a vacuum—the distillate was free from hydrochloric acid. When the hydrochloric acid added to the solution of alkali citrates exceeded the above proportions, the distillates were always acid (HCl).

Aqueous solutions of the neutral tartrates of ammonium, sodium, and potassium were mixed with hydrochloric acid equal to half the base, and distilled over a water-bath. The distillates were all neutral. When mixed with a larger quantity of hydrochloric acid the distillates were acid (HCl). Hydrochloric acid added to Rochelle salt precipitates acid tartrate of potassium; acetic, oxalic, citric, nitric, and sulphuric acids act likewise.

XLIV.—*On the Chemical Aspect of Vegetable Physiology.*

[A Lecture delivered before the Chemical Society, May 3rd, 1878.]

By SYDNEY H. VINES, B.A., F.L.S., Fellow of Christ's College, Cambridge.

THE investigation of the various substances which compose the tissues and which are contained in the cells of plants, has been for a long time zealously pursued by chemists, and the study of the decompositions which they undergo under the action of various reagents has afforded results which have contributed largely to the philosophy of chemistry. In fact it may be said that Organic Chemistry owes its existence to the numerous researches which have been made in this direction. And yet, strange to say, comparatively few attempts have been made to discover the significance of these substances in the economy of the plant. In discussing the subject which we have to consider this evening, I will attempt to lay before you as clearly as possible some at least of the conclusions arrived at on this point by the combined efforts of chemists and physiologists.

I will begin with the consideration of a substance which occurs in the majority of plants—chlorophyll. This substance plays an essential part in the performance of a function which is characteristic of green plants, and is perhaps the most important of all physiological functions—the function of "assimilation," which consists in the absorption of carbonic anhydride from the air; in its decomposition in the chlorophyll-corpuscles, with evolution of oxygen; and in the formation of starch-grains in the chlorophyll-corpuscles by the combination of the retained carbon with the elements of water. The history of the discovery of this function, and of the gradually in-

creasing appreciation of its importance, is of great interest, but time will not allow me to do more than to sketch it very briefly.

De la Hire,[*] and, after him, Bonnet,[†] found that green plants, or parts of plants, immersed in water and exposed to sunlight gave off bubbles of gas; and Bonnet further observed that no bubbles were given off if the water had been previously boiled. Priestly[‡] pointed out that the air evolved by leaves under these circumstances was "dephlogisticated," and Ingenhouss[§] showed that this evolution of gas is due, not to the warmth of the sun, but chiefly, if not only, to its light. Sénébier[||] insisted upon the importance of "fixed air" (CO_2) in the process, and proved that the amount of "pure air" evolved by green plants in water is greater when a considerable amount of "fixed air" is held in solution. De Saussure[¶] observed that the volume of the oxygen exhaled was less than that of the carbonic anhydride absorbed, and that the decomposition of carbonic anhydride by green plants is accompanied by an increase in their weight.

At the beginning of the present century the sum total of knowledge upon this subject amounted to this, that green parts of plants, when exposed to sunlight, decompose the carbonic anhydride contained in the air, evolving a volume of oxygen which is less than that of the absorbed carbonic anhydride, and that at the same time they increase in weight.

For several years no important publication on this subject appeared. In 1837[**] von Mohl drew attention to the almost universal occurrence of starch-grains in chlorophyll-corpuscles, and especially pointed out that these starch-grains were secondary formations within the corpuscles. These observations were confirmed and extended by Nägeli and Cramer.[††] In 1862 Sachs[‡‡] showed that starch-grains do not occur in etiolated chlorophyll-corpuscles, and that their formation in normal corpuscles is dependent upon exposure to light.[§§] He tacitly

