

PERIODIC PHENOMENA IN PHOTOSYNTHESIS

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INTRODUCTION

PHOTOSYNTHESIS, i.e., the process of assimilation of carbon dioxide by plants under the influence of light, is one of the fundamental processes in the vital activity of plants. Many studies, both biological and physicochemical, have been devoted to this process, beginning with those of Timiryazev. We may consider that at present the basic features of photosynthesis have already been elucidated. Nevertheless, certain characteristic peculiarities of this process are not yet completely clear. This is especially true of the kinetics of photosynthesis. For example, it is still not completely clear on what factors the rate (or in other words, the intensity) of photosynthesis depends, and how it is determined. (This quantity is measured in milligrams of carbon dioxide absorbed per unit of leaf surface or unit of mass in unit time.)

The latter problem is very important from the theoretical standpoint, since it is essential to an understanding of the mechanism of the photosynthetic process. In addition, it is of great practical significance, since the rate of growth, ripening, and in the final analysis, the productivity of the plant, depend on the rate of photosynthesis.

A very great number of studies have been devoted to the rate of photosynthesis, and a vast amount of data has been accumulated. First, these studies have examined the relation of the rate of photosynthesis to the illumination; second, they have examined its relation to the concentration of carbon dioxide in the external medium; and third, they have shown that the rate of photosynthesis may vary periodically under constant external conditions (i.e., with constant illumination and carbon-dioxide concentration).

The two former problems have been treated in detail in many monographs, in particular, the book of

Rabinowitch.¹ With respect to the latter problem, the causes of the periodic changes in the rate of photosynthesis are not yet completely clear. Most of the studies devoted to this latter problem have been of a phenomenological, descriptive character. However, there have been some studies which have attempted to relate this peculiarity in the kinetics of photosynthesis to other theoretical and experimental data on the mechanism (and the chemistry) of photosynthesis as a whole (e.g., with the apparatus of the stomata).*

We have given in this article a review of the fundamental studies devoted to the phenomenon of periodicity in the kinetics of photosynthesis, and in addition have presented in detail the studies of the authors² on the same problem.

1. REVIEW OF THE EXPERIMENTAL AND THEORETICAL DATA

We shall discuss first the fundamental features of photosynthesis as a whole. In a green plant, the radiant energy of the sun is used to transform simple inorganic compounds (water, carbon dioxide, and nitrogen compounds) into carbohydrates, proteins, fats, and other organic compounds. The absorption of energy is brought about by a pigment system occurring in special structures, the chloroplasts or plastids, which are distributed in the leaf plasm. Being very small in dimensions (4-10 microns), they comprise about 100 grana each (< 0.1 micron), which contain the pigment system of the leaf (chlorophyll, carotenoids, and other pigments).

The process of photosynthesis consists in: (1) the photochemical reactions, in which the light-absorbing pigment system of the chloroplast participates, and

*See below for more detail on this question.

(2) the dark chemical reactions, which proceed with the participation of enzymes.

As a result of the photochemical reactions, an active reduced form of chlorophyll (ChH) is formed; this is a compound of chlorophyll with hydrogen obtained from water. The photoproducts enter into the system of dark reactions, which amount essentially to the reduction of carbon dioxide to sugar.

The reduction of carbon dioxide takes place in the plasm or stroma of the chloroplasts, while the chlorophyll is localized in the grana. The transfer of hydrogen from (ChH) is carried out by bio-catalysts (hydrogen-carriers). The universal bio-catalysts carrying hydrogen in the cell are: the pyridine nucleotides (the prosthetic group of the dehydrogenase enzymes), the flavins, and the cytochromes. The pyridine nucleotides are the strongest reducing agents of those mentioned.

The presence of CO_2 is necessary, of course, for the dark reactions to take place. This substance enters the cytoplasm from the external medium. In the higher plants, the penetration of CO_2 into the leaf takes place through the openings of the stomata, while in the unicellular algae, CO_2 is absorbed from the water through the entire surface of the cell.

The problem of the nature of the concrete chain of dark reactions has been the subject of many studies which have been presented in detail in the monograph of Rabinowitch.¹ At present, the most plausible system of dark reactions seems to be that proposed by Calvin^{8,9} and his coworkers.

In this system, carbon dioxide is initially combined with the so-called acceptor, a substance having the structure of a pentose (ribulose). Then, from the ribulose and CO_2 are formed glyceric acid, triose phosphate, etc., in the sequence shown in Fig. 1.

Since the process takes place continuously, the CO_2 acceptor must be continuously regenerated in the process. That is, the chain of chemical reactions in this case is closed, or forms a cycle, as is shown in the diagram.

The material balance as a whole in the cycle may be represented as follows. Six CO_2 molecules are joined to six molecules of ribulose diphosphate, forming twelve molecules of phosphoglyceric acid. (This reaction is denoted as carboxylation.) Then, as a result of reduction, twelve molecules of triose phosphate are formed. Of these, ten are transformed into six molecules of ribulose diphosphate, and are thus returned to the cycle. Two molecules of the triose phosphate are transformed into one molecule of a monosaccharide (six-membered sugar), which leaves the site of reaction, representing the "net production" of the cycle.

The sequence of reactions between the various sugars is shown in more detail in Fig. 2. The names of the enzymes catalyzing the individual reactions in the cycle are also given there.

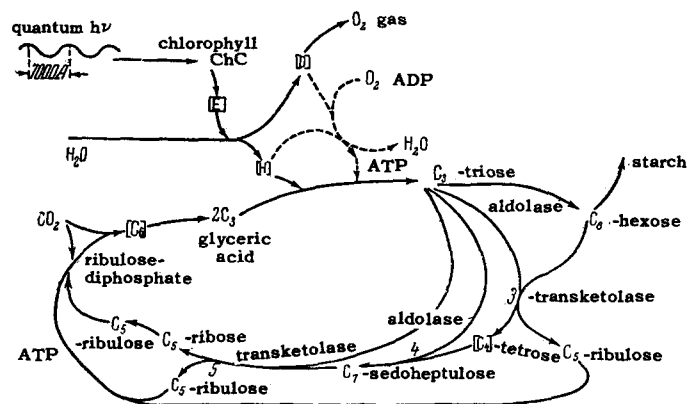


FIG. 1. The scheme of dark reactions in photosynthesis (according to Calvin).

Most of the reactions take place with the aid of enzymes, and thus they proceed rapidly, and apparently reversibly. Only the reactions accompanied by dephosphorylation take place irreversibly, since in these reactions the free energy of the final compound is lower than that of the initial compound.

We note that a supply of free energy is required at two points in the system. First, it is necessary in producing the acceptor, ribulose diphosphate, from ribulose monophosphate. Second, it is necessary in producing triose phosphate from phosphoglyceric acid and the reduced hydrogen-carrier (as was mentioned above, the hydrogen-carrier is triphosphopyridine nucleotide, indicated in the diagram (Fig. 2) as TPN).

In both cases, the free energy is supplied in the form of the energy-rich (high-energy) compound, adenosine triphosphate (ATP). The ATP itself is formed from adenosine diphosphate,* the energy for this process being derived ultimately from that of the absorbed quanta of light.

We must note that Calvin's system is not yet an absolutely established fact. It is possible that further studies will alter essentially many of its parts. However, its fundamental features must remain. Of these, the following seem to us to be important: the closure of the cycle (i.e., the regeneration of the CO_2 acceptor) and the presence in the cycle of practically irreversible reactions associated with phosphorylation and dephosphorylation.

Recently, studies of Calvin and his co-workers¹⁰⁻¹² have shown some indications of a possible assimilation of carbon by another pathway, other than by way of phosphoglyceric acid. These pathways of transformation of carbon in the process of photosynthesis have also been studied in a series of other papers, both in the Soviet Union^{13,14} and abroad.¹⁵⁻¹⁹

* * *

*In the studies of Calvin and his co-workers,⁸ the processes of formation of ATP have been examined in considerable detail. However, we shall not present them here, as this question is not directly related to our topic.

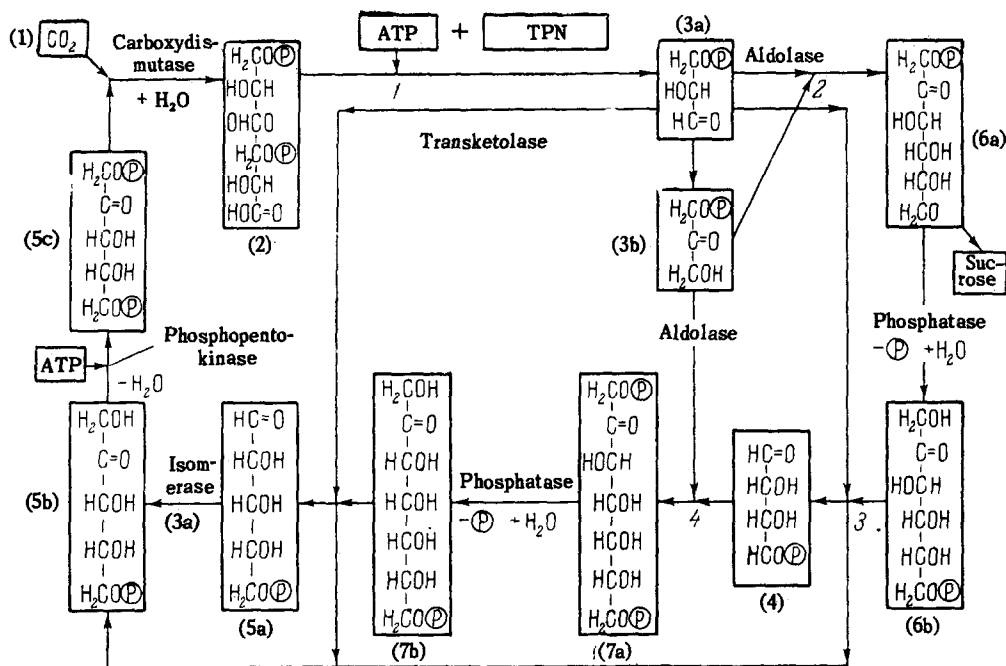


FIG. 2. Scheme of the dark reactions in the Calvin cycle.

