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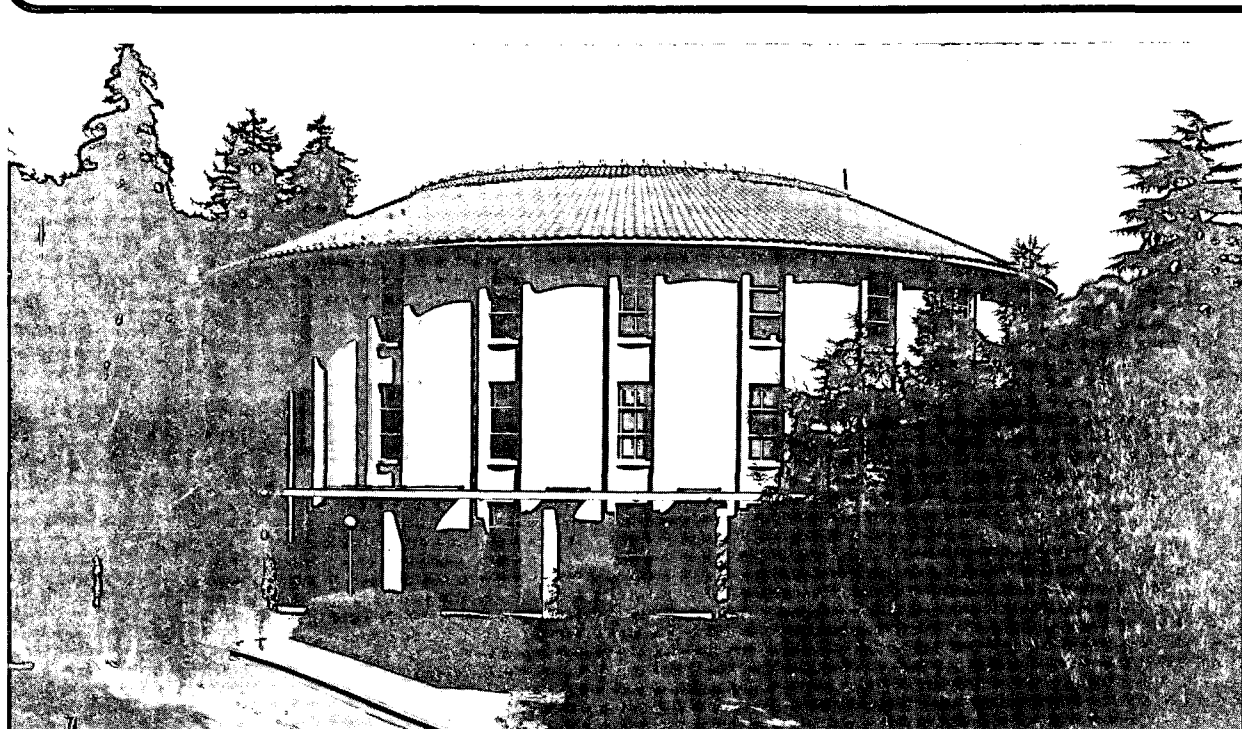
Intermediates in the Photosynthetic Cycle: An Essay

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INTERMEDIATES IN THE PHOTOSYNTHETIC CYCLE:

AN ESSAY

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ABSTRACT

A brief review of the research leading to the elucidation of the path of carbon in photosynthesis is presented, together with information on more recent research in the areas of hydrocarbon-producing plants and artificial photosynthesis.

## INTERMEDIATES IN THE PHOTOSYNTHETIC CYCLE:

## AN ESSAY

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The first article that we published in *Biochimica et Biophysica Acta* was in 1954 when the volume number was only fifteen, and the article which the editors chose for this special volume was published in 1956, in volume twenty-one. In the early days, of course, there was only one principal volume of BBA and it was not published as frequently as now. But then, as now, the journal represented the most exciting and far-reaching international science. It seems almost impossible that BBA has now reached Vol. 1000!

The importance of this particular article in 1956 was that it contained for the first time the entire photosynthetic carbon cycle with all of the various constituents identified.<sup>1</sup> This cycle has remained identical to this day and is the base from which many other plant molecular biology studies begin.