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* *Mém. de l'Acad.* 1690.   † *Usage des Feuilles.* 1754.
‡ *Phil. Trans.* 1772.
§ *Experiments on Vegetables.* 1779.
|| " Expériences sur l' action de la lumière solaire. 1788." Macbride had pointed out as early as 1764, that "fixed air," is absorbed by green plants when exposed to sunlight.
¶ *Recherches Chimiques sur la Végétation.* 1804.
** " Unters. üb. die Anatom. Verhältnisse des Chlorophylls." Reprinted in the *Vermischte Schriften.* 1845.
†† *Pflanzenphysiologische Untersuchungen.* Heft ii. 1858.
‡‡ *Bot. Zeitung.* No. 44. " Ueber den Einfluss des Lichts auf die Bildung des Amylums in den Chlorophyllkörnern." See also *Bot. Zeitung.* 1864. No. 38.
§§ Böhm, however, has found that when normal plants are exposed to feeble light the starch disappears from the chlorophyll-corpuscles, but reappears after an in-

assumes, though he gives no facts in proof, that this formation of starch-grains can take place only when the assimilating organ is supplied with carbonic anhydride, an assumption which has since been fully substantiated by Godlewski.* It will be seen at once that the appearance of starch-grains in the chlorophyll-corpuscles and the decomposition of carbonic anhydride, with evolution of oxygen, are dependent upon the same conditions, viz., (1) presence of CO_2 in the air ;† (2) presence of chlorophyll; (3) exposure to light. Sachs is therefore justified in concluding that these phenomena belong to the same function, that the formation of starch in the assimilating organ is a consequence of the decomposition of the carbonic anhydride: and in this way the increase of weight observed by De Saussure to take place in plants, which for some time had been actively decomposing carbonic anhydride and evolving oxygen, can be satisfactorily explained.

Hitherto it has been assumed that starch is always the product of assimilation, but this is not a universal rule. In some Monocotyledons (e.g., the onion) no starch can at any time be detected in the chlorophyll-corpuscles, and it appears that in these plants another carbohydrate, glucose, is formed instead. Recently it was stated‡ (Briosi) that oil was produced in certain plants (*Musa* and *Strelitzia*) by assimilation, but the researches of Holle§ and Godlewski§ have shown that this assertion is without foundation. That a carbohydrate is the product of assimilation may be deduced from some of De Saussure's results. He found that the increase of weight observed in some of his experiments amounted to rather more than twice the weight of the carbon contained in the absorbed carbonic anhydride. (In one case the increase in weight was 531 grams, and that of carbon 217 grams.) This proportion nearly corresponds with that which the carbon contained in a carbohydrate bears to the total weight of the carbohydrate ($C_6H_{10}O_5 = 162$ and $C_6 = 72$).

Further, Boussingault‖ determined that the volume of oxygen

terval, which may extend over two or three weeks. Under these circumstances the starch-grains cannot be regarded as products of assimilation; they must have been supplied from the reserve carbohydrates stored up in the plant. This does not, however, alter the fact that the starch-grains which appear in the chlorophyll-corpuscles under ordinary circumstances are produced by assimilation. (See *Sitzungsber. der K. Akad. d. Wissensch. Wien*. Bd. LXIX. 1874. Bd. LXXIII. 1876; and *Ber. d. Deutsch. Chem. Gesellsch. Jahrg.* 10. 1877.)

* *Flora*. 1873.

† See a paper by J. Moll, in the *Landwirthschaftliches Jahrbuch of Nathusius und Thiel*. 1877. "Ueber die Herkunft des Kohlenstoffs der Pflanzen."

‡ *Bot. Zeitung*. 1873.

§ *Flora*. 1877.

‖ *Comptes rendus*, t. liii. 1861.

exhaled by assimilating organs is approximately equal to that of the carbonic anhydride absorbed, a proportion which favours the assumption that a carbohydrate has been formed, according to the following equation :—

