

teenth, seventeenth and twentieth minutes it made twelve, eight, six and one half, six and one half and five beats respectively. Then pouring in water around the edges to make a water-seal resulted in the beats diminishing to three per minute; after a three-minute interval, one and one half, and after two more minutes the gargoyle became stationary and no further beats were noted as long as it was kept in this saturated air. After awhile the instrument was taken out of the casserole and placed in the current of air from the electric fan and it made 107 beats. The instrument was then taken outdoors where the temperature was

1° C. with scarcely any breeze blowing. The instrument made five beats for each of four different minutes that were counted at irregular intervals. Then brought back into the room it made forty beats.

The use of the atmometer arrangement in greenhouse practice such as was written up by J. D. Wilson in a recent article¹ will no doubt give more exact data of amount of evaporation, but a gargoyle would be a much simpler instrument to utilize under ordinary conditions of greenhouse practice.

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SPECIAL ARTICLES

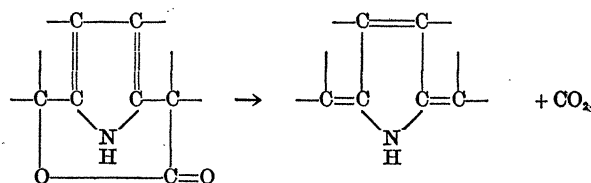
THE RELATIONSHIP OF CHLOROPHYLL TO THE PORPHYRINS

CHLOROPHYLL a and b and a group of substances obtained from them by the removal of magnesium and the hydrolysis of the ester groups may be transformed by drastic treatment with alkali into porphyrins which are substances characterized by the type of their absorption spectra. Hans Fischer has established by synthesis the general constitution of the porphyrins and very recently has proved in detail the structure of aetioporphyrin,¹ the final decomposition product of the chlorophyll series. The relationship between the porphyrins and chlorophyll is still unknown. We have discovered a few facts which throw some light on this problem.

The magnesium-free chlorophyll derivatives (the phaeophorbides, phytochlorin e and phytorhodin g) have been found to differ from typical porphyrins (from chlorophyll and blood) in the following respects (1) In dilute alkaline solution they are reduced by sodium hydrosulphite and by the action of hydrogen in the presence of palladinized asbestos (about 2 moles of hydrogen are absorbed): neither of these reagents affects porphyrins. (2) Catalytic hydrogenation in glacial acetic acid yields colorless solutions with the absorption of 3 or 4 moles of hydrogen; on exposure to air reoxidation occurs but the product is different from the original material. Under the same conditions the porphyrins absorb about the same amount of hydrogen² but the product of oxidation is also a porphyrin. Phaeophorbide a and b and phytochlorin e yield substances that appear to be porphyrins; phytorhodin g is transformed to a substance with an absorption spectrum more like that of the bile pigments. It is clear that the porphyrin structure represents a more stable and less reactive grouping of unsaturated linkages and pyrrole nuclei than are present in the chlorophylls and related substances. It

also seems extremely probable that the carbon skeleton characteristic of the porphyrins is already present in the chlorophylls.

We have also found that the phaeophorbides, phytochlorin e and phytorhodin g lose carbon dioxide and water at 150°–250° in diphenyl solution. The formation of carbon dioxide, at least in the case of the non-acidic substance methyl phaeophorbide a, can not be due to a free carboxyl group; the trimethyl ester of phytochlorin e does not lose carbon dioxide, therefore the ester groups are not involved. One of the two crystalline products of the decomposition of phytochlorin e is a porphyrin. We suggest that a lactone linkage is responsible for part of the thermal formation of carbon dioxide, perhaps as follows:



The presence of this same linkage would explain the transformations for which Willstaetter postulated a lactam grouping. The presence of hydroxyl groups was indicated by the recent analyses of Treibs.³ Our own analytical data point in the same direction. It thus seems probable that the carbon skeleton of the porphyrins is modified in chlorophyll by the presence of one or more hydroxyl and carboxyl groups (or lactone groups) on the atoms connecting the pyrrole nuclei. The work is being continued and the details will be published elsewhere as soon as possible.

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¹ H. Fischer and A. Treibs, *Ann.* 466, 188 (1928).

² Compare Kuhn, *Ber.* 61, 2509 (1928).

³ *Ecology*, 9: 412–420. 1928.

³ Treibs and Wiedemann, *Ann.* 466, 264 (1928).