book is clearly written, and the mathematics necessary for complete understanding as well as application of the subject matter are well balanced and precise. The incorporation of specific problems at the end of every chapter materially increases the value of the book, which fills one of the remaining gaps in our scientific and technological literature. It therefore should be of real value to anyone—student, teacher and men in industry alike—who is faced with problems in which systems containing small particles are involved. Besides being an excellent textbook, it should serve admirably as a reference book, particularly in view of the selected bibliography and a list of useful constants and conversion factors appended to the main text.

The print as well as the many illustrations are excellent.

In the chapter on methods of particle size measurements no reference could be found to the valuable contributions of A. Casagrande, as well as those of Norton and Speil.

In the discussion of light scattering the contributions of Pihlblad would have deserved mentioning.

In the chapter dealing with fine grinding reference to the work of men like von Weimarn, Stein and Utzino would have contributed to completeness.

Entirely omitted in the discussion of ball mill operations is the well-known phenomenon of mechanical coagulation, a factor which may not be overlooked even with particles larger than colloidal.

Although the author purposely omits the discussion of colloidal systems, the influence of surface properties of matter particularly during disintegration or comminution may no longer be entirely overlooked.

These statements, however, do in no way reduce the interest this book should have and are offered merely as suggestions for future developments in micromeritics.

If any unfavorable criticism of the book could be made at all it would be the price, which may seriously hamper the distribution it deserves.

E. A. HAUSER

A Textbook of Elementary Quantitative Analysis. By CARL J. ENGELDER. Third edition. John Wiley and Sons, Inc., New York, N. Y., 1943. viii + 283 pp. 14 figs. Price, $2.75.

The third revision of this textbook for a one semester course in quantitative analysis is not unlike the previous edition. It contains a selection of the simpler procedures of volumetric and gravimetric analysis and a discussion of the principles on which they are based. In addition there appears a new chapter on "Systematic Quantitative Analysis" which outlines some of the separation procedures used in rock and alloy analysis and gives a tabular summary of methods for the determination of the elements. The appendix contains pages devoted to the literature of analytical chemistry, plans and suggestions for the instructor, density tables for solutions of acids and bases, five-place logarithms, and chemical factors.

With respect to the treatment of practical matters such as directions to the student for performing the experiments, the principal criticism of the material presented is that much of it is repetitious. For example, directions for the reduction of ferric ion given on page 130 are repeated al-