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, Zscheile 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.

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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).