the American Museum of Natural History. On Friday the congress enjoyed the hospitality of Mr. Frederick B. Pratt, at Glenn Cove.

At the closing meeting it was voted to hold the next session of the congress in 1930 in Hamburg. Professor G. Thilenius, Professor W. Küchler and Dr. A. Warburg were appointed the organizing committee.

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PHOTOSYNTHESIS[1]

THERE is no process within the confines of chemistry which is of greater interest and importance than that by means of which the living plant prepares the food on which its life and growth depend. This food consists of starch and sugars, together grouped under the general name of carbohydrates, and of certain nitrogen-containing compounds known as proteins. The material from which the plant starts is carbonic acid, or a solution of carbon dioxide, which it obtains from the air, in water which it obtains through its roots from the soil. From this substance alone the plant is able to prepare its supply of carbohydrates, and it is true to say that this chemical process is the fundamental basis of the whole of terrestrial life. This may truly be asserted because the production of the proteins is very closely associated with it and the initial stage is common to the two.

The formation of carbohydrates from carbonic acid when expressed by a chemical equation looks simple enough. There is no doubt that the first product of the process that can be recognized in the plant is a simple sugar, and thus the equation can be written

$$6H_2CO_3 = C_6H_{12}O_6 + 6O_2$$

where the simple carbohydrate is either glucose or fructose. These simple sugars undergo condensation immediately they are formed to give cane sugar or one of the starches, and these changes can readily be written as simple chemical equations.

The mechanism by means of which the plant achieves the synthesis of these complex compounds from carbonic acid has long been a mystery to chemists and to botanists. It is known that the agency used by the plant to effect its purpose is sunlight, and thus the term photosynthesis has been applied to the operation. It is also known that the plant makes use of certain pigments, such as chlorophyll, and it is to these that the color of the leaves is due. The mystery of it all lay in the fact that no one knew what actually takes place, and, indeed, the more chemists and botanists explored, the more puzzling did the problem seem to be.

Perhaps the most puzzling fact of all is that the plant only makes use of sunlight, when all our previous knowledge of light reactions leads us to believe that such light is quite incapable of inducing photosynthesis. This may readily be understood if the amount of energy involved in the synthesis is considered. It has been proved experimentally that in order to synthesize one gram molecule (180 grams) of glucose or fructose there must be supplied to the carbonic acid a minimum quantity of energy equal to 673,800 calories. Whilst it is known that the plant manages in some way to absorb the necessary energy in the form of light, the physicist tells us that it can not directly absorb enough energy from sunlight. Thus the photosynthesis can be brought about by red light of the wave-length 660 $\mu\mu$ when the energy directly absorbed can only be 260,000 calories, which is far below the minimum quantity required.

The experience gained from the ordinary reactions of photochemistry leads to the belief that if it is required to convert carbonic acid into sugars by means of light alone, it will be necessary to use ultra-violet light which is absorbed by carbonic acid, that is to say, light of wave-length 210 $\mu\mu$. It is obvious from this that some unknown factor is operating in vital photosynthesis.

In any endeavor to elucidate the mystery, it is evident that the first line of inquiry must be to study the action of the short wave ultra-violet light upon carbonic acid. This was first investigated by Moore and Webster in 1913, who found no evidence of any reaction taking place. They found, however, that in the presence of certain catalysts, such as colloidal iron hydroxide, small quantities of formaldehyde were produced. Since these results appeared to be at variance with general experience in photochemical investigations, they were again examined some years later in Liverpool, and it was then found that when a stream of carbon dioxide was passed through water irradiated by the light from a quartz mercury lamp, small quantities of formaldehyde were produced. This result seemed to be very satisfactory, since the formaldehyde could be looked upon as an intermediate stage on the way to carbohydrates, especially in view of the fact that Moore and Webster had proved that formaldehyde was converted by light into a substance with properties similar to the simple sugars.

