

schreiben ist. Zusatz einer geringen Menge Al (z.B. 0.01 Gew. %) zum deformierten, weissen Zinn erhöht die U.G. derart, dass eine „akute“ Zinnpest eintritt, welche in kurzer Zeit zur völligen Disgregation des weissen Zinns zu führen im Stande ist. Es wurde auf die Bedeutung hingewiesen, welche diesen Erscheinungen auch für das Studium der Polymorphie anderer Metalle zukommt. Hier erschliesst sich ein weites Forschungsgebiet, welches wir bereits in Angriff genommen haben.

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VAN 'T HOFF-Laboratorium.

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**Botany.** — *Note on the mechanism of photosynthesis.* By L. G. M. BAAS BECKING and E. A. HANSON. (From the Botanical Laboratory, the University, Leiden.)

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The chlorophyll is not evenly distributed within the plastid, but is concentrated in small granules, of about  $0.3 \mu$  in diameter (1). These granules possess a great absorptive power for light and contain more than 12 % by volume of chlorophyll (2). Earlier investigations have shown that the chlorophyll is present in these structures probably in monomolecular films, in which the pigment, on its hydrophilic side, is bound to a, probably proteinaceous, carrier (3), while on the lipophilic side, (the phytol) the structure is stabilized by a lipid, lecithinoid or carotinoid in nature.

Moreover, the porphin nucleus of the molecule appears always as a flat plate, whether spread in monomolecular layer on water, or in its amorphous, solid, state, and even in crystals of ethyl chlorophyllid. The porphin-nucleus of chlorophyll shows a surface of  $108 \text{ \AA}^2$  and a thickness of  $4.2 \text{ \AA}$  (4).

There is, therefore, reason to assume that also in the living plastid the porphin-nucleus will show these dimensions in the tangential interphases of the granule. The molecules cannot form a continuous pattern for at physiological pH, they appear to be hydrated, at pH 7 the hydration increasing the area of the nucleus by 9 % (5). Radial movement of assimilates in a granule of this structure is therefore possible, while tangential movement of assimilates might take place on the protein film or between the stabilized phytol chains. The entire granule is therefore in communication with the rest of the plastid.

The porphin-nucleus is asymmetrical. This asymmetry is caused partly by the cyclopentanone ring between the  $\gamma$  methine-carbon and the third pyrrol-ring (6). This ring contains an enolizable keto-group, in which the enol form is favoured by the action of light. The hydrogen of the outer hydroxyl appears to be active; quinone being reduced to hydroquinone in the light (7). This pentanone ring may be, therefore, important

in the chemism of photosynthesis. Other important features of the molecule are its large number of conjugated double bonds and its central Magnesium-atom.

Chlorophyll is fluorescent in the living plastid (8). The conjugated double bonds cause the molecule to absorb strongly in the red end of the spectrum. Fluorescence of molecules in the peripheral shell of the granules may excite molecules in the next shell to fluoresce, as the fluorescence- and absorption-bands of the chlorophyll overlap for the largest part. The carrier molecules do not show any absorption-bands in the red, and do not interfere. Therefore an effective optical energy-transmission is given in the granule. The Magnesium atom in the centre of the molecule seems to regulate the hydration and the activity of the enol-hydrogen (9).

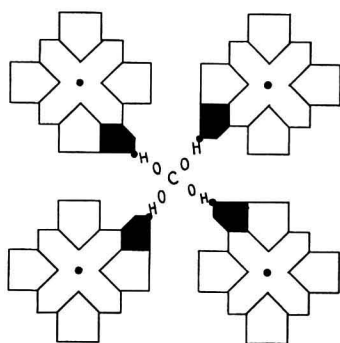
With minor variations, the modern theories on the mechanism of photosynthesis may be divided into two groups. The first group assumes the formation of hydrogen peroxide which, by the action of catalase is decomposed into oxygen and water (10). This idea seems to be untenable both because of recent experimental evidence and because of the fact that in other forms of carbon dioxide-assimilation (whether photosynthetic or chemosynthetic) other peroxides should be formed of which substances chemistry has never heard.