Provisional notation: ATP – adenosine triphosphate, TPN – triphosphopyridine nucleotide (denoted by X for short), (1) – carbon dioxide (C_1); (2) – phosphoglyceric acid; (3a) – triose phosphate (aldo-form); (3b) – triose phosphate (keto-form) (C_3); (4) – tetrose phosphate (C_4); (5a) – ribose phosphate; (5b) – ribulose phosphate (C_5); (6a) – hexose phosphate; (6b) – hexose diphosphate (C_6); (7a) – sedoheptulose diphosphate; (7b) – sedoheptulose phosphate (C_7); The fundamental reactions taking place at points 1-5 are:

1. $C_5 + C_1 + X \rightarrow 2C_3$.
2. $2C_3 \rightarrow C_6$.
3. $C_6 + C_3 \rightleftharpoons C_4 + C_5$.
4. $C_4 + C_3 \rightleftharpoons C_7$.
5. $C_7 + C_3 \rightleftharpoons 2C_5$.

These reactions are catalyzed by the enzymes: aldolase and transketolase.

We shall now consider in greater detail the experimental data on periodic changes in the rate of photosynthesis.

Three phenomena are of interest here:

1. The phenomenon of midday depression.
2. Photoperiodism.
3. The oscillation in the rate of the initiation of photosynthesis.

1. Midday depression. It has been shown experimentally that in the course of the day, with more or less constant illumination, the rate of photosynthesis does not remain constant, but varies periodically. As a rule, the minimum rate is found in the middle of the day, and has been called the midday depression.

There has been a voluminous literature on the phenomenon of depression and the irregularity of the diurnal variation of photosynthesis. A considerable part of this literature is cited in reference 1, as well as in the later reference 20. We shall discuss only a few studies.

Detailed studies have been carried out by the school of Kostychev and Votchak. Much space in the papers of Nichiporovich²¹⁻²³ has been devoted to this problem.

It has been shown that depression occurs in plants from varying geographical latitudes.^{24,25} The following characteristic peculiarities of this phenomenon have been elucidated: (a) the depression is especially marked at high light intensities.²⁶⁻²⁹ When the light intensity is reduced, depression is not observed at all, or in any case, is less clearly marked;^{27,30} (b) the depth of the depression, as well as whether it occurs, depends on the age of the plant: it is deeper in old plants, while it is hardly noticeable in young ones.^{24,31} Further, many authors (Kostychev, Filzer^{25,27,32})

have found that the depth of depression depends on the prior history of the plant.

Above all, all these data are evidence that the depression is to a considerable degree associated with the state of the products of photosynthesis, i.e., with the dark reactions.

Most of these studies have been carried out under natural conditions. That is, the illumination, temperature, etc., were not kept constant. For the elucidation of the nature of the phenomenon, those studies are of interest which have been carried out with constant prolonged illumination under laboratory conditions.^{32,24,25}

The fundamental conclusion from these studies which has been formulated especially clearly in some recent articles,^{34,35} consists in the following: the diurnal course of photosynthesis, practically under any given experimental conditions, is inhomogeneous and periodic. Periodicity is shown even under constant conditions in the surroundings (light, temperature, humidity).

There have been many attempts to explain this phenomenon, or in any case, to find its basic causes. The first explanation subjected to study was that of overheating of the plant. However, the studies of Kostychev et al. showed that the variation in temperature (the time-dependence of the temperature) and the rate of photosynthesis are not correlated.^{24,25} In addition, cases are known in which depression begins without any overheating whatever.²⁵ Finally, the depression phenomenon is also found in aquatic plants,²⁶ for which there can be no question of overheating.

In many of the studies, attempts were made to explain the depression phenomenon by the action of the

stomatal apparatus.^{36,33} In order to clarify this point, we must discuss the mechanism of the stomatal system. The orifices of the stomata are distributed on the leaf surfaces of higher plants. They play a fundamental role in regulating the water balance of the leaf, since transpiration (evaporation of water) takes place through these orifices. Besides, it is also primarily through them that the gas exchange of the plant with the external medium takes place, namely the absorption of carbon dioxide from the air by the leaf and the evolution of oxygen.

The stomata are bordered by special guard cells. Depending on the water content of the leaf, and hence on the osmotic pressure, these cells may swell (this phenomenon is denoted as turgor). As a result, the orifice is expanded and the transpiration increases. Upon increase of the osmotic pressure of the intercellular fluid (i.e., upon decrease of its water content), the stomatal cells contract, and the stomatal orifice becomes smaller, even to the point of complete closure of the stoma. When the stomata are completely closed, transpiration is interrupted, as well as any gas exchange. Thus we see that in the higher plants, the stomatal apparatus may in fact influence the rate of gas exchange, and consequently, of photosynthesis.

This has been confirmed experimentally recently.³⁷ Even earlier, Stalfelt³⁶ also found that the rate of photosynthesis depends on the degree of opening of the stomata. However, these experiments were performed under conditions far from those in which depression occurs, and they did not answer the question whether the stomata play the fundamental role in the phenomenon of depression.

On the other hand, Kostychev²⁶ has shown that depression occurs in aquatic plants, in spite of the absence of stomata. In a recent study,³⁰ depression was found at the most varied degrees of opening of the stomata. It was shown in the same study that in many plants, the stomata are less open at the time of depression than at the maximum of photosynthesis. Thus, the stomatal mechanism can apparently play a certain role in the depression phenomena, namely that of increasing the depth of depression. However, it is not the principal cause of the depression.

The attempts to explain the periodicity of photosynthesis in terms of internal factors, which have been given the general designation of "plasmatic factors," are of great interest.^{38,39} Here, the rhythmicity of photosynthesis is considered to be an internal characteristic of the plant. That is, in the terminology of Bünning,^{40,41} it is a manifestation of an "endogenous rhythm."*

We must note that in the studies cited above, no attempts were made to elucidate the nature of the

*According to Bünning, an "endogenous rhythm" is a biological process which varies periodically, although the external conditions are constant.

plasmatic factor or the mechanism (or chemistry) of the endogenous rhythm. Thus the discussions on this subject have been quite abstract.

At present it seems to us possible and appropriate to examine the question of just what plasmatic processes are capable of giving rise to an internal (endogenous) rhythm, and to relate this rhythm to the chemistry of the dark stages of photosynthesis. Such an attempt is presented in the following sections of this article.

2. Photoperiodism. It has been established from extensive experimental material that every type of plant possesses its own optimal rhythm of external illumination (i.e., optimal length of light and dark periods in the course of the day).

Plants are classified according to their nature into long-day plants (for which a schedule of long light periods and relatively short dark periods is optimal) and short-day plants. The former group are mainly distributed at more northern latitudes, while the latter are distributed relatively farther south.

A change in the light schedule, e.g., a transfer of a short-day plant to long-day conditions, does not as a rule kill the plant, but has a negative influence on its blooming, fruit-bearing growth, and other physiological processes.

In problems related to photoperiodism, the primary attention of researchers has been attracted not to the process of photoperiodism itself, but above all, to the reproductive processes. It has been shown that it is not necessary that plants remain for their entire lifetime at the optimal length of day for flowering and fruit-bearing to take place. Rather, the influence of the optimal photoperiods for a relatively short time was sufficient (Razumov,⁴² Égiz,⁴³ Lyubimenko and Shchegolova⁴⁴).

We may distinguish two hypotheses in the understanding and elucidation of the internal causes of photoperiodism: (1) the existence of an internal endogenous rhythm,^{40,41} and (2) the direct action of the light on specific products necessary for reproduction. The latter viewpoint has been developed by Chaïlakhyan.^{45,46} He has advanced the hypothesis that specific reproductive substances are sensitive to light, decomposing in the light in short-day plants, while they are more stable in long-day plants.*

It seems to us that the first viewpoint agrees better with reality. Evidence for this is given by the data of references 40, 41, 47, 34, as well as 48 — 50. In these studies, under constant illumination, periodic changes were observed not only in the rate of photosynthesis, but also in the relations between products. It was found that both quantities varied periodically.

*We must emphasize that the photochemical decomposition of specific reproductive substances according to reference 46 must take place in a rather unusual fashion. Namely, it must be only slightly sensitive to the frequency of the light and the temperature, a behavior not usual in photochemical reactions.

It seems to us that in the case in which plants have an internal endogenous rhythm, they will develop normally when the external illumination is synchronized with the internal rhythm. In the opposite case, the composition of the products in the plant will oscillate widely and will differ from the normal composition. Above all, this will affect the reproductive processes, which are most sensitive to the internal state of the plant. This idea will be developed in somewhat greater detail below.

3. Oscillation in rate at the initiation of photosynthesis. When a plant is transferred from darkness to light, oscillations in the rate of photosynthesis are found.⁵¹⁻⁵⁴ The period of these oscillations amounts to several minutes. The amplitude of the oscillations gradually decays.

The nature of this phenomenon is not yet very clear. It is highly probable that it is closely related to the damped periodic phenomena in respiration and transpiration which appear when the light status of the plant is changed (i.e., upon replacing light by darkness or vice versa).³⁷

The possibility of a relation between these periodic phenomena and the internal rhythm of photosynthesis will be discussed somewhat later on.

