after the adsorption with aluminum hydroxide as above described is markedly more active in tumor production than the most concentrated filtrate, although some of the tumor producing material is carried down with the aluminum. No other explanation seems possible than that both tumor producing principle and some substance or condition inhibiting its activity existed in the fluid prior to adsorption with aluminum hydroxide, the process removing far more of the inhibitor than of the principle. While there is less activity in the aluminum supernatant fluid than in the original extract, yet, unhampered by the inhibitor, it is more active.

The details of the experiments and a discussion of the results will be published later.

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THE DEHYDROGENATION OF CHLORO-PHYLL AND THE MECHANISM OF PHOTOSYNTHESIS

IN a recent paper,¹ it was shown that the allomerization of chlorophyll is essentially a dehydrogenation (oxidation) reaction. We have now been able to obtain additional evidence in favor of this view in a study of the dehydrogenation of the magnesium-free compound methyl phaeophorbide a. In a pyridineacetone solution this compound is oxidized by potassium molybdicyanide; approximately two equivalents of reagent are required per mole. The product (methyl dehydrophaeophorbide a) yields the same hydrolysis products with hot alkali as allomerized phaeophorbide, and like this substance is not further oxidized by molybdicyanide. The difference between the spectra of methyl phaeophorbide a and methyl dehydrophaeophorbide a is slight in the visible range, but considerable in the near ultraviolet.

These facts, which prove that the chlorophyll molecule contains an easily dehydrogenated group, suggest at once a possible mechanism for photosynthesis. Emerson's recent work² has proved that chlorophyll is involved in the so-called Blackman dark reaction, and hence must be a participant in some strictly chemical step in the photochemical process. We suggest that this step is the reduction of carbon dioxide by chlorophyll itself, the other product being dehydrochlorophyll. In order to make the system chlorophyll-dehydrochlorophyll mobile, an enzyme would undoubtedly be necessary; this would account for the sensitivity of the Blackman reaction to hydrocyanic acid. The

¹ Conant, Hyde, Moyer and Dietz, J. Am. Chem. Soc., 53: 359, 1931.

² Robert Emerson, Jour. Gen. Physiol., 12: 609, 623, 1929.

regeneration of chlorophyll would require energy furnished by the light. The steps can be represented thus:

$$Ch = chlorophyll Ch(-2H) = dehydrochlorophyll$$

(1) Dark reaction 12 Ch + 6 CO₂ + enzyme \rightarrow 12 Ch (- 2H) + C₆H₁₂O₆ + 6 H₂O glucose

(2) Light reaction 12 Ch(-2H) + light + 12 H₂O \rightarrow 12 Ch + 6 O₂

This mechanism would appear to account for most of the facts now known about photosynthesis, including Warburg's experiments with a rotating sector. A calculation of the free energy of reduction of carbon dioxide (in the atmosphere) to glucose (in dilute solution) yields information in regard to the necessary reducing intensity of the chlorophyll-dehydrochlorophyll system if it is to function in reaction 1. A reducing intensity of 50 millivolts greater than the hydrogen electrode would be sufficient for reaction 1 to run very far towards completion. A reducing intensity equal to the hydrogen electrode would produce glucose in a thousandth molar solution, if the ratio of chlorophyll to dehydrochlorophyll were kept at about 100 to 1 in a steady state by a combination of reactions 1 and 2. Presumably the glucose or other primary reduction product of carbon dioxide is removed continually from the reaction by a series of irreversible processes. These calculations and a more detailed discussion will be published in full elsewhere.

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