Our observations were criticized by Porter and Ramsperger, who stated that if rigid precautions were taken to guard against the presence of every trace of impurity, no formaldehyde was produced. The suggestion was implied by them that the origin of the formaldehyde was to be found in some unknown im-

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[1] Address given before the Royal Institution of Great Britain, on February 3, 1928.

purity. There is, however, an alternative possibility, and one which is more in keeping with the known facts of the natural photosynthesis in the living leaf. There is no doubt that in this reaction the carbonic acid is converted directly into carbohydrates and that formaldehyde as such is not produced, and it seemed that the most probable explanation of the discrepancy between our results and those of Porter and Ramsperger was that the action of the ultra-violet light is to establish a photochemical equilibrium,

$$6H_2CO_3 \rightleftarrows C_6H_{12}O_6 + 6O_2,$$

which reverts to carbonic acid again in the dark. In the presence of oxidizable impurities a small amount of carbohydrates will be formed, which will be photochemically decomposed to formaldehyde. This decomposition of all the carbohydrates by means of ultra-violet light is well known.

There is no need to give here the details of the experiments which were carried out to test this view, and it is sufficient to say that conclusive proof was obtained of the reality of the equilibrium: that is to say, carbohydrates were found to be present in the solution during irradiation by ultra-violet light, and these vanished very quickly after the irradiation was stopped.

This gave us at once a starting point, because it seems evident that if a harmless inorganic reducing agent were added to the solution, carbohydrates should be formed in quantity on exposure to the ultra-violet light. Such a reducing agent is ferrous bicarbonate, and great hopes were raised when it was found that a saturated solution of this compound, which was completely colorless when prepared, gave a copious precipitate of ferric oxide on exposure to ultra-violet light. It was evident that the oxidation took place by reason of the oxygen in the carbohydrate equilibrium in accordance with the equation

$$4Fe\,(HCO_3)_2 + O_2 = 2Fe_2O_3 + 4H_2O + 8CO_2$$

and indeed it was found that on evaporation of the exposed solution a simple sugar was obtained. The quantity produced was very disappointing and far less than was anticipated, and the conclusion was forced upon us that some unknown factor was taking part in the process.

During many unsuccessful endeavors to improve the yield of the carbohydrates, it was noticed that the ferric oxide was not produced in the body of the solution, but only on the walls of the quartz containing vessels and on the surface of the iron rods used to make the bicarbonate. This led us to suspect that the surface was a determining factor, and we at once changed the experimental method so as to increase the surface as much as possible. In order to secure this a suspension of pure aluminium powder in water, maintained by a stream of carbon dioxide, was exposed to ultra-violet light. Increased yields of carbohydrates were at once obtained, but it was also found that the best yields were obtained when the aluminium powder had been allowed to coat itself with hydroxide by remaining in contact with the water before the exposure to light. This latter observation very materially changed our ideas, since it established the fact that the surface phenomenon is of far greater importance than the reducing action, and indeed raised the question as to whether the latter plays any rôle at all in the process.

In order finally to decide this question an aqueous suspension of pure and freshly prepared aluminium hydroxide, maintained by a stream of carbon dioxide, was exposed to ultra-violet light. There was obtained after filtration and evaporation of the solution a quantity of carbohydrates equal in weight to that produced when aluminium powder was used. This conclusively proved the fundamental significance of the rôle played by the surface, and at the same time the reducing action was found to be entirely unnecessary. Identical results were obtained with other powders, such as aluminium, zinc and magnesium carbonates.

During the course of these experiments it occurred to one of my students (Dr. W. E. Stephen) that if a green powder were used in place of the white ones the photosynthesis might take place in visible light, the green color being suggested by the green color of the plant-pigment chlorophyll. This was found actually to be the case, since a suspension of nickel carbonate maintained by a stream of carbon dioxide in water, on exposure to the light from an ordinary tungsten filament lamp, gave a larger yield of carbohydrates than any of the white powders in ultra-violet light. We soon found that there was no especial virtue in the green color, and that equally good results were given by pink cobalt carbonate.

Apart from the interest which accrues from the fact that the photosynthesis is thus achieved in a way which shows a real analogy with the natural phenomenon, the method with a colored surface and visible light has a very material advantage in that the danger of photochemical decomposition by ultra-violet light is completely eliminated, with the result that the products are obtained in a purer state.