Introduction

My own interest in the basic process of solar energy conversion by green plants began some time in the years between 1935 and 1937 during my postdoctoral studies with Michael Polanyi at the University of Manchester. It was there that I first became conscious of the remarkable properties of coordinated metal compounds, particularly metalloporphyrins, as represented by heme and chlorophyll. At that time I was working with Polanyi on platinum-hydrogen activation systems and Polanyi

speculated that it might be possible to use the same principles involved in platinum hydrogenation to study porphyrin molecules which mediated most biological oxidation-reduction reactions. He felt that if biological oxidation was a dehydrogenation and reduction it should be possible to use porphyrin molecules, similar to heme and chlorophyll, to study natural biological oxidation-reductions, using molecular hydrogen as one of the reagents. Polanyi felt that the proteins on the natural porphyrin molecules were simply "wires" for moving electrons around to match the protons which needed to be moved and the reactions took place on the porphyrin molecules themselves. This, at least to my mind, was a remarkable feat of association, and it became important for me to find porphyrin molecules which might be useful in studying hydrogen activation.

About that time, Polanyi heard of the synthesis of a porphyrin analog (phthalocyanine) in London by R. P. Linstead and I was sent down to Imperial College to learn how to synthesize this material. After a few days there I was able to make the phthalocyanine, as the procedure involved was relatively simple, and I then returned to Manchester to study the activation of molecular hydrogen in the gas phase by crystals of the phthalocyanine.

When I came to Berkeley in 1937 I continued work with metalloporphyrins generalized by the stimulus of Gilbert N. Lewis. During World War II we studied cobalt coordination compounds of a specific type to reversibly bind oxygen. This was a direct result of the study on the porphyrins which had begun with Polanyi in Manchester and also the knowledge that reversible oxygen binding by hemoglobin (a porphyrin of

structure similar to that of chlorophyll) was a property associated with the porphyrin molecule itself. During the next several years we prepared a series of coordination (or chelation) compounds which could be used to bind metal ions by chelating groups, in many cases for solvent extraction.

The studies on phthalocyanine dyes, begun at the University of Manchester, led to interest in other coordination compounds which were developed during the war and eventually to chlorophyll itself, which is the natural compound of photosynthesis and which is similar in structure to heme, a porphyrin compound.