$$6CO_2 + 5H_2O = C_6H_{10}O_5 + 6O_2.$$
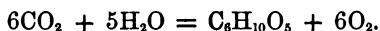
We have now to inquire in what way this process takes place ; how it is that the chlorophyll-corpuscle is capable of forming starch within it. It is obvious that any satisfactory answer to such an inquiry must be based upon an accurate knowledge of the composition and properties of chlorophyll. Unfortunately we are not at present in possession of such knowledge, although many investigators have endeavoured to attain it. It is not certainly known whether chlorophyll is a definite substance (according to Pringsheim,[*] Wiesner,[†] and Karl Kraus[‡]), or a mixture of one or more blue with one or more yellow constituents (Frémy, Filhol, Stokes, Sorby, Gregor Kraus[§]). A priori the former view would appear to be the more probable, and all the more recent experiments tend to establish it. The supporters of this view give the name of "chlorophyll" to a substance which corresponds generally with the "blue constituents" of chlorophyll according to the latter view ; and they regard the "yellow constituents" as being colouring matters which coexist with the chlorophyll, and either give rise to it or are formed from it. This diversity of opinion is doubtless to be attributed to the fact that none of the solvents as yet employed dissolve chlorophyll without more or less decomposing it. For the same reason its ultimate composition is still not accurately determined. The earlier analyses (those of Mulder, Morren and Morot) represent chlorophyll to be a nitrogenous substance. Pfaundler[‖] could detect only 0.037 per cent. of nitrogen in it, which he regarded as being due to impurities. Kromayer,[¶] however, found 7 per cent. of nitrogen in chlorophyll obtained by extraction of the leaves of the wheat with alcoholic potash, and Timiriaseff[**] goes so far as to say that chlorophyll contains an ammonia compound, to which he gives the name of *chlorophyllin.* Probably iron also enters into the molecule of chlorophyll, and this probability is reduced almost to a certainty by Wiesner's recent researches.[††] All

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[*] *Monatsbericht d. Berl. Akad.,* 1874, p. 628 ; 1875, p. 745. See also Conrad, *Flora.* 1872.

[†] *Entstehung des Chlorophylls,* Wien. 1877.

[‡] *Flora.* 1875.

[§] *Zur Kenntniss der Chlorophyll-farbstoffe.* 1872.

[‖] *Liebig's Annalen,* vol. 115.

[¶] *Arch. Pharm.,* vol. 156, and *Chem. Centralblatt,* 1861.

[**] *Bot. Zeitung.* 1869.

[††] *Loc. cit.*

these moot points, however, must necessarily remain undecided until a satisfactory solvent for chlorophyll is discovered.

Since our knowledge of the composition of chlorophyll is so incomplete, it is not surprising that its significance in the function of assimilation should have been explained on theories which differ widely. There seems to be a general concurrence in the opinion that the chlorophyll in assimilating organs is constantly undergoing change, but the nature of this change is very variously described. Wiesner* considers that the chlorophyll becomes oxidised, the oxygen being derived from the absorbed carbonic anhydride, and he bases his view upon the fact that an alcoholic solution of chlorophyll becomes oxidised when exposed to light. Without attempting to enter upon a discussion of this view, it may be pointed out that, if this be the case, it is difficult to account for the elimination of oxygen which accompanies assimilation, for Wiesner's own experiments seem to show that the evolution of oxygen and the decomposition of chlorophyll take place simultaneously. It is also not easy to suggest in what way a continuous supply of fresh reducing material (chlorophyll) is kept up.

Another hypothesis has been brought forward by Karl Kraus.† He suggests that chlorophyll is a product of assimilation, for it is formed in consequence of it, and is at the same time the cause of it, for assimilation cannot take place without it; that is to say, that the chlorophyll in process of development, and not the chlorophyll which is already formed, is the cause of assimilation. He considers that chlorophyll is the result of the combination of the products of the decomposition of carbonic anhydride with a substance to which he gives the name of *leucophyll*. The chlorophyll is then decomposed by the rays of light which it absorbs, the leucophyll is set free to combine again with the products of the decomposition of carbonic anhydride, and the formation of starch commences. This hypothesis can hardly be accepted at present as a satisfactory explanation, for it is unsupported by experimental evidence, and it presents obvious difficulties. A third explanation has been offered by Sachsse.‡ He regards chlorophyll as being the first product of the process of assimilation, and considers that under the influence of light it is converted into starch or some substance of the same physiological value. In support of his views he draws attention to the fact that the chlorophyll of the living plant is constantly undergoing decomposition, and he infers that consequently a fresh formation of it is continually taking place. In order to prove a genetic connection between chlorophyll and carbo-

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* *Sitz. Ber. d. Wien. Akad. Math.-naturw. Classe*, vol. 69.

