

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.

(6) White, Zscheile and Brunson, *THIS JOURNAL*, **64**, 2603 (1942).
STANFORD UNIVERSITY, CALIF. RECEIVED MAY 10, 1943

COMMUNICATIONS TO THE EDITOR

$\alpha,\beta,\gamma,\delta$ -TETRAPHENYLCHLORIN

Sir:

In 1939 Rothemund¹ described the preparation of tetraphenylporphyrin 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 Calvin² 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 chlorins³ indicated that the spectra of the first two most abundant materials obtained in the tetraphenylporphyrin 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 m μ , 596 m μ and 518 m μ .

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

(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.

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 m μ , 600 m μ and 559 m μ . 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 m μ and 615 m μ 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 m μ 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.

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RECEIVED OCTOBER 13, 1943

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 suggested¹ 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 Hwang² has reported the occurrence of

(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. Camson³ 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 Goodhue⁴ 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 $[\alpha]^{25}_D -236^\circ$; 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.

Rothenone 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.

(3) E. J. Camson, Orbis Products Corp., Newark, N. J., personal communication.

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

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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-epoxy-cyclohexane 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}_D 1.4477, M^{20}_D 27.65. *Anal.* Calcd. for C₆H₁₀O: C, 73.47; H, 10.20. 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.

(1) V. N. Ipatieff, "Catalytic Reactions at High Pressures and Temperatures," The MacMillan Company, New York, 1931, p. 106.

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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 recently¹ may be used successfully for the potentiometric determination of K⁺, Na⁺, Li⁺, NH₄⁺, 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's² clay membranes in that the presence of other cations seriously interferes in all instances.

Collodion membranes impregnated with protamine³ 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⁻, ClO₃⁻, ClO₄⁻, BrO₃⁻, IO₃⁻, NO₃⁻, 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-

(1) K. Sollner, I. Abrams and C. W. Carr, *J. Gen. Physiol.*, **25**, 7 (1941); C. W. Carr, Ph.D. Thesis, University of Minnesota, 1943.

(2) C. E. Marshall and W. E. Bergman, *THIS JOURNAL*, **63**, 1911 (1941), *J. Phys. Chem.*, **46**, 32, 325 (1942); C. E. Marshall and C. A. Krimbill, *THIS JOURNAL*, **64**, 1814 (1942).

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