2. THE HYPOTHESIS OF THE SELF-OSCILLATING MODE OF THE DARK REACTIONS OF PHOTOSYNTHESIS

In its very nature, every internal rhythm is nothing other than a self-oscillating mode in the internal chemical reactions. In the given case, this is most likely a self-oscillation in the dark reactions of photosynthesis. A process is designated as self-oscillating when the rate of the chemical reactions itself is not constant, but varies periodically, under constant external conditions (temperature, light intensity, CO₂ concentration). Thus we see that the definitions of self-oscillating and endogenous rhythms given by Bünning simply coincide. Self-oscillating processes are already known, and have been described in chemical kinetics (e.g., self-oscillation in flame processes). It follows from the theory of self-oscillation that such phenomena may arise under the following conditions: (a) The presence of positive feedback. In chemical kinetics, positive feedback means that the rate of the process is increased as the concentration of intermediate or final products is increased. In other words, such a process is called self-accelerating or autocatalytic. (b) The presence of negative feedback, i.e., a process such that the rate of the chemical reactions is diminished upon accumulation of a large amount of the products. Negative feedback is necessary, as a rule, in order that the rate of the self-accelerating process should not become too great (i.e., in order that its rate be limited). It is also necessary that the dependence of the negative feedback on the concentration of

the final or intermediate products should be of a different character from that of the positive feedback. Otherwise, these two factors would simply compensate for each other, and self-oscillation would not set in.

In other words, positive feedback means that the rate of any given reaction is proportional to some positive power of the concentration of the final or intermediate products (the proportionality constant being positive). Negative feedback means that the rate of the process is proportional to the concentration of final or intermediate products, but with a negative proportionality constant.

We must state that the existence of these conditions is necessary for the appearance of self-oscillation, but not sufficient. In other words, even when these conditions are fulfilled, the process may occur in a steady state, rather than in an oscillating fashion, if the steady state of the process is stable. The occurrence of stability itself depends on the external conditions (the values of the light intensity, etc.)

We must note that both necessary conditions for the appearance of self-oscillation occur in the photosynthesis process. In fact, it can no longer be doubted that the process of photosynthesis is autocatalytic,¹ and hence, positive feedback actually occurs.* With regard to negative feedback, it generally occurs in all self-regulating systems, and consequently, is unconditionally present in any process in a living organism.

The stability or instability of the steady-state process (and hence, the appearance of self-oscillation) may be studied only for some concrete scheme of photosynthesis. As a concrete scheme, we may use the Calvin cycle (see above). We must note that in the calculations given below, this cycle enters only as a concrete example, corresponding to reality in its basic features. For these calculations, certain characteristic features of this cycle are primary, namely: its closure, the regeneration of the CO₂ acceptor, and the participation of a hydrogen donor (nucleoprotein).

The system of calculations given below has a certain independent value. We can easily study with its aid the appearance of an oscillatory state in any other cycle of dark reactions of photosynthesis which might have more experimental basis than the Calvin cycle.

Here we must note that we have used certain assumptions in the calculations which did not take part directly in the Calvin cycle. Namely, we have as-

*Concretely, the autocatalytic character of photosynthesis is manifested in the fact that the primary CO₂ acceptor (which is the catalyst for the given process) is regenerated in the process of photosynthesis from the intermediate or final products. Hence, its concentration is proportional to the concentration of final products. This fact of the regeneration of the acceptor (or in other words, the fact that the cycle of dark reactions is closed) does not depend on the concrete scheme of the process, and according to reference 55, must always take place.

sumed that: (1) the nucleoprotein (hydrogen donor) itself is formed in the process of photosynthesis, and its concentration is proportional to that of the primary intermediate products of photosynthesis (ribulose and phosphotriose), and also (2) the photosynthetic cycle is associated with the respiratory Krebs cycle, and even in the absence of photosynthesis or when its rate is exceedingly low, triose and ribulose are formed at constant rate as a result of the hydrolysis of starch, and (3) as was mentioned above, we have assumed that the enzymatic reactions proceed rapidly and are completely reversible. Certain reactions in the Calvin scheme involve dephosphorylation. Such, for example, is the reaction of formation of glucose from triose. These reactions proceed more slowly than the enzymatic reactions, and are irreversible.

3. KINETIC EQUATIONS OF PHOTOSYNTHESIS

The study of the Calvin cycle with regard to the appearance of self-oscillation was carried out as follows: According to Calvin's scheme, we may write a system of chemical kinetic equations as follows:

1. The equation for the change in the concentration of triose C_3 :

$$\frac{dC_3}{dt} = \alpha_1 C_5 [CO_2] X - \alpha_2 C_3^2 - \alpha_3 C_3 C_6 + \alpha_0 - \alpha_4 C_3 C_4 - \alpha_5 C_3 C_7. \quad (1)$$

Here, the term $\alpha_1 C_5 [CO_2] X$ is the amount of triose formed from ribulose (C_5) and carbon dioxide (the concentration of which we shall consider hereinafter as constant, and which we shall include in the coefficient α_1) with the participation of the hydrogen donor X. (As was mentioned above, we shall consider the latter to be proportional to the concentration of triose C_3 , $X = aC_3$.) The term $\alpha_2 C_3^2$ is the amount of triose removed as glucose. The order of this reaction (the exponent) was assumed from stoichiometry.

The terms $\alpha_3 C_3 C_6$, $\alpha_4 C_3 C_4$, and $\alpha_5 C_3 C_7$ describe the change in concentration of triose due to the reactions at points 3, 4, and 5 (see Figs. 1-2), which are considered to be reversible according to the Calvin cycle, as has been mentioned above.

Finally, the constant positive term α_0 describes the formation of triose due to respiration.

2. The equation for the balance of hexose C_6 is:

$$\frac{dC_6}{dt} = \beta_1 C_3^2 - \beta_2 C_6^2 - \beta_3 C_6 C_3 + \beta_4 C_5 C_4. \quad (2)$$

Here, $\beta_1 C_3^2$ gives the amount of hexose formed from triose; $\beta_2 C_6^2$ is the decrease of hexose due to conversion to starch; $\beta_3 C_6 C_3$ is the decrease of hexose due to formation of pentose and tetrose (according to the Calvin scheme); and $\beta_4 C_5 C_4$ is the increase in hexose due to the reversibility of the reaction at point 3.

In order to determine the concentrations C_4 , C_5 , C_7 , we shall make use of the fact that the reactions at points 3, 4, and 5 are reversible, that the rate of establishment of equilibrium at these points is great,

and hence, that equilibrium is quickly established.* This gives the relations

$$\frac{C_3 C_6}{C_4 C_5} = K_1, \quad \frac{C_7}{C_4 C_3} = K_2, \quad \frac{C_3 C_7}{C_5^2} = K_3, \quad (3)$$

where K_1 , K_2 , and K_3 are equilibrium constants independent of the concentrations. Hence, we find

$$C_4 = \left(\frac{K_3}{K_1 K_2}\right)^{1/3} C_6^{2/3}, \quad C_5 = \left(\frac{K_2}{K_3}\right)^{1/2} \left(\frac{K_3}{K_1 K_2}\right)^{1/6} C_6^{1/3} C_3, \\ C_7 = K_2 \left(\frac{K_3}{K_1 K_2}\right)^{1/3} C_6^{2/3} C_3. \quad (4)$$

Substituting these values into the equation for C_3 and C_6 , we find

$$\alpha_1 C_5 X = \alpha_1 \left(\frac{K_2}{K_3}\right)^{1/2} \left(\frac{K_3}{K_1 K_2}\right)^{1/6} C_6^{1/3} C_3, \quad \alpha C_3 = \alpha_1' C_6^{1/3} C_3^2. \quad (5)$$

Here α_1' is a new coefficient, which is a combination of all the quantities not depending on the concentrations C_6 and C_3 . Hence,†

$$C_4 C_5 \propto \frac{1}{K_1} C_3 C_6, \quad C_4 C_3 \propto C_7 \propto C_3 C_6^{2/3}, \quad C_5^2 \propto C_3 C_7 \propto C_6^{2/3} C_3^2. \quad (6)$$

Now the equation may be rewritten as

$$\frac{dC_3}{dt} = \alpha_1' C_3^2 C_6^{1/3} - \alpha_2' C_3^2 - \alpha_3' C_3 C_6 - \alpha_4' C_3 C_6^{2/3} - \alpha_5' C_3^2 C_6^{2/3} + \alpha_0. \quad (7)$$

To simplify the equation, we shall neglect the terms in the series having fractional exponents.‡ Namely, we shall assume that

*These relations might be derived in another manner, by using only the equations of chemical kinetics; for example, we may write the following equation for tetrose C_4 :

$$\frac{dC_4}{dt} = \eta_1 C_3 C_6 - \eta_2 C_4 C_5 + \eta_3 C_7 - \eta_4 C_4 C_3.$$

Further, we must take into account the fact that the quantity dC_4/dt must be of the same order of magnitude as dC_3/dt , while the absolute value of each of the terms on the right-hand side is considerably greater than that of dC_3/dt , since each term on the right-hand side is the rate of an enzymatic process, and hence, is much larger than dC_3/dt (which is the rate of a non-enzymatic, irreversible process). Hence, in order to satisfy the equation, it is necessary, for example, that the terms $\eta_1 C_3 C_6$ and $-\eta_2 C_4 C_5$ and the terms $\eta_3 C_7$ and $-\eta_4 C_4 C_3$ should compensate each other to a high degree of accuracy. That is, they should satisfy $\eta_1 C_3 C_6 = \eta_2 C_4 C_5$, and $\eta_3 C_7 = \eta_4 C_4 C_3$. Hence the relations follow:

$$\frac{C_3 C_6}{C_4 C_5} = K_1, \quad \frac{C_4 C_3}{C_7} = K_2.$$

†In these relations, the fact of proportionality itself (denoted by the symbol \propto) is of importance to us. The proportionality coefficients and their expressions in terms of K_1 , K_2 , and K_3 have not been written out here, since their values will be determined below from other considerations.