#### Photosynthesis Studies

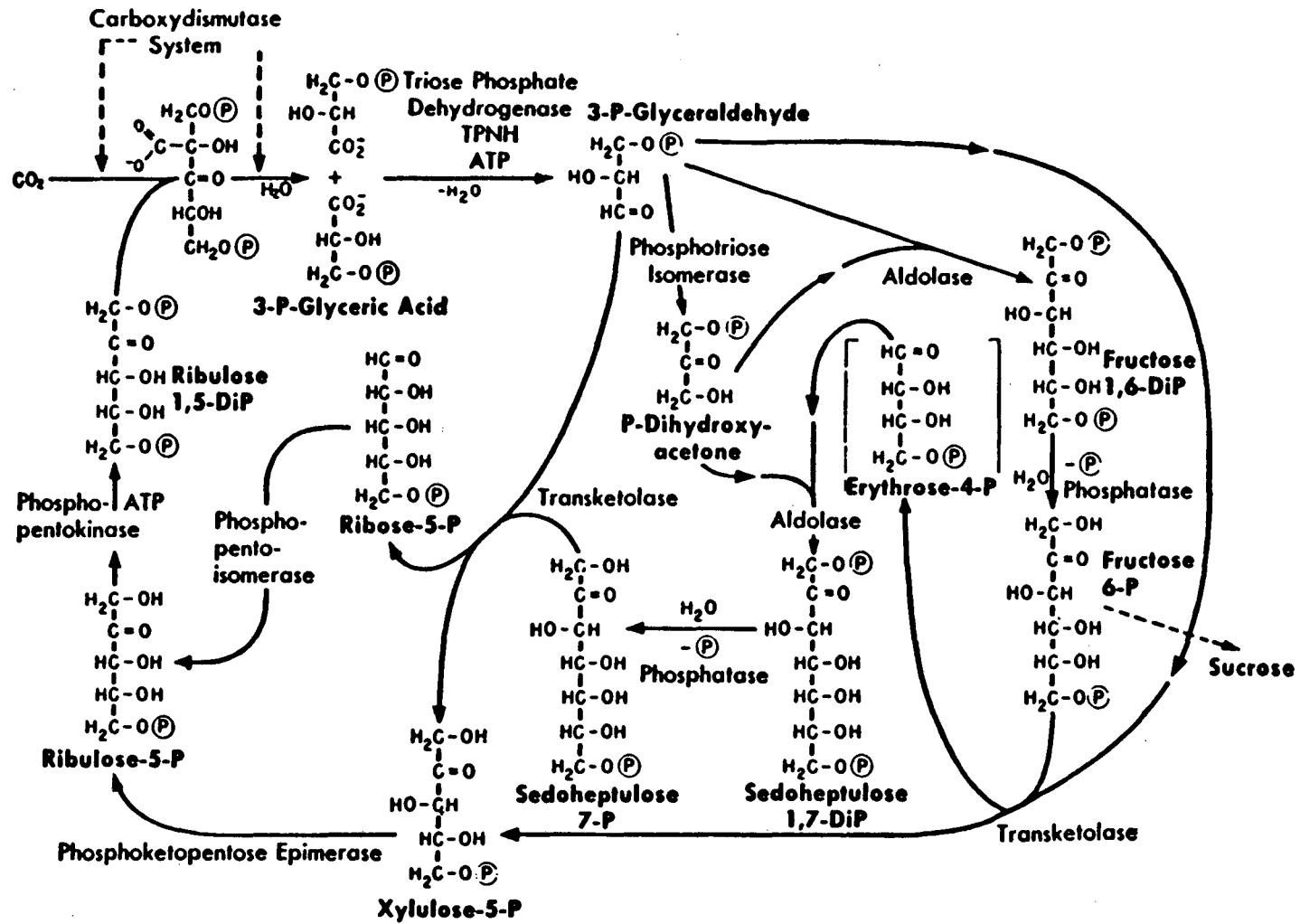
One of the principal difficulties in the investigation of photosynthesis, in which the machinery which converts the carbon dioxide to carbohydrate and the substrate upon which it operates are made with the same atoms--namely, carbon and its near relatives--is that ordinary analytical methods do not allow us to distinguish easily between the machinery and its substrate. However, the discovery of the long-lived isotope of carbon, carbon-14, by Samuel Ruben and Martin Kamen in 1939, provided the ideal tool for tracing the route along which CO<sub>2</sub> travels on its way to carbohydrate.<sup>2</sup> In 1945 it became apparent that carbon-14 would be available cheaply and in large amounts by virtue of the nuclear reactors which had been constructed, and with the encouragement and support of Ernest O. Lawrence, the director of the Radiation Laboratory, we undertook to study that part of the energy-converting process of photosynthesis represented by the carbon reduction sequence, making use of <sup>14</sup>C as our principal tool.

The principle of the experiment was simple. We knew that ultimately the  $\text{CO}_2$  which enters the plant appears in all of the plant materials but primarily, and in the first instance, in carbohydrate. Using green algae as the reproducible starting material and using the sophisticated paper chromatographic methods developed by Consden, Gordon, Martin and Synge in England, we were able to identify the various constituents of the photosynthetic carbon cycle by shortening the experimental times to discern that path from  $\text{CO}_2$  to carbohydrate as the radioactivity which entered with the  $\text{CO}_2$  passed through the successive compounds. Some of the variables that were studied and altered during this search were the period for the uptake of the radiocarbon by the algae, analysis of the distribution of the radioactivity in the various sugar segments, identification of the "two-carbon acceptor" (leading to phosphoglyceric acid), carbon-14 saturation experiments including the relationship of light and  $\text{CO}_2$  availability.