† *Loc. cit.*

‡ *Chemie u. Physiologie der Farbstoffe, etc.* 1877.

hydrates, he cites Baeyer's* experiments, [in which a colouring matter was synthetically formed (by the action of an aldehyde, furfurol, upon a member of the aromatic group, pyrogallol or resorcin), resembling chlorophyll in some of its chemical and optical properties. Of course this substance is not identical with chlorophyll; but, if it be admitted that it is related to the colouring matters of the chlorophyll group, the mode of its formation indicates a genetic connection between chlorophyll and the carbohydrates. It is known that the carbohydrates can be oxidised to aldehydes, and that under certain circumstances they can be decomposed in such a way that various aromatic substances are produced. It appears, then, from Baeyer's experiments, that it is possible to form a colouring matter allied to chlorophyll by a synthesis of the products of the decomposition of carbohydrates.

The question now arises as to the possibility of the occurrence of such a synthesis in the living plant. It has already been suggested by Baeyer† that the first product of the simultaneous decomposition of carbonic anhydride and of water in assimilating cells is formic aldehyde, according to the formula—

$$CO_2 + H_2O = COH_2 + O_2.$$

Karl Kraus‡ has recently (1875) made some interesting experiments which seem to support this view. He grew maize plants in the dark, and supplied some of them with a dilute solution of methyl alcohol, a substance which is readily oxidised to formic aldehyde. He found that the leaves of the plants growing in the dilute alcohol became distinctly green in the dark, whereas those of the plants grown in pure water were etiolated. It appears, therefore, to be probable that a formation of aldehyde takes place under normal conditions. As to the occurrence of aromatic substance, which is essential to the formation of chlorophyll, there can be no uncertainty. Substances belonging to this group have been found in so many plants that it is not unreasonable to infer that they exist in all. Moreover, the presence of one member of this group, pyrocatechin, first detected in a living plant (*Ampelopsis hederacea*) by von Gorup-Besanez,§ has been demonstrated by Karl Kraus in the growing parts of many plants, more especially of those which contain no tannin. Evidence of another kind is afforded by the observations of Wiesner,‖ of

* *Deut. Chem. Ges Ber.*, v, 1096.
† *Deut. Chem. Ges. Ber.*, iii.
‡ *Loc. cit.*
§ *Sitzungsber. d. phys.-med. Soc. Erlangen.*, 1871 and 1874.
‖ *Jahrb. f. Wiss.* Bd. viii.

Drude,* and of Prillieux,† upon the presence and mode of origin of chlorophyll in parasitic and saprophytic plants, such as *Neottia, Nidus-avis, Monotropa Hypopitys,* and the *Orobanchaceæ,* and by those of Sachs‡ and Weiss§ upon the coloration of chlorophyll corpuscles. In all these cases the starch present in the cells was seen to diminish in quantity as the amount of colouring matter increased. That a genetic connection exists between carbohydrates and chlorophyll seems therefore to be placed beyond doubt. According to Sachsse's view, the carbohydrates stored up in a seed undergo, at the time of germination, a decomposition, probably of the nature of oxidation, as a result of which aldehyde and aromatic substances are formed, which combine to form a yellow chlorophylloïd colouring matter, *etiolin.* If the seedling be not exposed to light, no further change takes place (except in the case of Ferns and Conifers), but under the influence of light the etiolin is converted into chlorophyll, probably by a process of reduction.

The next question to be considered is, whether chlorophyll is converted into carbohydrates in the process of assimilation, that is, whether it forms part of a cycle of chemical changes, which begins with carbohydrates and goes on, through chlorophyll formed from the products of their decomposition, to the reconstitution of carbohydrates by a reduction of the chlorophyll, or whether chlorophyll simply causes the decomposition of the carbonic anhydride of the air, and thus renders possible a combination of carbon with the elements of water to form carbohydrates.