‡Such a dependence, e.g., $C_6^{1/3}$, is a weak dependence. Thus, if we replace the term $C_6^{1/3}$ by a constant, this will hardly influence the results of a qualitative study of the equations. Besides, we have assumed in deriving the equations that the order of the reaction, i.e., the exponent of the concentration, is determined by stoichiometry. However, as is known, the true order of a reaction may be somewhat different from the stoichiometric. Hence, it is in agreement with the accuracy of the derivation of the equations if we neglect the fractional powers in this case. On the other hand, the further study is considerably simplified by neglecting them and simplifying the corresponding terms.

$$\alpha'_1 C_3^2 C_6^{1/3} \simeq \alpha'_1 C_3^2, \quad \alpha'_4 C_3 C_6^{2/3} \simeq \alpha'_4 C_3 C_6, \quad \alpha'_2 C_3^2 C_6^{2/3} \simeq \alpha'_2 C_3^2. \quad (8)$$

Then

$$\frac{dC_3}{dt} = \alpha''_1 C_3^2 - \alpha''_2 C_3 C_6 + \alpha_0, \quad (9)$$

where

$$\alpha''_1 = \alpha'_1 - \alpha'_2 - \alpha'_3, \quad \alpha''_2 = \alpha'_3 + \alpha'_4.$$

Since the previously derived coefficients α and α'_1 will no longer enter into the treatment below, we shall omit the prime and the designations of the coefficients, and shall write finally

$$\frac{dC_3}{dt} = \alpha C_3^2 - \alpha_2 C_3 C_6 + \alpha_0. \quad (10)$$

The analogous equation for hexose will have the form

$$\frac{dC_6}{dt} = \beta_1 C_3^2 - \beta_2 C_6^2 - \beta_3 C_6 C_3. \quad (11)$$

Let us now study the system of equations which we have derived. In a steady state of the photosynthesis process, in which the coefficients are independent of time, the quantities $dC_3/dt = dC_6/dt = 0$, and consequently,

$$\beta_1 C_3^2 - \beta_2 C_6^2 - \beta_3 C_6 C_3 = 0, \quad \alpha_1 C_3^2 - \alpha_2 C_3 C_6 + \alpha_0 = 0. \quad (12)$$

Here C_3^0 and C_6^0 are the concentrations of triose and hexose in the steady state.

For the sake of convenience, we shall now transform to dimensionless concentrations \bar{C}_3 and \bar{C}_6 , taking the steady-state concentrations as units: $\bar{C}_3^0 = \bar{C}_6^0 = 1$. In other words, we shall measure the concentrations \bar{C}_3 and \bar{C}_6 not in moles per liter, but in fractions of the steady-state concentrations.* In terms of the new symbols, the kinetic equations retain their previous form

$$\frac{d\bar{C}_3}{dt} = \bar{\alpha}_1 \bar{C}_3^2 - \bar{\alpha}_2 \bar{C}_3 \bar{C}_6 + \bar{\alpha}_0; \quad (13a)$$

$$\frac{d\bar{C}_6}{dt} = \bar{\beta}_1 \bar{C}_3^2 - \bar{\beta}_2 \bar{C}_6^2 - \bar{\beta}_3 \bar{C}_6 \bar{C}_3, \quad (13b)$$

where

$$\bar{\alpha}_1 = \alpha_1 C_3^0, \quad \bar{\alpha}_2 = \alpha_2 C_6^0, \quad \bar{\alpha}_0 = \alpha_0 \frac{1}{C_3^0},$$

$$\bar{\beta}_1 = \beta_1 \frac{C_3^0}{C_6^0}, \quad \bar{\beta}_2 = \beta_2 C_6^1, \quad \bar{\beta}_3 = \beta_3 C_3^0.$$

The equations of material balance in the steady state [Eqs. (12)] acquire the following form in terms of the new variables

*We must note that if the concentrations C_3^0 and C_6^0 expressed in moles per liter differ greatly from one another (by several orders of magnitude), then this transformation to dimensionless concentrations (for which $\bar{C}_3^0 = \bar{C}_6^0 = 1$) may introduce a certain inconvenience. This is because the ratio of \bar{C}_3 to \bar{C}_6 then will not give the true ratio of concentrations C_3/C_6 . However, in this case, for example according to references 49-50, in the steady-state the concentrations of triose and hexose (expressed in moles per liter) are of the same order of magnitude. Hence, in the present case, the ratio of the dimensionless concentrations \bar{C}_3 and \bar{C}_6 will give the order of magnitude of the true ratio of concentrations.

$$\left. \begin{aligned} \bar{\beta}_1 - \bar{\beta}_2 - \bar{\beta}_3 &= 0, \\ \bar{\alpha}_1 - \bar{\alpha}_2 - \bar{\alpha}_0 &= 0. \end{aligned} \right\} \quad (14)$$

Hereinafter, since we shall be dealing with quantities in terms of the new variables, we may omit the bars:

$$\beta_1 - \beta_2 - \beta_3 = 0, \quad (15a)$$

$$\alpha_1 - \alpha_2 + \alpha_0 = 0, \quad (15b)$$

or

$$\beta_1 \left(1 - \frac{\beta_2}{\beta_1} - \frac{\beta_3}{\beta_1} \right) = 0, \quad \alpha_1 \left(1 - \frac{\alpha_2}{\alpha_1} + \frac{\alpha_0}{\alpha_1} \right) = 0.$$

We must note that the coefficients α and β here are not dimensionless, but, as may be easily seen from Eq. (18), have the dimensions of reciprocal time (since the left-hand side of the equations contains the time-derivative of a dimensionless quantity, and on the right, besides the coefficients α and β , there are only dimensionless quantities).

We shall now estimate the orders of magnitude of the ratios of the coefficients

$$\frac{\beta_2}{\beta_1} \text{ and } \frac{\beta_3}{\beta_1}, \quad \frac{\alpha_0}{\alpha_1} \text{ and } \frac{\alpha_2}{\alpha_1}.$$

In the steady state, the coefficient β_1 is the quantity of hexose formed from triose per unit time, the coefficient β_2 is the amount of hexose removed from the Calvin cycle as starch in the same time, and β_3 is the amount of hexose returned to the cycle. In each turn of the cycle, i.e., in the assimilation of one molecule of carbon dioxide, one molecule of hexose takes part. Hence, in order that one molecule of hexose may leave the cycle as starch, six turns of the cycle are necessary. Thus, the amount of glucose leaving the cycle per unit time as starch (coefficient β_2) must be one-sixth as large as the amount which is returned to the cycle in the same time (coefficient β_3):

$$\beta_2 = \frac{1}{6} \beta_3.$$

By use of Eq. (15a), we find

$$\beta_2 = \frac{1}{7} \beta_1, \quad \beta_3 = \frac{6}{7} \beta_1. \quad (16)$$

We shall now estimate the coefficient α_0 . It is the amount of triose formed per unit time in the steady state from starch, due to the respiration process. This quantity must be small, not only in comparison with the amount of triose transformed into pentose, tetrose, and sedoheptulose (the latter is expressed by the coefficient α_2), but also in comparison with the amount of triose leaving the cycle. In the contrary case, the net production of photosynthesis in the steady state would be negative.

Thus, the condition $\alpha_0/\alpha_2 \ll \beta_2/\beta_1$ must be satisfied. Then, from the equation of material balance (15b),

$$\frac{\alpha_2}{\alpha_1} = 1 + \frac{\alpha_0}{\alpha_1} \sim 1. \quad (17)$$

Thus, of the six quantities $(\alpha_0, \alpha_1, \alpha_2, \beta_1, \beta_2, \beta_3)$,

only two remain undetermined: β_1 and α_1 . In view of the considerations given above (see the footnote on p. 856), the ratio of these quantities must be of the order of unity. However, we shall discuss the value of this ratio in more detail below.

The absolute magnitude of any of these quantities (e.g., α_1) is not essential to the study of the equations. In fact, by introducing the dimensionless time $\tau = \alpha_1 t$, we may rewrite Eqs. (13) in such a way that the coefficient α_1 does not enter into them:*

$$\frac{dC_3}{d\tau} = C_3^2 - \frac{\alpha_2}{\alpha_1} C_3 C_6 + \frac{\alpha_0}{\alpha_1}; \quad (18a)$$

$$\frac{dC}{d\tau} = \frac{\beta_1}{\alpha_1} \left\{ C_3^2 - \frac{\beta_2}{\beta_1} C_6^2 - \frac{\beta_3}{\beta_1} C_3 C_6 \right\}. \quad (18b)$$

However, we shall need to know the absolute magnitude of α_1 below, in the interpretation of the results and their comparison with the experimental data. We must state that it is impossible to define the value of α_1 unambiguously, since it depends on the external conditions. In fact, the concentrations of carbon dioxide and the hydrogen donor enter into the coefficient α_1 . In turn, the latter depends on the light intensity. Thus, the coefficient α_1 must be increased by increasing the light intensity or the concentration of carbon dioxide.

The coefficient β_1 must also depend on the light intensity and the carbon dioxide concentration, since β_1 [in terms of the previous symbols, $\bar{\beta}_1 = \beta_1 (\bar{C}_3^2 / \bar{C}_6^2)$] depends on the steady-state concentrations C_3^0 and C_6^0 . Thus it becomes larger as the rate of the photosynthesis process increases. Hence the size of the ratio α_1 / β_1 must depend more weakly on the external conditions than the coefficient α_1 itself does.