From the above description of the direct photosynthesis of carbohydrates from carbonic acid in the laboratory several points arise which require discussion and explanation. In the first place it may be stated that the most rigid control experiments which we could devise have definitely established the fact that the carbohydrates are not due to the presence of impurities.

One of the greatest difficulties met with in this work was the preparation of the various materials used for the surfaces, since it is absolutely essential that these be completely free from any trace of alkali. It is well known that when metallic hydroxides and carbonates are precipitated they tend to absorb the alkali, and the removal of this is extraordinarily troublesome. The absence of any alkaline reaction in the filtrate after the powder has been boiled with water is no criterion of purity, and the only satisfactory method is to pass carbon dioxide into a suspension of the powder in water for two hours in the dark, and the filtrate after concentration must yield no weighable quantity of alkaline carbonate.

It was frequently found that the carbonates of nickel and cobalt, even when completely freed from alkali, were entirely ineffective in promoting photosynthesis. These can, however, be activated either by heating to 120° or by exposure in thin layers to ultraviolet light, and this fact afforded a very convincing method of carrying out controls. A quantity of one of these inactive powders gives no trace of carbohydrates when exposed to visible light in the manner described. The same sample of powder when activated and used in the same apparatus, with the same water, the same light, and carbon dioxide from the same source, gives a good yield of carbohydrates. So, once and for all, is all doubt removed as to the possible effect of impurities.

For the benefit of those who may wish to repeat these experiments, it may be stated that more recently it has been found possible to prepare nickel carbonate by a new method which is free from the objections characteristic of its precipitation by means of alkali carbonate. A solution of carbonic acid in conductivity water is electrolyzed, the electrodes being made of nickel plates. The current is taken from a 220 volt circuit, and sufficient resistance is intercalated to reduce the current density to from one or two amperes per square decimeter. The electrolyte is cooled by glass coils through which a stream of water is maintained. With electrodes 190 square centimeters in area it is possible to prepare thirty grams of pure carbonate in twenty-four hours. The carbonate should be collected every day by filtration, and it is advisable to clean the electrodes with emery paper every third day.

To sum up the results, so far as they have been described, it has been found possible in the laboratory to produce carbohydrates directly from carbonic acid by a process which is physically similar to that of the living plant. The essential difficulty in our understanding of the natural photosynthesis has been solved, namely, the use of visible light as the agent in a process which the elementary laws of photochemistry taught us to believe could only be achieved by means of ultra-violet light. As so often happens the explanation when found is very simple. The great amount of energy required to convert the carbonic acid into carbohydrates is supplied to it in two portions, one by the surface and the other by the visible light.

Nothing has as yet been said of the actual carbohydrates which have been photosynthesized in the laboratory. Although as yet our information is still meager, there is no doubt that the photosynthetic syrup is a mixture containing glucose or fructose, or both. There are also present more complex carbohydrates, which can be resolved to the simple sugars by the action of dilute acid. The analogy with the products of natural photosynthesis is too close to be passed by without comment.

Although it has not as yet been possible to carry out a complete analysis of this syrup, owing to the difficulty of preparing a sufficiently large amount, interesting information has been gained from the investigation of the sugar syrup obtained by the action of light upon formaldehyde solution. This has been pursued during the last three years. We owe a debt of gratitude to Sir James Irvine for the signal help he has given us in this work. He himself was the first, in association with Dr. Francis, to prove that glucose is one of the substances actually produced. By oxidation of the sugars to the acids by means of bromine, and the crystallization of the salts of these with brucine, cinchonine and quinine, we have obtained d-gluconic and also d-erythronic acids. This not only confirms Irvine and Francis in their proof of glucose, but it also proves that fructose is formed just as in the living plant. In addition to that, there is produced a mixture of complex acids which afford convincing evidence of the synthesis of complex carbohydrates.

Although it may be thought that the use of formaldehyde as the starting-point takes away something from the interest, yet it must be remembered that it makes but little difference whether in actual fact we start from carbonic acid or formaldehyde. Without doubt the first substance, transiently formed in either case, is the same, namely, activated formaldehyde which polymerizes to the sugars.