Sachsse argues that chlorophyll is actually converted into a carbohydrate either by a simple reduction, that is, by a continuation of the reducing process by which chlorophyll is formed from etiolin, or by a re-arrangement of its molecules with the absorption of the elements of water. From a purely chemical point of view it is not easy to imagine how this conversion of an aromatic into a fatty body can readily take place in the plant. A good deal may, however, be said in favour of the other view. If we accept Baeyer's above-mentioned suggestion, that formic aldehyde is the immediate product of assimilation, we may follow him in regarding it as giving rise by condensation to the polymeric substance glucose, or to starch, the anhydride of glucose. That a process of this kind is not impossible is shown by the fact that Butlerow succeeded in producing a saccharoïd substance from formic aldehyde by the action of alkalis. If this be the process which actually occurs in the plant the function of chlorophyll is simply

* *Biologie von Monotropa.* 1873.
† *Comptes rendus,* lxxvi, and *Ann. d. Sci. Nat.* 1874.
‡ *Experimental-Physiologie,* p. 315.
§ *Sitzungsber. d. Wien. Akad. Math.-naturw. Classe,* liv.

the decomposition of carbonic anhydride into carbonic oxide and oxygen.

At present there are no facts which could be brought forward to prove either the one or the other of these two hypotheses, and the question of the part played by chlorophyll in the process of assimilation must for the present remain an open one. It is interesting, however, to note in connection with this subject the importance of the salts of potassium (more particularly the chloride and nitrate), in the process. Speaking generally, it may be said that no appreciable increase in weight takes place in a plant—that is, that the plant does not assimilate—from which all supplies of potassium salts are cut off.* Liebig long ago pointed out that potassium salts always occur in considerable quantity in those parts of plants in which carbohydrates are being formed or deposited, and he explained the fact in a manner which will be subsequently discussed, and shown to be unsatisfactory. It may be that the alkali is liberated from its combination, and is then available for use in the formation of carbohydrates from the first products of assimilation in the manner above mentioned.

In concluding this portion of the subject, I will mention very briefly the probable fate of the carbohydrates—the raw material of the plant —formed by assimilation. One portion becomes converted into cellulose to form the walls of the cells in growing organs, and this cellulose becomes subsequently converted into lignin or cork, or gum or mucilage. A second portion is devoted to the nutrition of the existing protoplasm, and to a formation of new proteid material by the combination of carbohydrates with derivatives of the nitrogenous compounds (ammonia and nitrates) absorbed by the roots. We have at present no certain knowledge of the nature of this important process, the investigation of which offers a promising field for research. The researches which have been made in this direction all tend to prove its actual occurrence, but the results obtained are not sufficiently definite to afford a satisfactory explanation of it. Time will not permit me to do more than refer to the researches of Schutzenberger† upon albuminoïd substances. He finds that not only do such substances as chondrin and chitin (" *véritables glucosides azotés complexes* ") exist, which, as is well known, yield on decomposition glucose and various nitrogenous substances, but that the true albumins contain, as an integral part of their molecule, amides of cellulose (*amides cellulosiques*). A third portion probably undergoes decomposition to form the colouring matters, acids, &c., and furnishes in consequence energy to the plant, and the remainder of the carbohydrates is stored up in the

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* Nobbe, *Ueb. die organische Leistung des Kaliums in der Pflanze.* 1871.

† *Les fermentations.* 1876.

persisting parts of the plant, either as carbohydrate, or as oil and fat.

We may now pass on to consider the physiological significance of some other substances which are found in the cells of plants, in the same manner as we have done that of chlorophyll. Those which occur most frequently are the numerous colouring matters, the vegetable acids, the glucosides, and the alkaloïds. Of these I propose to select the acids, partly because their function is more fully understood and their chemical constitution is more clearly known than is the case with the other substances, but more especially because they have been connected by some great authorities with the subject which we have just discussed.

Mulder and Liebig * considered that the first products of assimilation were the vegetable acids, which combined with bases derived from the soil to form salts, and in this way Liebig explained how it is that a plant will not grow in a soil which does not contain a certain proportion of bases. This view was supported by Berthelot, who showed that carbonic oxide will combine directly with water to produce formic acid—

$$CO + H_2O = CH_2O_2.$$

On the other hand, Davy considered that the first products of assimilation were neutral substances, such as dextrin and sugar, a view which was also held by the botanists von Mohl,† Schleiden, Schacht, and others. They regarded the vegetable acids as being produced by the oxidation of the organic substances of the plant, a view which, as we shall see, has much in its favour.