4. A STUDY OF THE KINETIC EQUATIONS

We shall carry out the study of the system (18) as follows.

First, we shall study whether the steady state is stable (and if it is stable, under what conditions). If it is stable, photosynthesis will occur at a constant rate, and self-oscillations will not appear. Second, if it is unstable, then we shall find the pattern (no longer steady-state) which actually is established. Third, we shall try to interpret the results obtained by comparison with experimental data (Sec. 5).

1. The study of stability is ordinarily conducted by the method of small variations.

*The meaning of this dimensionless time consists in the following: the time τ or t is measured not in seconds or minutes, but in units $1/\alpha$, that is, a certain characteristic period is taken as the unit. In the present case, this characteristic period is equal to the time for one "turn" of the Calvin cycle, i.e., the time during which any labeled carbon atom introduced in the form of ribulose passes through the entire cycle of Calvin's chemical reactions, and again becomes ribulose. This time may be estimated (indeed very roughly) from the experimental data.⁵⁰ It turns out to be of the order of minutes. Thus, $1/\alpha_1$ is a quantity of the order of minutes.

Let us consider the system (18) in the region in which the concentrations C_3 and C_6 differ slightly from unity:

$$C_3 = 1 + x, \quad C_6 = 1 + y, \quad x, y \ll 1. \quad (19)$$

In this region, we may neglect the quantities x^2 , y^2 , and xy in comparison with x and y . Consequently, system (18) is transformed into a linear homogeneous system:

$$\frac{dx}{d\tau} = \left(1 - \frac{\alpha_0}{\alpha_1}\right)x - \left(1 - \frac{\alpha_0}{\alpha_1}\right)y, \quad (20a)$$

$$\frac{dy}{d\tau} = \frac{\beta_1}{\alpha_1} \frac{8}{7} x - \frac{\beta_1}{\alpha_1} \frac{8}{7} y. \quad (20b)$$

In writing down this system of equations, we have used the relations (see above):

$$\frac{\beta_2}{\beta_1} = \frac{1}{7}, \quad \frac{\beta_3}{\beta_1} = \frac{6}{7}, \quad \frac{\alpha_2}{\alpha_1} = 1 + \frac{\alpha_0}{\alpha_1}.$$

We shall seek a solution of these equations in the form

$$x = x_0 e^{\lambda \tau}, \quad y = y_0 e^{\lambda \tau},$$

where x_0 and y_0 are the small initial deviations. Substituting these expressions into Eqs. (20), we obtain the algebraic system:

$$\left. \begin{aligned} \lambda x_0 &= \left(1 - \frac{\alpha_0}{\alpha_1}\right)x_0 - \left(1 + \frac{\alpha_0}{\alpha_1}\right)y_0, \\ \lambda y_0 &= \frac{\beta_1}{\alpha_1} \frac{8}{7} x_0 - \frac{\beta_1}{\alpha_1} \frac{8}{7} y_0. \end{aligned} \right\} \quad (21)$$

These equations form a consistent system only in case that the following condition is satisfied:

$$\left| \begin{aligned} \left(1 - \frac{\alpha_0}{\alpha_1}\right) - \lambda, & \left(1 + \frac{\alpha_0}{\alpha_1}\right) \\ \frac{\beta_1}{\alpha_1} \frac{8}{7}, & -\frac{8}{7} \frac{\beta_1}{\alpha_1} - \lambda \end{aligned} \right| = - \left[\left(1 - \frac{\alpha_0}{\alpha_1}\right) - \lambda \right] \left(\frac{8}{7} \frac{\beta_1}{\alpha_1} + \lambda \right) + \frac{8}{7} \left(1 + \frac{\alpha_0}{\alpha_1}\right) \frac{\beta_1}{\alpha_1} = 0. \quad (22)$$

We may easily find the roots of the latter quadratic equation for λ :

$$\lambda_{1,2} = -\frac{1}{2} \left[\frac{8}{7} \frac{\beta_1}{\alpha_1} - 1 + \frac{\alpha_0}{\alpha_1} \right] \pm \sqrt{\frac{1}{4} \left[\frac{8}{7} \frac{\beta_1}{\alpha_1} - 1 + \frac{\alpha_0}{\alpha_1} \right]^2 - \frac{8}{7} \frac{\beta_1}{\alpha_1} \frac{2\alpha_0}{\alpha_1}}. \quad (23)$$

Thus we see the sign of the real part of the roots $\lambda_{1,2}$ is determined by the first term $-\frac{1}{2} [(8\beta_1/7\alpha_1) - 1 + (\alpha_0/\alpha_1)]$.

In order to solve the problem of stability, the important fact for us is the sign of the quantity λ . In particular, if λ is negative, then the quantities $x, y \sim \exp \lambda \tau$ will decrease in time. In this case, the steady state is stable, since any initial deviation will decay in time according to the law $\exp(-|\lambda| \tau)$, and the system will return to its initial state.

If λ is positive, then any perturbation will increase in time as $\exp \lambda \tau$, and sooner or later, will become of the order of magnitude of the steady-state concentration itself. In this case, the steady state will be un-

stable, and will actually not be realized. We cannot answer the question of what state will actually occur by means of the method of small variations (since the deviations increase, and in time cease to be small, so that it becomes incorrect to neglect y^2 and x^2 in comparison with x and y).

Thus, in the present case, the steady state is stable if

$$-\frac{1}{2} \frac{8}{7} \frac{\beta_1}{\alpha_1} + \left(1 - \frac{\alpha_0}{\alpha_1}\right) \frac{1}{2} < 0,$$

and unstable if

$$-\frac{1}{2} \frac{8}{7} \frac{\beta_1}{\alpha_1} + \left(1 - \frac{\alpha_0}{\alpha_1}\right) \frac{1}{2} > 0.$$

The transition from stability to instability will take place when

$$\left. \begin{aligned} -\frac{1}{2} \frac{8}{7} \frac{\beta_1}{\alpha_1} + \left(1 - \frac{\alpha_0}{\alpha_1}\right) \frac{1}{2} &= 0, \\ \frac{\beta_1}{\alpha_1} &= \frac{7}{8} \left(1 - \frac{\alpha_0}{\alpha_1}\right) \approx 0.87 \end{aligned} \right\} \quad (24)$$

(since $\alpha_0/\alpha_1 \ll 1$). Thus we see that as α_1 increases (as might be associated, for example, with an increase in the light intensity), the stable state may become unstable.

2. We shall study now the case in which the steady state is unstable, and

$$\frac{\beta_1}{\alpha_1} < \frac{7}{8} \left(1 - \frac{\alpha_0}{\alpha_1}\right).$$

For this purpose, we must solve the system of nonlinear equations (18). It is not possible to find an analytic solution of this system, and hence, we shall use the graphic method of isoclines. Indeed, the solution may be found (as in any numerical or graphical method) only for some concrete case, i.e., by assigning all of the numerical values entering into the parametric equation. It has already been determined that $\alpha_0/\alpha_1 \ll 1/7$; now we shall assume for the sake of concreteness that $\alpha_0/\alpha_1 \sim (1/3)(1/7) \approx (1/20)$. We shall select a value of the coefficient β_1/α_1 in the region of instability of the steady-state solution, but near the transition point, i.e., we shall assume $\beta_1/\alpha_1 = 0.67$.

The solution by the method of isoclines is carried out as follows: we shall divide (18a) by (18b):

$$\frac{dC_6}{dC_3} = \frac{\beta_1}{\alpha_1} \left(\frac{C_3^2 - \frac{1}{7} C_3^2 - \frac{6}{7} C_6 C_3}{C_3^2 - \frac{21}{20} C_6 C_3 + \frac{1}{20}} \right); \quad (25)$$

where $\beta_1/\alpha_1 = 0.67$. The solutions of this differential equation in the general case will be the integral curves $C_6(C_3)$. In order to find this family of integral curves, we shall construct a rectangular system of coordinates in a plane (Fig. 3). We shall plot the concentration C_6 as the ordinate, and C_3 as the abscissa.* Upon assigning any definite values to C_3 and C_6 (thus defining a

*Such a coordinate system is called the characteristic plane of Eq. (25).

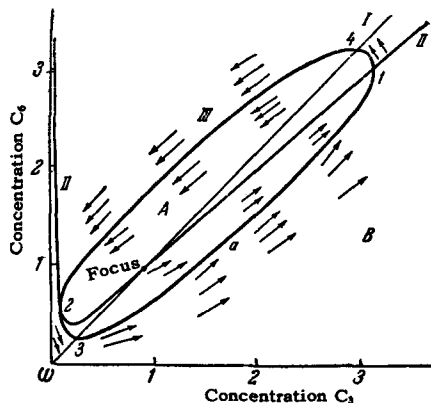


FIG. 3. The characteristic plane and field of isoclines. Abscissa: concentration of triose C_3 ; ordinate: concentration of hexose C_6 .

point on the characteristic plane), we can calculate the right-hand side of Eq. (25). According to Eq. (25), this quantity will be equal to the slope of the integral curve at the point (C_3, C_6) . If we select a sufficient number of such points, and at each point draw a line segment with the slope given by Eq. (25), then such a field of directions (or field of isoclines) will make it possible to construct any given integral curve. When we have the integral curves, we may follow the course of the whole process. Namely, if at any given moment τ the system is in a state represented by the point (a) [i.e., the concentrations are $C_3^{(a)}$ and $C_6^{(a)}$], then in the course of time, the concentrations C_3 and C_6 will vary, but not arbitrarily. The concentration C_6 will depend on C_3 , and this dependence will be graphically represented by the integral curve passing through the point $[C_3^{(a)}, C_6^{(a)}]$. That is, the change of concentration with time will be described by the motion of the representative point along the integral curve. In the present case, a field of isoclines of about 100 points was constructed (see Fig. 3). For convenience of construction, the following curves were drawn:

$$\left. \begin{aligned} I. \quad C_3^2 - \frac{1}{7} C_3^2 - \frac{6}{7} C_3 C_6 &= 0, \\ II. \quad C_3^2 - \frac{21}{20} C_6 C_3 + \frac{1}{20} &= 0. \end{aligned} \right\} \quad (26)$$

The first curve degenerates into two straight lines: $C_6 = C_3$, and $C_6 = -7C_3$, of which only $C_6 = C_3$ is of interest to us, since negative values of the concentrations can have no physical meaning.