The individual steps in the path of carbon were assembled in a sequence, called the photosynthetic carbon cycle (Figure 1) was first published in its entirety in the BBA paper cited here. There were twenty-three publications entitled "The Path of Carbon in Photosynthesis" and two books.<sup>3,4</sup> The significance of the elucidation of the multisteps in the path of carbon was recognized by the award of the Nobel Prize in Chemistry in 1961.<sup>5</sup>

This work encompassed ten years (1946-1956) by many students and collaborators, with the two major investigators being Andrew A. Benson and James A. Bassham.





The photosynthetic carbon cycle.

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One of the most interesting personal occurrences during this period was the recognition of the identification of the two-carbon acceptor in the photosynthetic cycle. Some years ago I described this as follows:<sup>6</sup>

"I would like to describe the moment (and, curiously enough it was a moment) when the recognition of one of the basic facets of the photosynthetic carbon dioxide cycle occurred. One day I was waiting in my car while my wife was on an errand. I had had for some time some basic information from the laboratory which was incompatible with everything which, up until then, I knew. I was waiting, sitting at the wheel, probably parked in the red zone, when the recognition of the missing compound occurred. It occurred just like that--quite suddenly--and suddenly, also, in the matter of seconds, the cyclic character of the path of carbon became apparent to me, not in the detail which I shall describe here, of course, but the original recognition of phosphoglyceric acid, and how it got there, and how the acceptor might be regenerated, all occurred in a matter of 30 seconds. So there is such a thing as inspiration, I suppose, but one has to be ready for it. I don't know what made me ready for it at that moment, except I didn't have anything else to do. I had to sit and wait, and perhaps that in itself has some moral."

Perhaps the sudden insight into the cyclic character of the path of carbon might have resulted from the fact that the right answer came about as the result of an instinctive creative trick. That is to get the right answer as a result of having only half of the data in hand, and half of it is wrong, and you don't know which half is wrong. When you get the right answer under those circumstances you are doing something

creative, which is certainly what happened in the instance described above.

It may perhaps be worth stating that one of the practical results of the elucidation of the path of carbon has been our more recent research in the area of hydrocarbon-producing plants as alternate energy sources. One of the endpoints of carbon accumulation in plants is, of course, hydrocarbon, and the trick here is to use the hydrocarbon pathway to plant products, such as terpenoids, which would be important sources for energy and materials.<sup>7</sup> We used arid land plants, which would not require good soil for their production. Enough experimental information was obtained through the growth of these plants on experimental plantations to realize that the products could be cracked to the usual suite of materials that are obtained from normal petroleum cracking. The stumbling block to expansion of this research comes from the fact that the costs of the final fuel and/or materials from these plants are not yet competitive with the products of fossilized photosynthesis.

An interesting recent development indicates that algae can become an economic source of oil and chemicals and might even supply 8% of America's motor fuel by the year 2010.<sup>8</sup> Researchers at the Solar Energy Research Institute are studying algae which produce a large amount of lipids which can be extracted to make diesel oil. The algae can thrive in salty water and grow in ponds where sunshine can be guaranteed for at least six months a year. The secret of the process is to induce the algae to use their energy to make lipids by controlling the supply of nitrogen and silicon during the growth process. It has been estimated that the algae can convert over two-thirds of their mass to lipids with

an 80% conversion of lipids to diesel oil. This is a most hopeful development for future fuel supplies.

It is perhaps appropriate in this biochemical discussion to say a few words about our ongoing work toward the construction of a totally synthetic system designed upon the basis of our knowledge of how the natural photoelectron transfer systems functions in the green plant.<sup>9</sup> The purpose of this exercise, called artificial photosynthesis, is to achieve efficient photoelectron transfer with energy capture and storage and an inhibition of the back reaction. We believe the efficiency of the photoelectron transfer in green plants resides in the circumstance that the primary electron transfer event in photosynthesis is efficient because it is a transfer of an electron across a phase boundary from one environment to another. In nature the phase boundary is the photosynthetic membrane while in artificial photosynthesis a variety of phase boundaries (micelles, vesicles, colloids) have been investigated.