The fact which afforded the strongest evidence in favour of Liebig's view was the gradual diminution in the acidity of ripening fruits, which he attributed to the conversion of the acids into sugar. This he regarded as a striking example of the process which, according to his views, takes place in every assimilating organ. It is very strange that no attempt was made to verify this hypothesis by estimating the amount of acids in a fruit at various stages of development. The mere disappearance of the strongly acid taste and the increasing sweetness afford no conclusive evidence that the acids have undergone conversion into sugar. The change of flavour may be as satisfactorily accounted for in a variety of ways; for instance, by supposing that the acids are gradually neutralised, and that sugar is brought to the ripening fruit from other parts of the plant. It is obvious that the experimental evidence cited in support of Liebig's view completely breaks

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* *Agricultural Chemistry;* see also Rochleder, *Chemie und Physiologie der Pflanze,* 1858, for a discussion of the subject.

† *Anatomy and Physiology of the Vegetable Cell,* 1852, p. 90.

down, and the theory is totally demolished by the consideration that if acids are the first products of assimilation, it is impossible that the volume·of oxygen exhaled should be equal to that of the carbonic anhydride absorbed, a proportion which we have already found to have been accurately determined.

We have now to consider the other view, according to which the vegetable acids are products of the oxidation of the organic substance of the plant. The supporters of this theory did not bring forward any definite experimental evidence in its favour, for they probably considered that the *onus probandi* lay rather upon those who controverted it. Von Mohl, however, pointed out the important fact that the vegetable acids occur in very many plants deposited in their cells as insoluble salts, for the most part of lime; and the researches of Hilgers* upon the formation of calcic oxalate in the parenchyma of Monocotyledons, show that the crystals when once fully formed undergo no further change. This fact affords a strong argument against Liebig's view of the derivation of plastic substance from acids, and suggests that substances which are thus for ever removed from the active metabolism of the plant, are to be regarded as by-products of some of the various processes which are included under that expression.

With which of these processes are we to associate the formation of the acids in the plant? At present it is impossible to give a satis-factory reply to this question, but it seems reasonable to suggest that they may be formed in connection with the process of respiration—a process which is essentially one of oxidation, though as yet there is no decisive evidence to show that this is actually the case. However, it has long been known that acids, more particularly formic and oxalic, may be produced by the oxidation of various vegetable substances, such as starch, sawdust, &c., and that if the process be carried far enough, carbonic anhydride and water are the final products. Hoppe-Seyler† found that, on treating grape sugar with alkalis, the access of oxygen being prevented as far as possible, it was decomposed into formic and carbonic acids and pyrocatechin, and further, that on heating starch with water in closed tubes, pyrocatechin, together with formic acid and carbonic anhydride (formed perhaps by the decomposition of oxalic acid), were produced. These facts suggest the inference that something of the same kind may occur in the living plant; that carbohydrates are split up into acids and aromatic substances; that a portion of the acid thus produced combines with the

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* *Ueber das Auftreten der Krystalle von oxalsaurem Kalk im Parenchym einiger Monocotylen.* Jahrb. fur Wiss. Bot., Bd. vi, 1867.

† *Medicinish-Chemische Untersuchungen.* 1866–71, p. 586.

oxybenzenes, with elimination of water, to form chlorophylloïd colouring matters; and that the remainder is either neutralised and deposited as crystals of insoluble salts in the cells of the plants, or is decomposed into carbonic anhydride and water. Karl Kraus* has shown that one part, at any rate, of this hypothesis admits of experimental proof. He finds that the external dry scales of the onion contain crystals of calcic oxalate and pyrocatechin, but no grape-sugar; whereas the internal juicy scales contain much grape-sugar, but neither calcic oxalate nor pyrocatechin. If, however, the internal scales be allowed to become dry, they assume the brown colour of the external scales, the grape-sugar disappears from the cells, and pyrocatechin and crystals of calcic oxalate make their appearance.