At each point of line I, the numerator of Eq. (25) is zero, and hence, the isoclines are parallel to the axis of abscissas. At every point of curve II, the denominator of Eq. (25) is zero, and hence, the isoclines are perpendicular to the axis of abscissas.

The point of intersection of curves I and II (with the coordinates $C_3 = 1$, $C_6 = 1$) is a singular point, at which the isoclines may have all possible directions. Consequently, an infinite number of integral curves

passes through this point at various angles. This point represents the steady state of the process.

In the present case, in which the steady state is unstable, the integral curves, as is shown in Fig. 3, lead out from the point of the steady state. As may be seen from Fig. 3, the integral curves show still another peculiarity: any integral curve passing through any point (C_3, C_6) occurring within the region A (see Fig. 3) does not go to infinity, but winds around within the closed curve III. On the other hand, any integral curve originating in region B cannot enter into region A, but winds around outside the same closed curve III. If, however, we select any point $[C_3^{(a)}, C_6^{(a)}]$ on curve III as the initial state, then in the course of time, the representative point will move along the closed curve III, and after a certain period of time, will return again to its initial position $[C_3^{(a)}, C_6^{(a)}]$. In this case, the change in the concentrations C_3 and C_6 will be periodic, while the system of the entire process will be self-oscillating.

The closed curve III is called the limit cycle, and is a fundamental characteristic of a self-oscillating system. In the present case, the graphically-found limit cycle is drawn in Fig. 3 (curve III).

With the use of the limit cycle, we may easily find an explicit form of the time-dependence of C_3 and C_6 in the self-oscillating state. To do this, it is sufficient to integrate Eq. (18a):

$$\frac{dC_3}{d\tau} = C_3^2 - 1.05 C_3 C_6 + 0.05, \quad \tau = \int_{C_3^1}^{C_3^2} \frac{dC_3}{(C_3^2 - 1.05 C_3 C_6 + 0.05)} \quad (27)$$

Here the quantity C_6 is a function of C_3 , as given graphically in the form of the limit cycle.

In view of this, the integral as a whole must be determined graphically or numerically. We must note that the integrand at points 1 and 2 (Fig. 3), at which the denominator vanishes, shows singularities (although integrable). These points are the intersections of the limit cycle with curve II (since at all points on curve II, $C_3^2 - 1.05 C_3 C_6 + 0.05 = 0$). Numerical integration within the small regions in the neighborhood of these points is impossible. The contribution of these regions was calculated analytically by series expansion of the differential equation in terms of the small deviations of the concentrations from the values at points 1 and 2. We note that the contribution from the region near singular point (1) turned out to be small in comparison with that of the entire period, while that from the region near singular point (2) was substantial.

As a result, the time-dependence of the concentration $C_3(\tau)$ was obtained, from which the dependence $C_6(\tau)$ was then obtained. This dependence is shown graphically in Fig. 4. We may see from Fig. 4 that the period of self-oscillation in dimensionless units of time $(1/\alpha_1)$ is equal to 36. The problem of what time interval in hours or minutes this quantity corresponds to will be discussed below. We may also see

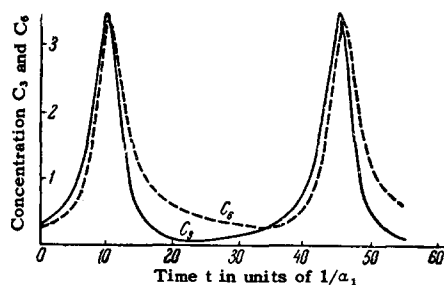


FIG. 4. The time-dependence of the concentrations of triose C_3 and hexose C_6 .

from the diagram that the form of the dependence reminds us, in fact, of the diurnal variation of photosynthesis under conditions of deep midday depression.

In concluding this section, we shall clarify the physical meaning of the results obtained. We shall examine the reasons for the appearance of self-oscillations in the present concrete case. In order to do this, we shall distinguish the processes which play the principal role during the various stages of the process.

1. In the stage in which the concentrations C_3 and C_6 are small, and C_3 is increasing while C_6 is decreasing with time, the principal term in Eq. (18a) for C_3 is α_0 (this phase is indicated in Fig. 3 by points 2 and 3). The principal process is the accumulation of C_3 due to respiration.

2. Then, in the stage from point 3 to point 1, the concentrations C_3 and C_6 are both increasing. As may easily be seen, the principal terms here are the autocatalytic terms $\sim C_3^2$ in both of the equations of (18).

3. In the stage from point 4 to point 2, the principal terms are the negative terms $C_3 \cdot C_6$ and $(1/\gamma) C_6^2$. In this phase, both concentrations are decreasing; the principal process bringing about their decrease is the binding of these substances, removing them from the Calvin cycle as starch. The fall of the concentrations below point 4 takes place because too much hexose had been accumulated in the previous stage, and consequently, triose must be consumed wastefully in this stage. The decrease in the concentration of triose is interrupted again when at point 2 the constant source of this substance, or respiration, "comes into action" (more precisely, this source acts continually, but at point 2 the supply of triose from it becomes greater than the loss due to the other processes).

Thus, the "reason" for the appearance of self-oscillation is the too-rapid increase in the concentrations (due to the autocatalytic character of the reaction) in the first stage, and the then unavoidable rapid decline in the concentrations due to the "overproduction" of hexose.

5. INTERPRETATION OF THE RESULTS OBTAINED

In the calculation given above, specific values were chosen for the parameters ($\beta_1/\alpha_1 = 0.67$ and $\alpha_0/\alpha_1 = 1/20$). Hence, this calculation is mainly an illustrative

concrete example of the appearance of a self-oscillating state, and makes no pretense of agreeing with the self-oscillations taking place in nature. However, we may expect that the most general features of this calculation will reproduce the qualitative peculiarities of the actual self-oscillating process in photosynthesis.

In order to compare the curves obtained with the curves for the rate of photosynthesis, we note that in the present case the rate of photosynthesis (in particular, the rate of absorption of CO_2 from the air) is proportional to the concentration of the acceptor, ribulose, which is itself proportional to C_3 . Thus, the time-dependence of the rate of photosynthesis must be given by the curve $C_3(\tau)$. This curve, as well as the similar curve $C_6(\tau)$ (see Fig. 4), actually has much in common with the curve of the midday depression.

The period of self-oscillation, which is equal in dimensionless units to $\tau_0 \sim 36$, may be expressed in concrete time in units of $1/\alpha_1$, i.e., $T \sim 35(1/\alpha_1)$. It was shown above that the quantity $1/\alpha_1$ is quite indeterminate, and may vary depending on the external conditions; its order of magnitude is such that $1/\alpha_1$ approximately amounts to several minutes. Hence, the period of self-oscillation T is of the order of several hours, which is not in contradiction to the data on depression.

We shall follow qualitatively how the nature of the self-oscillation will vary as we vary the parameter β_1/α_1 . As the ratio β_1/α_1 is increased, i.e., as it approaches the value $\beta_1/\alpha_1 = 0.85$, the region enclosed by the limit cycle will diminish.* Hence, the amplitude of the self-oscillation will also diminish. That is, the difference between the maximum and minimum values of C_3 and C_6 will diminish. The nature of the dependence of C_3 and C_6 on τ becomes shallower, and the depression not so deep.

The dimensionless period of self-oscillation τ_0 depends weakly on the parameter β_1/α_1 . Thus, at the point $\beta_1/\alpha_1 = 0.85$ and in its vicinity, $\tau_0 = 2\pi/\omega$, where ω is equal to the imaginary part of the root λ [see Eq. (23)]. That is

$$\omega = \sqrt{\frac{8}{7} \frac{\beta_1}{\alpha_1} 2 \frac{\alpha_0}{\alpha_1}} \simeq 0.31 \quad \text{for} \quad \frac{\alpha_0}{\alpha_1} = \frac{1}{20}, \quad \tau_0 = 21. \quad (28)$$

It was found above that $\tau_0 = 35$ when $\beta_1/\alpha_1 = 0.67$. Thus we see that τ_0 does not depend very strongly on the parameter β_1/α_1 .

On the other hand, a slight increase in the ratio β_1/α_1 , as was mentioned above, must be accompanied by a more significant decrease in the absolute magnitude of the coefficient α_1 . (In practice, it is possible to bring about such a decrease in α_1 with an increase in β_1/α_1 by decreasing the light intensity or the CO_2 concentration.) Thus, the real period (measured in hours) $T = (1/\alpha_1)\tau_0$ must also increase as β_1/α_1

is increased, due to the "lengthening" of the time unit $1/\alpha_1$.

Thus, on approaching the stable steady state (by increasing β_1/α_1), the real period of the self-oscillations is lengthened, while their character becomes shallower.