The similarity between the vital and the laboratory processes is not confined to the fact that the products from the two are the same. Botanists tell us that in the living plant the photosynthesis takes place on a surface, so also is a surface necessary in the laboratory. It has been found possible to compare the quantities of carbohydrates synthesized for equal areas exposed to light in the case of living leaves and the glass vessels of the laboratory. These quantities are about the same. Some plants produce more and others produce less than we are able to synthesize. This similarity may be emphasized, because surely Dame Nature in the living leaf has produced the best machine she could for her purpose of food production for her children of the vegetable kingdom.

There is yet another striking feature which is common to the two, photosynthesis *in vivo* and *in vitro*. The light must not be too strong in either, for if it is too strong then harmful results at once supervene. This is due to the poisoning of the surface by the oxygen which is set free. In both cases this poisoning slowly rights itself, and in both the synthesis must not proceed at a greater rate than that of the recovery of the surface from its poisoning.

In fine, so far as we have been able to carry the investigations, the processes in the living plant and in the laboratory show most striking resemblance, not only in the compounds which are formed, but in every feature which is characteristic of either of them.

For my own part I would go further than this, because I believe that these experimental results help us to gain some understanding of the chemistry of life, the chemistry which is so different from that of man's achievements with his test-tube, flask and beaker. Within the confines of vital chemistry reactions take place which are so far outside our own experimental experience that it came to be believed by many that they were under the control of a mysterious force, to which the name of *vis vitalis* was given. One of these processes has come within our purview to-night, the condensation of the simple sugars, glucose and fructose, to form cane sugar, starch and inulin. No one has yet succeeded in effecting these syntheses in his laboratory, but it would seem that something of that nature takes place in our photosynthesis. Why, then, is it that even this step forward has been gained?

The one lesson that we have gained from photosynthesis is that the definitive factor is the very large amount of energy which must be supplied to the carbonic acid before the synthesis of the simple sugars takes place. The means of supplying that energy do not concern the argument. The synthesis proceeds at an energy level which is far higher than is the case in the reactions of ordinary chemistry, and the sugars are formed at that high energy level. I myself believe that the condensation reactions to give the more complex carbohydrates are those which are characteristic of the simple sugars when they exist at the high energy level. The reason why no one has succeeded up till now in inducing these reactions to take place is because no one has hitherto been able to supply the large energy increment necessary.

I myself believe that we find in this the key which unlocks the door of vital chemistry, and that the chemistry of all life is one of high energy, our laboratory experience being confined to the chemistry of low energy. From this viewpoint I see a wondrous vista unfold itself, wherein new understanding, new hopes and new possibilities reveal themselves. Health and vitality must essentially depend on the high energy level being maintained; any lowering of that level will lead to poor health and weak vitality. Knowledge comes to us of the means whereby the high level may be kept unimpaired. The most important sources from which we can absorb high energy are fresh food and ultra-violet light. From the one we learn the necessity of the rapid distribution of our food supply before its high energy is lost, from the other we gain a real understanding of the benefits of ultra-violet light therapy, and, more important still, of the dangers of its misuse. We gain an insight into the chemistry of vitamins, which in the light of our new knowledge reveal themselves as stores of high energy, bottled sunshine so to speak, which yield their energy to restore and maintain the vitality of decadent tissues. A vision thus comes to us of a new chemistry with limits far flung beyond those which constrain our knowledge of to-day, a chemistry which will embrace and coordinate not only the properties of inanimate matter upon this earth, not only the wondrous mechanism of the life of man in health and in disease, but in addition the stupendous marvels of the birth and growth of the worlds outside our own. From those who would decry this as a mere speculation I beg forgiveness, and plead that speculation based on sure experimental fact is the life blood of true scientific research.

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MILLIONTH SCALE MAP OF HISPANIC AMERICA[1]

The department of Hispanic-American research of the American Geographical Society has been engaged for the past seven years in the preparation of a new map of Hispanic America and the West Indies. An exhaustive search has been made for original surveys and other source material, and a completely new map is being compiled. The map follows the scheme of the International Map of the World on a scale of 1: 1,000,000 and will consist of one hundred sheets,

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[1] Résumé of a paper read at a recent meeting of the Federal Board of Surveys and Maps.