It may, therefore, be regarded as a fact that acids are formed from carbohydrates in the living plant by a process of decomposition, which is necessarily one of oxidation. That this is the case is shown by the following equations:—In the first, 2 molecules of grape-sugar are regarded as giving rise to 1 molecule of pyrocatechin and to 1 of oxalic acid, with evolution of carbonic anhydride and formation of water, 5 molecules of oxygen being required:

$$2C_6H_{12}O_6 + 5O_2 = C_6H_6O_2 + C_2H_2O_4 + 4CO_2 + 8H_2O.$$
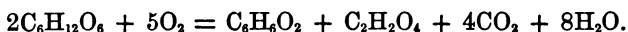
In the second, 2 molecules of grape-sugar are regarded as giving rise to 1 molecule of pyrocatechin and to 3 of oxalic acid, no carbonic anhydride, but only water being formed, and 4 molecules, the minimum quantity, of oxygen being required:

$$2C_6H_{12}O_6 + 4O_2 = C_6H_6O_2 + 3C_2H_2O_4 + 6H_2O.$$

With reference to the connection of this formation of acids with the respiration of the plant, it is to be noted that possibly it may be accompanied by an evolution of carbonic anhydride, as is shown in the first equation, even when so highly oxidised an acid as oxalic is the product, and that when a less highly oxidised acid is produced, the evolution of carbonic anhydride is inevitable. The following equation illustrates this with regard to an acid of frequent occurrence in plants, the tartaric—

$$2C_6H_{12}O_6 + 3O_2 = C_6H_6O_2 + C_4H_6O_6 + 2CO_2 + 6H_2O.$$
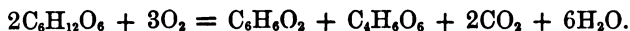
Whether it be or be not admitted that the formation of acids in the plant is accompanied by an evolution of carbonic anhydride, it is certain that this is one of the products of their final decomposition. It must be remembered that oxalic acid is singular among the acids occurring in plants in being deposited in an insoluble form, and in being thus excluded from any further participation in the active

* *Flora.* 1875, p. 253.

chemical processes. The other acids remain for the most part dissolved in the cell-sap of living cells under circumstances which favour their further oxidation.

The whole subject may be thus briefly summed up. The decomposition of carbohydrates gives rise in the first instance to substances (oxybenzenes) which contain a smaller proportion of oxygen in their molecule, and to substances (acids) which contain a larger proportion. Probably the acids first formed contain a relatively small proportion of oxygen, and are capable of further oxidation, each process of oxidation giving rise to a substance with an increased proportion of oxygen in its molecule, until carbonic anhydride is formed as the final product.

I will add only a few words as to the function discharged by the acids in the economy of the plant. All that is known on this subject has reference more particularly to oxalic acid. It appears from the researches of Holzner* and of Emmerling,† that the oxalic acid formed in the plant decomposes phosphates, sulphates, and nitrates, and sets the acids at liberty to be used in the nutrition of the tissues.

There is yet one more substance of particular interest to which I would draw your attention. This substance is asparagine. It has been found to occur in very many plants, and is particularly abundant in those which have undergone etiolation. Its physiological significance has, however, been made clear in the case of leguminous plants. Baeyer‡ has shown that in *Lupinus luteus*, as the legumin gradually diminishes in the cotyledons of the seedling, so does asparagine gradually increase in quantity in the stem and roots. From this it is inferred that the legumin stored up in the cotyledons is made available for the nutrition of the seedling by conversion into a soluble and diffusible substance. The researches of Pfeffer§ show that if the seedling be kept in the dark, the conversion of legumin into asparagine proceeds, but that the asparagine accumulates in the cells. He finds that this is the case also if the seedling be exposed to light in an atmosphere which contains no carbonic anhydride.

It appears therefore that the asparagine can only be made available if the process of assimilation be allowed to proceed. The probable explanation of this is that asparagine combines with the carbohydrates formed by assimilation to reproduce proteïd substance.

We have therefore a tolerably clear general idea of the origin and use of asparagine in these plants, but many details have yet to be sup-

* *Flora.* 1867.
† *Ber. d. Deut. Chem. Ges.* 1872.
‡ *Landwirthsch. Versuchs.-Stat.*, vol. ix.
§ *Jahrb. f. Wiss. Bot.*, viii. 1872.

plied.   The actual mode of origin, for instance, of asparagine from the reserve proteïds has not yet been fully explained.