It seems possible to us to relate the self-oscillating state in the vicinity of the bifurcation value of the parameter β_1/α_1 to the rhythm of photoperiodism. In order to do this, we must assume that at a normal light intensity (for a given type of plant), the coefficient α_1 is several (3–4) times smaller than under the external conditions causing depression. Under "normal" light intensity, the period will be correspondingly longer than the period under conditions of depression, i.e., it will be of the order of a day.

In fact, according to references 34 and 35, photosynthesis does not proceed at constant rate under continuous illumination, but varies periodically. The period of these changes is of the order of a day. Apparently, this is evidence that the rhythm of photoperiodism is being manifested here. On the other hand, the oscillations established in this study were shallower (with lower amplitude) than the oscillations in depression. This is evidence that the self-oscillating state under constant illumination is closer to the stable state than in the case of depression.

We must now consider the basic process of photoperiodism, or the distinction between short-day and long-day plants. Obviously, this distinction is due to the adaptation to external influences of different types found in different geographic latitudes. However, the total period of the external influence is the same in all latitudes, being equal to the length of the day. The difference in the external influences is manifested in differing ratios of the lengths of light and darkness. It is natural to make the hypothesis: the adaptation of the plants amounts to the fact that the internal rhythm is tuned in resonance with the external influence.* Here we must consider resonance not only in the sense of an equality of the overall periods of the external and internal rhythms, but also in the sense of the agreement between the lengths of the different phases, i.e., agreement of the length of the light phase with the duration of rapid photosynthesis in the intrinsic rhythm, etc.† Hence, we must seek the difference in the internal rhythms of long-day and short-day plants in the difference in form of cycle, the overall periods being one and the same. In our scheme, such a difference in the form of the cycles may be ex-

*Experimental data have recently been published in evidence of this hypothesis. It was shown in references 34 and 35 that the internal rhythm of plants is actually "tuned" to the external periodic influence. Then, when the plants are transferred to conditions of continuous illumination, for some time the periodicity of the previously-existing state is manifested.

†In physical terms, this implies the coincidence of the overtones of the external and internal rhythms.

*At the value of the "parameter" $\beta_1/\alpha_1 = 0.85$, the entire limit cycle shrinks to a point. This value of the parameters is called the bifurcation value, at which instability gives way to stability.

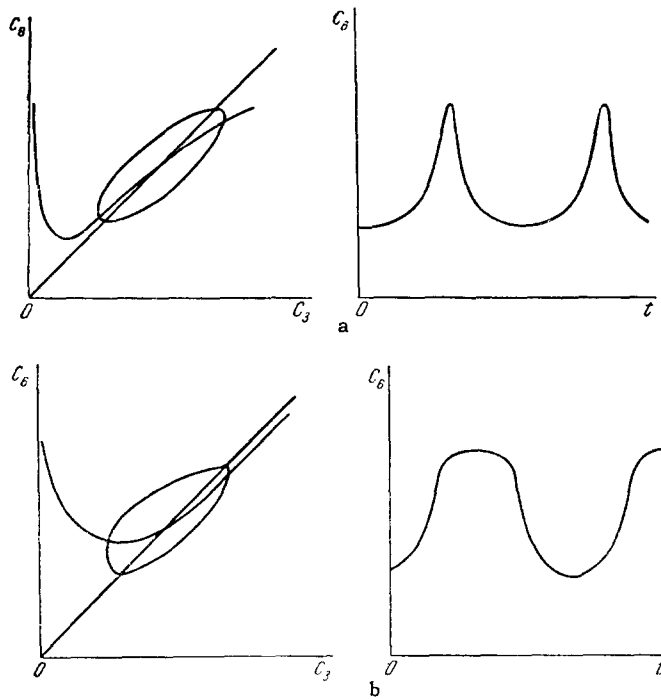


FIG. 5. The limit cycle and the corresponding time-dependence of photosynthesis: a) for a short-day plant; b) for a long-day plant.

plained, e.g., in terms of the difference in the parameters α_0/α_1 . In Fig. 5 are given the cycles for different values of α_0/α_1 , with the corresponding functions $C_6(\tau)$. Figure 5a (with small α_0/α_1) corresponds to a short-day rhythm while Fig. 5b (with large α_0/α_1) gives a rhythm more similar to that of a long-day plant.

On the other hand, the light intensity during the daylight hours under short-day conditions (i.e., at southern latitudes) is greater, as a rule, than under long-day conditions. Hence, the "normal" light intensity for a short-day plant (i.e., the intensity at which the overall period is equal to a day) is greater than that for a long-day plant. Hence, when a long-day plant is put on a short-day schedule, the intrinsic period of photosynthesis will decrease, bringing about a deep midday depression. On the other hand, the transfer of a short-day plant to a schedule of "normal" days for long-day plants will bring about a lengthening of the intrinsic period.

Thus, at the beginning of the next day, the plant will not be prepared, being still in a stage of falling rate of photosynthesis.

Thus, the transfer of plants to rhythms not characteristic of them, from our point of view, disturbs the resonance between the internal rhythm and the external influence. This causes "beats," which are a pathological factor according to the hypothesis advanced above.

In concluding this section, we must state that the problem of photoperiodism, and how to explain and calculate it, is more complex than the problem of

depression. First, the basic hypothesis of resonance, in spite of its apparent plausibility, is not entirely firmly grounded. Second, in order to study the problem of behavior of short-day plants on long-day schedules, etc., strictly speaking, we must solve the equations given above, taking into account the fact that the coefficients α and β are explicitly time-dependent in this case. Third, the question of the relation of photosynthesis to the reproductive processes, which is important in photoperiodism, is completely outside the framework of the present study.

Hence it seems expedient to us to test experimentally the hypotheses advanced above before proceeding to the calculations.

* * *

We shall study now the initiation of photosynthesis, i.e., the process in which a leaf which has remained for a long time in the darkness and has been deprived of assimilated material ($C_3 = 0, C_6 = 0$) is brought out into light of normal intensity. We shall assume that the parameter β_1/α_1 has such a value that the self-oscillating state corresponds to the rhythm of photoperiodism (i.e., the amplitude of the oscillations is small, while the period T is of the order of a day). The limit cycle in such a case is given in Fig. 6. The initial position of the representative point is at the origin [$C_3^{(1)} = 0, C_6^{(1)} = 0$].

In Fig. 6 is given the integral curve, and in Fig. 7, the corresponding function $C_6(\tau)$. We see from Fig. 7 that, in fact, before the state corresponding to the limit cycle sets in, the system undergoes oscillations of large amplitude.

We must note, however, that the oscillations obtained here hardly correspond to those observed upon initiating photosynthesis.

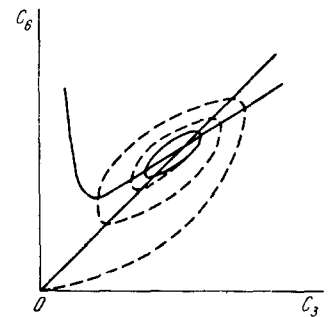


FIG. 6. Motion of the representative point in the characteristic plane upon initiation of photosynthesis.

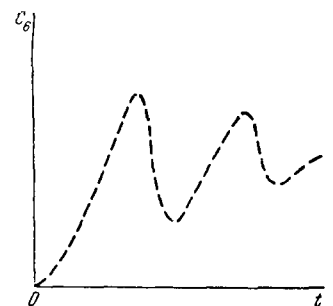


FIG. 7. Time-dependence of the concentration of triose C_3 at the initiation of photosynthesis.

First, the period of the oscillations obtained is of the same order of magnitude as the schedule of the limit cycle (with regard to the latter, we assume that it is here of the order of a day). However, the observed periods are of the order of several minutes. Second, in the present case, the maxima at first must necessarily be larger than those of the limit cycle (this is a consequence of the fact that the integral curve proceeding from the origin must necessarily wind around the outside of the cycle).

Experimentally, such a regularity of the maxima is not observed. All of this means that the periodicity of the initiation of photosynthesis can hardly be described by a scheme based solely on the Calvin cycle or any other scheme involving only the dark reactions of photosynthesis. In order to do this, we must apparently make a more detailed study of the relation of the photosynthetic cycle to the respiratory Krebs cycle. The experimental data give evidence supporting this, since at the initiation of photosynthesis, there occurs a momentary very intensive respiration, which does not occur under other conditions. Besides, in studying the oscillations at the initiation of photosynthesis, we can no longer limit ourselves to two equations in two unknowns (C_3 and C_6), but must include a third variable related to the respiratory cycle. Then we shall be able to explain the fact that the maxima in the rate of photosynthesis at the initiation of the process still lie lower than those occurring in the further course of the process. However, the solution of such a problem is much harder than that with two variables.

6. CONCLUSION AND DISCUSSION OF EXPERIMENTAL POSSIBILITIES

The studies presented here are based on one fundamental hypothesis that the internal rhythm of photosynthesis is a result of a self-oscillating state in the dark reactions. The calculation given shows that such a state is quite possible in the Calvin cycle. Further, it has been shown that this calculated rhythm agrees in its fundamental features with the observed rhythm of depression.

As may be seen from all of this treatment, this study is of a somewhat theoretical character. That is, many of the assumptions have not been confirmed by experiment, but have been derived speculatively.

There exists at present a rather large amount of experimental material on depression during the diurnal course of photosynthesis. However, it is not now possible to obtain data from the existing experiments to confirm systematically the stated hypothesis. From the viewpoint of a study of the kinetics of photosynthesis, the existing experimental data are highly unsystematic and incomplete. In this regard, it seems of interest to us to carry out a series of experiments to test systematically the theory presented here:

1. It will be necessary to carry out a determination of the products of assimilation (by chromatog-

raphy) during various phases of depression. The presence of a correlation between the rate of photosynthesis and the content of triose phosphate and hexose phosphate will give a direct indication of the relation of these phenomena.