For if hydrogen sulphide should act as hydrogen donor analogy should require a substance of the type  $H_2S_2$  to be formed, while, in the assimilation of the anorgoxidants, or when hydrogen itself is directly brought into the  $CO_2$  molecule, it is hard to imagine which compound of peroxidic nature might originate. The second group of theories consider the chlorophyll itself as a hydrogen donor. Four molecules of chlorophyll contributing the four hydrogens required to reduce one molecule of  $CO_2$ . After this reaction, the chlorophyll should be rehydrogenated at the expense of some hydrogen donor (11). In the case of the green plant, this hydrogen donor should be water; oxygen being liberated. Now it has been established, not only for the green plant but also for the green- and the purple bacteria that the reduction of one molecule of  $CO_2$  requires four energy quanta (12). If the rehydrogenation of the chlorophyll takes place at the expense of two water molecules, this process should also require a large amount of energy, which cannot be found in the four quanta necessary for the transference of the four hydrogen atoms on the  $CO_2$ . If the chlorophyll were rehydrogenated at the expense of  $H_2S$ , less energy would be needed, so that we might expect a different quantum-requirement. As a matter of fact, this requirement is always the same, therefore it is most unlikely that the chlorophyll should act as a hydrogen donor. GAFFRON has pointed out that chlorophyll should only act as a photosensitizer and not as a "photoc enzyme" (13).

The chlorophyll molecules being situated in planes, with their active hydrogens also situated in the same plane, we assume that there exists an active constellation of four chlorophyll molecules, their respective

pentanon rings pointing to the same centre, in which centre the  $\text{CO}_2$  is reduced. The assumption of a porphin "tetrad", fixed to a carrier-molecule, is not improbable when we keep in mind the existence of a similar tetrad in the haemoglobin. In the latter case we have a structure, capable of the binding of two atoms of oxygen, in the former we have a structure with four active hydrogens. In as much as the central Magnesium-atom in the chlorophyll seems to increase the hydration-capacity of the molecule, the porphin-nuclei will be in heat-motion and the statistical probability of the active constellation is rather small. In an orthogonal pattern the probability of the active constellation is  $1/256$ , and the actual geometrical probability will be even smaller. If we assume the presence of an active constellation dictated by chance, only one in a thousand, or even less, molecules of chlorophyll would be active per molecule of  $\text{CO}_2$  reduced. This hypothesis agrees with the experimental data of EMERSON and ARNOLD (14).

We do not know whether the  $\text{CO}_2$  is hydrated by an enzyme, such as found in the blood, nor do we know whether this substance is fixed on the protein as a carbaminic compound, as is shown for haemoglobin (15). We only know that the living plastid has a great affinity for carbon dioxide and that some such process should take place. Several reasons have led us to believe that, if the active porphin-tetrad should be a reality, the carbon dioxide, held in its centre might be present in the form of orthocarbonic acid. The low dissociation-constant of an aqueous solution of carbon dioxide already urged SCHAUM in 1909 to propose this substance rather than  $\text{H}_2\text{CO}_3$ , as the raw material for photosynthesis (16). The pentanon ring being also the centre of hydration we might expect a large hydration tendency in the centre of the porphin tetrad. Here the molecule of orthocarbonic acid may be placed in such a fashion that the distance of its four hydroxyl-hydrogens to the four enol-hydrogens of the pentanon-rings is both short and equal. This may be seen from the structure of a model of this tetrad and is, very schematically, represented in the accompanying figure, which only shows the orthocarbonic acid in



projection. The components of the tetrad, which emit quanta by fluorescence, will cease to emit visible light when a molecule of carbon dioxide is "caught". The hetero-polar character of the orthocarbonic acid is changed by the quanta absorbed and, after the fourth quantum is absorbed, the molecule breaks apart into a glucose-radical, oxygen and water. In the green plant, this oxygen partly enters into to respiratory metabolism, and is partly liberated. Where active hydrogen-donors are present, the

oxygen enters into combination with these compounds (such as

hydrogen, hydrogen sulphide, sulphur, etc.). It is very unlikely that any of such reactions should be endothermic. Therefore all the energy required is furnished by the four light-quanta, the pigment remaining unchanged during the process. The recent findings of NAKAMURA on the photic oxygen emission of "starved" purple bacteria agrees with the above-mentioned hypothesis (17). The only place of the BLACKMAN reaction in the reaction-scheme given in this paper is prior to the photochemical reaction, and consists of the hydration of the carbon dioxide. In this, and in several other respects our hypothesis shows similarity with the ideas of GAFFRON (18).

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