Since the total amount of nitrogen contained in the seed does not vary throughout the whole process of germination, whereas oxygen is absorbed and carbonic anhydride is evolved, the formation of asparagine is usually regarded as being the result of a simple process of oxidation.   Von Gorup-Besanez* has, however, shown that a peptic ferment exists in the germinating seeds of leguminous plants (vetches), and it seems therefore pertinent to enquire whether or not this ferment has anything to do with the production of asparagine which they contain in such abundance.   According to Hoppe-Seyler† leucine and tyrosine are produced when proteïds are submitted to long-continued gastric digestion, and it is admitted on all hands that they are formed when proteïds undergo pancreatic digestion.   It is interesting to note here that von Gorup-Besanez‡ has detected leucine in the germinating seeds of leguminosæ.   Further, Radziejewsky and Salkowsky§ have shown that aspartic acid is one of the products of the pancreatic digestion of fibrin, and Knieriem‖ has proved the same in the case of gluten.   It is well known how readily asparagine can be decomposed into aspartic acid and ammonia, and it may therefore be fairly assumed that in these digestive experiments the occurrence of aspartic acid among the final products is an indication that asparagine has been formed during the process.   These facts afford some ground for regarding the formation of asparagine in germinating seeds as dependent, not upon simple oxidation, but upon the action of the proteolytic ferment which they contain.¶   It is worthy of note that the reaction of germinating seeds is acid; if therefore asparagine be produced in them by the agency of a proteolytic ferment, a well-marked distinction is set up between it and the pancreatic ferment (trypsin), for the latter can form aspartic acid only in an alkaline fluid.

Further researches are required to elucidate these points, and perhaps they may succeed in enabling us to connect these products of decomposition with certain groups of proteïds, as, for example, asparagine with the caseins, and leucine with the albumins and globulins of the seed.   That something of this kind is the case is suggested by the

* *Ber. d. Deut. Chem. Ges.*, vii.   1874.

† *Physiologische Chemie*, ii Theil.   1878, p. 228.

‡ *Ber. d. Deut. Chem. Ges.*, vii; see also Cossa, *ibid.*, viii.

§ *Ber. d. Deut. Chem. Ges.*, vii.   1874.

‖ *Zeitschr. f. Biologie*, Bd. ii.

¶ The detection of tyrosin (together with aspartic acid) in seedlings of *Cucurbita*, by E. Schultze and J. Barbieri (*Ber. d. Deut. Chem. Ges.*, xi, 1878), tends to confirm this view.

fact that the seed of the castor-oil plant, according to Ritthausen, contains no legumin, and Pfeffer was unable to discover any asparagine in the seedling.

It appears that other substances exist which are analogous to asparagine in their physiological significance. Such are solanine and chenopodine, for example. The former has been usually regarded as an alkaloïd, but it has not been suggested that it may be allied to asparagine in its chemical constitution.* The latter has been shown by Dragendorff† to be probably identical with leucine.

Although I have by no means exhausted the points of chemical interest which present themselves in the physiology of plants, I am compelled to content myself with those which I have brought to your notice. The account which I have given of them will suffice to show that the physiologist has already received much assistance from the chemist in his attempts to explain the phenomena of plant life, but it suggests at the same time that further assistance of the same kind is yet required. The researches above mentioned of Adolf Baeyer may be cited as a striking example of the valuable aid which the chemist can afford to the physiologist, and of the particular kind of information which the physiologist is anxious to obtain. The importance of various substances in the economy of the plant, and the conditions under which these substances are formed, can only be fully understood when we are in possession of accurate quantitative estimations of the amount of such substances present in the plant under different circumstances. These determinations involve considerable difficulties, for it is by no means easy to extract the whole amount of a substance present in a plant from the cells in which it occurs, and the isolation of the substance when extracted is even more perplexing. These difficulties, however, are doubtless to be overcome by patient endeavour, and by the gradual improvement of the chemical methods employed.

XLV.—*On some Fluorine-Compounds of Vanadium.*

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ALTHOUGH no fluorides or oxyfluorides of vanadium have been described, it would appear from the general relationships of the metal that a series of vanadium oxyfluorides corresponding with those of niobium discovered by Marignac (*Compt. rend.*, lx, 234, 1355; *Ann. Chem.*

* For the literature on this subject, see *De Vries-Landwirthsch. Jahrb.* 1878.
† See Husemann, *Pflanzenstoffe.*