2. It will be of interest to study how an increase in the hexose concentration in the leaf affects the photosynthetic process. An increase in the concentration C_6 by the amount ΔC in the characteristic diagram brings about a shift of the representative point upward by the distance ΔC (Fig. 8). By using the field of isoclines, we may construct the integral curve proceeding from the shifted point. This is shown in Fig. 8 for two cases:

(1) The increase in concentration is carried out at the position of maximum C_6 , and (2) at some intermediate position, in which the initial position (prior to the shift) of the representative point is near the steady-state point.

The explicit time-dependences $C_6(\tau)$ obtained from these integral curves are given in Fig. 9. We see from

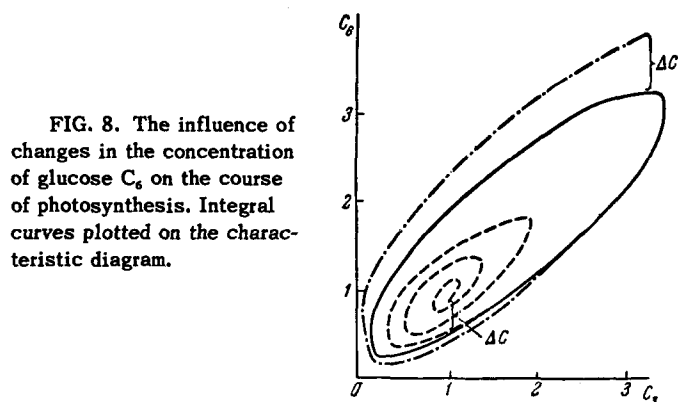


FIG. 8. The influence of changes in the concentration of glucose C_6 on the course of photosynthesis. Integral curves plotted on the characteristic diagram.

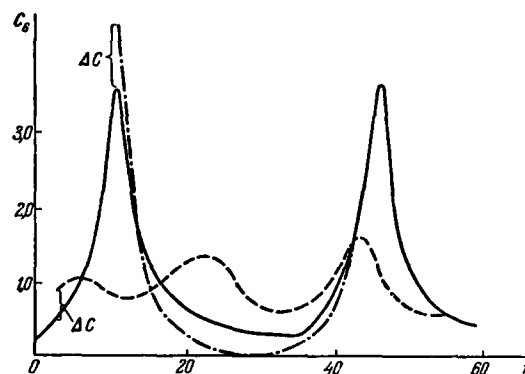


FIG. 9. The influence of injection at various instants of time on the course of photosynthesis.

the diagram that in the first case, after the increase in the concentration C_6 , it then falls rapidly, going below the value which it would have had without external interference, and then increases again, finally merging with the basic curve corresponding to the limit cycle. That is, in this case the amplitude of the oscillations is increased at first. On the contrary, in the second case, the amplitude of the oscillations is small at first, and the process follows a more shallow course, as a

result of the external influence. Then the amplitude of the oscillations increases, and the curve finally merges with that of the limit cycle. Thus, influences identical in nature, but exerted at varying moments of time, lead here during the initial period to diametrically opposite consequences.*

We must emphasize that the given example is characteristic of any self-oscillating process in general, rather than of the given concrete example alone. Namely, an increase in the concentration of any component at the moment when it is at a maximum (or in general, any shift of the representative point outside the limit cycle) brings about a temporary increase in the amplitude of the oscillations. On the other hand, an increase in this concentration at the moment when it is at a minimum (or a shift of the point to within the cycle) will bring about a temporary weakening or diminution of the amplitude of the oscillations.

The increase in concentration may be brought about experimentally by injection of triose or hexose phosphate into the leaf. According to the theoretical predictions, the effect of the injection must differ in the different phases. If the experiment gives such a pattern, this will be a direct confirmation of the entire hypothesis developed here.†

3. It would be of great interest to carry out a more systematic study of depression, and of the internal rhythms of photosynthesis in general. In most studies, depression has been studied under ordinary conditions, i.e., under daylight. Strictly speaking, the external conditions were not constant. Here, there always arose the question of the influence of a change in the external conditions on the rhythm itself. Hence, for a phenomenological study of depression, we must carry out a series of experiments at constant illumination (for several days) by light of various intensities. Experiments in this direction have been set up,^{34,35} but the data are not yet complete enough (e.g., the influence of the light intensity was not studied).

According to our study, the state must be self-oscillating in this case, with a period of oscillation

*The fact that both curves return again finally to the limit cycle need not be perplexing, since as was mentioned above, this is a fundamental characteristic of the limit cycle. Every external influence which does not alter the coefficients, but merely shifts the representative point, must sooner or later lead back to the limit cycle.

†It is possible that the Calvin cycle does not exist at all in photosynthesis. Then the concrete calculations given above are of no effect, of course. However, the hypothesis itself of the self-oscillating character of the dark reactions remains. In such a case, it would be necessary for us to calculate analogously a new cycle proposed in place of the Calvin cycle, and convince ourselves as to whether self-oscillation is possible in it. Experiments on the correlation between photosynthesis and the products of assimilation, and especially experiments on injection, are still of interest to us in this case. Only, instead of triose and hexose phosphates, we must then operate with other intermediates playing the principal roles in the new cycle.

decreasing as the light intensity increases. It is of great interest to us to test this assumption directly.

4. The hypothesis was advanced above (not directly in connection with the basic hypothesis) that the rhythm of photoperiodism is of the same nature as the depression. To test this hypothesis, we may attempt, in the same experiments under continuous illumination, to alter the period of the rhythm from a day to several hours by changing the light intensity.

It would be highly interesting to set up such experiments with various plants belonging to various geographical zones (i.e., long-day and short-day plants).

It is important to find out here what the periods of these plants will be at identical light intensities. (According to our hypothesis, the period of the short-day plant will be longer than that of the long-day plant.) It will also be important to find out whether the long-day plant will exhibit depression under the light intensity "normal" to the short-day plant.

5. Finally, it will be interesting to test experimentally the hypothesis of the role of resonance between the external influence and the internal rhythm, and the corollary hypothesis of the pathological influence of the "beats." In order to do this, we must study the characteristic relation between the assimilation products in the state of resonance for the given plant. That is, it will be necessary to find the period and form of the cycle for the given plant under constant illumination with a certain intensity, and then to establish for this plant an illumination of the same period and form. Then we may put the plant into a light schedule with a rhythm foreign to it, i.e., artificially bring about "beating," and then study the relations of the assimilation products under these conditions. If the relations between the assimilation products (e.g., C_3 and C_6), or in general, between carbohydrates and proteins, are substantially different in these two cases, this will be evidence of an important role of resonance.

In conclusion, we must note that the self-oscillating state of photosynthesis studied above is by no means exceptional. The respiratory Krebs cycle can apparently proceed in an oscillatory state. It seems quite possible to us that most of the biological processes either occur in a self-oscillating state, or are near to it (i.e., in physical terms, their states are near the bifurcation point). This, it seems to us, is a distinguishing peculiarity of biological processes. We hope to carry out a more detailed study of this problem in the future.

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Translator's Comments: This paper is primarily a unified presentation of the authors' own mathematical treatment of periodicity in photosynthesis, rather than a complete review of the subject. Nevertheless, a considerable volume of literature is cited in the article in discussion of one or another point. The impression of the translator is that much of this material has been read hurriedly by the authors, with resultant minor errors.

However, the value of this article is not in reproducing the prior research, but in presenting a mathematical approach based on elementary cybernetic concepts, applied in this instance to the fluctuations in the photosynthetic process, but applicable in principle to any biological rhythm for which we can propose a model. The authors base their treatment on the assumption that such periodic phenomena as midday depression, photoperiodism, and certain induction effects are due to an oscillatory state being set up in the reactions of the Calvin cycle itself. They show this assumption to be quite plausible as an explanation of midday depression, and at least possibly a factor effective in photoperiodism, while involvement in the short-period induction effects is ruled out. Their assumption with regard to the cause of midday depression agrees qualitatively with the hypothesis¹ that this phenomenon is due to accumulation of carbohydrates in the leaf, but the treatment of the present authors is unique in subjecting the assumption to mathematical treatment. On the other hand, the existing studies of the kinetic equations of the photosynthetic process have generally involved such subjects as light-dependence and CO₂-dependence,² and have not considered the possibility of an oscillatory state. The study of Pirson³ on induced periodicity in photosynthesis reveals periods comparable to those studied by the present authors and highly suggestive of the mechanisms they propose, but no mathematical analysis is made by Pirson.

While the treatment given by the authors to their topic is admittedly quite speculative, their work is of value in showing how a concrete model of a series of biochemical reactions can be tested

mathematically for the possibility of oscillatory behavior, and indeed, that the Calvin cycle is an example which passes the test. However, since the abstract, quite approximate mathematical treatment only renders the assumed oscillation in the Calvin cycle plausible, rather than proving it, the authors provide a quite thorough list of proposed experiments to test the various assumptions made.

A collection of comparable studies of various other biological rhythms has recently appeared in a volume of the series of Cold Spring Harbor Symposia on Quantitative Biology.⁴ The papers presented in this volume are of especial interest in comparison with the present article because of the variety of biological rhythms studied, especially those of 24-hour period, and because of the similar mathematical concepts employed in some of them.

Further pertinent information on photosynthesis may be found in the recent monographic article by Gaffron,⁵ and in the AAAS volume on photoperiodism.⁶ The geometric study of differential equations is treated further in a number of treatises, including that of Lefschetz.⁷

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