Considerable efforts have been made both in our laboratory and elsewhere toward the goal of artificial photosynthesis, to lay the foundation for efficient and economically viable conversion of sunlight to storable high energy compounds. In other words, to harvest solar energy and store it as chemical energy. In order to achieve the goal of water decomposition to hydrogen and oxygen by visible light, two processes must be achieved: Charge separation by electron transfer across a phase boundary followed by two different catalytic reactions to transform the separated charge into stable separated products, oxygen for the positive charge and either hydrogen or some reduced  $\text{CO}_2$  for the negative charge. We have achieved each of these separately but not yet in a single reaction system.

### Organization of the Laboratory

The brief description of the development of the photosynthetic carbon cycle certainly does not give a true picture of the complexity of the research that was required to achieve this final result. The talents of many chemists, physicists, biologists, biochemists were utilized to draw the map. I believe that the actual elucidation of the cycle would not have been possible without the interdisciplinary effort that was brought to bear on the problem.

This effort was the result partly of the physical organization of the laboratory where the work was done. The photosynthesis work which began in 1945 was housed in the Old Radiation Laboratory (ORL), an old wooden structure which was the home of the original 37-inch cyclotron developed by Ernest Lawrence. The room where the cyclotron had been located was a large, open space, a laboratory without internal walls. After the removal of the cyclotron, we installed laboratory benches, each capable of holding two people on each side, and partitioned off a small corner which we used as office space. To go out of the laboratory and downstairs to the basement, where the concrete counting room and, later, the first nuclear magnetic resonance and electron spin resonance equipment were located, it was necessary to pass through the office where the blackboard was located. This caused almost instantaneous seminars to occur at all hours of the day, and wide ranging discussions were held about the results of the current experiments. Physicists, chemists, biologists and biochemists all talked together and brought their individual talents together to keep the science moving.

This particular type of open laboratory space with no walls separating the benches gave rise to a special degree of interaction

between the scientists of diverse disciplines who were working there. Everyone knew pretty much what everyone else was doing and could participate in discussion freely as well as to help with an experiment if necessary.

Therefore, when the time came for us to design a new building, (which was necessitated by the destruction of ORL to make room for the new chemistry complex) we created a structure which would have built into it the principles of interaction that we had discovered quite by accident in the Old Radiation Laboratory. The design of the Laboratory of Chemical Biodynamics (sometimes called the Round House) was a circle in keeping with the group's preference for the free flow of information and ideas. Ideally, all working areas would be equidistant from the coffee pot situated on a large, white central discussion table. The lab benches radiated outward like spokes of a wheel and there was a spiral staircase behind the coffee table to facilitate movement between floors of the building. The circular layout of the laboratories and offices offered distinct advantages for interdisciplinary research. The design evolved so that the several scientific disciplines housed there could interact with each other and to solve problems which we called "the dynamics of biological structure and function".

During the entire existence of the laboratory, we were fortunate to have a constant stream of visitors and graduate students, not only from the United States but from all over the world. These people brought to us new ideas, different backgrounds, and made the Laboratory a truly international group. Many of these "graduates" went on to establish laboratories of their own, imbued with the same scientific philosophy of the mixing of the disciplines to solve scientific problems. We are now

finding a third generation appearing--students/postdocs of students and postdocs--trained in the same scientific philosophy who are, in turn, creating mini-ORL's or mini-Round Houses. The atmosphere of daily interaction has always been conducive to nurturing creative science and the men who practice it, and the mixing of minds has been conducive to generating entirely new and original notions to solve a single scientific problem upon which all were working.

#### Concluding Remarks

The "umbrella" that brings together the seemingly unrelated scientific topics with which we have been concerned is the long-lived interest in coordination chemistry which began at the University of Manchester with Professor Michael Polanyi and which continued when I came to the University of California in 1937. The impulse to study photosynthesis arose not only from the original interest in chlorophyll but also from another interest in coordination chemistry which appeared during World War II. In fact, the interest in this type of coordination compound is still paramount today, and the scientific continuity extends to the area of artificial photosynthesis where the redox chemistry of manganese complexes of all types may eventually lead to the design of a device for the photolysis of water. This continuity might be a result of following the trail of "light", with the original light being coordination chemistry and phthalocyanine.

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