NATURE

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*" To the solid ground
Of Nature trusts the mind which builds for aye."*—WORDSWORTH.

SATURDAY, JULY 2, 1927.

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Scientific Worthies.

XLV.—RICHARD WILLSTÄTTER.

" For all flesh is as grass "—1 PETER i. 24.

" A child said, *What is the grass?* fetching it to me with full hands;
How could I answer the child? I do not know what it is any more than he.
I guess it must be the flag of my disposition, out of hopeful green stuff woven.

" Or I guess the grass is itself a child, the produced babe of the vegetation.
Or I guess it is a uniform hieroglyphic
And it means, Sprouting alike in broad and narrow zones.

" And now it seems to me the beautiful uncut hair of graves."

WALT WHITMAN, *Leaves of Grass.*

CHEMISTRY is both a craft and an art, one of the finest of arts—perhaps the art of arts, a veritable " sword of Aklis," wherewith the threads are cut which hold the secrets of our material world and the nature and character of its component units disclosed; it has a wondrous psychology of which but few as yet have gained feeling, mastery and reverence. A science only in the second degree, because so much of its burden cannot be quantified, chemistry is none the less a premier science, through the exquisite finish of the enviable craftsmanship exercised by the men of genius who have been successful in its service. Among the craftsmen who have most adorned our ranks, we can place none higher than the subject of this memoir, for he has reached to the highest pinnacle of technical proficiency to which our art has been carried. A striking feature in his conquests has been the sureness and swiftness of his approach, the courage of his attack and his deft handling of situations which previous workers have failed to master.

A biographer writes :[1] " It is an open secret to the few who know it but a mystery and a stumbling block to the many, that Science and Poetry are twin sisters : insomuch that in those branches of scientific inquiry which are most abstract, most formal and most remote from the grasp of the ordinary sensible imagination, a higher power of imagination akin to the creative instinct of the poet is most needed and most fruitful of lasting work."

The chemist who can teach so much of grass, who can go so far towards answering the question put by the child to which the poet confessedly had no answer, who can also lay bare the secret of colour in flowers, may be placed even above the poet. The poet but deals with the superficial and with fancies ; at best he is a mere painter. The full beauty of Nature, the structure of her wondrous mechanism, is patent only to the chemist : he is fast learning to interpret her ' uniform hieroglyphic ' in terms which admit of no dispute. Now that we can think in terms of the Ångström unit, our vision is become ultramicroscopic. Our science of chemistry, in fact, is no twin sister of poetry but poetry itself and at its highest. Its mysteries are as deserving of attention and as marvellous as are those of even the densest stars. Indeed, the saga of the universe is before us in grass, if we will but read it : we know that " all flesh *is* as grass." The alphabet in which the story is told, in reality, is one of remarkable simplicity and that so few care to make the attempt to master our shorthand, the language in which our story of flowers is told, is surprising, to say the least. The outward beauty of the flower is patent to every one—the inward beauty of its mechanism, to the seeing eye, is marvellous beyond compare—the man who has done so much to interpret its character may well be deemed worthy among us.

Richard Willstätter was born in Carlsruhe (Baden) on Aug. 13, 1872. At first, he was educated there but afterwards, on removal of his parents to Nürnberg, at the Realgymnasium of that town. When eighteen years old, he entered the University of Munich, where he began the study of chemistry under the great Adolf von Baeyer, a master of laboratory craft, known to the world as the first to prepare indigotin artificially, the colouring matter of the indigo plant. The fifteen years of his career were spent there as student and privat-docent, and finally, from 1902 onwards, as extraordinary professor and head of the organic chemical department. In the spring of 1902, he was appointed full professor (ordinarius) at the noted Zürich Technical High School. After spending seven years in Zürich, in 1912 he returned to Germany to take charge of the Chemical Research Department established by the Kaiser Wilhelm Society at Dahlem, Berlin. It was here that he carried out most of his work on plant-colouring matters. Ultimately, he became professor at Munich, in succession to Adolf von Baeyer. He was elected a member of the Prussian Royal Academy of Sciences in 1915 and received the Nobel Prize in 1920.

It appears to have been Willstätter's ambition, from an early stage in his career, to undertake the study of vegetable and animal pigments and he advisedly entered upon a considered course of original study to acquire the necessary technical proficiency in preparation for this task. Beginning with the vegetable alkaloids, atropine and cocaine, which he was able to prepare artificially, he passed to the study of the quinones, a class of compound to which at least a majority of dyestuffs belong. He made a notable addition to knowledge by his discovery of orthobenzoquinone. He then entered upon his great inquiry into the nature of chlorophyll. He next devoted himself to the study of the red and blue colouring matters of flowers. Of late years he has been engaged in the attempt to isolate enzymes. These, however, are only the main lines of inquiry which have occupied his attention. A German professor, especially if he be a man of established repute, is called upon to provide subjects for a large body of young workers : hence it comes that Willstätter has touched a great variety of themes other than those referred to above. He has thus been led to solve a number of problems of special interest and more than ordinary difficulty. Among the inquiries, that on hydrogenation under the influence of platinum may be referred to as one of prime importance.

The studies of the green colouring matter of plants are described in twenty-four memoirs, published in Liebig's *Annalen der Chemie* during the years 1906–14, and in a book written in conjunction with A. Stoll (Berlin, 1913). It will be remembered of Shibili Bagara that he " pre-

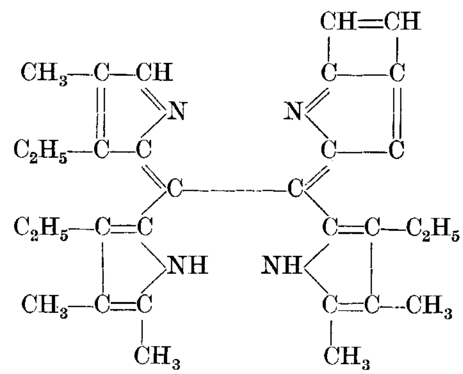
[1] F. Pollock in Leslie Stephen and Frederick Pollock's Lectures and Essays, by W. K. Clifford.

pared a rapid lather and dashed it over Shagpat and commenced shaving him with lightning sweeps of the blade (Aklis). 'Twas as a racing wheel of fire to see him." So Willstätter with chlorophyll. When he began the inquiry, the view prevailed that chlorophyll was but a group name and even that each plant might contain its specific chlorophyll. Not the least remarkable outcome of his work has been to show that, in more than two hundred species of Cryptogamic and Phanerogamic plants, the same mixture is to be found, in slightly different proportions, of two closely related compounds, which he has termed α-chlorophyll and β-chlorophyll, the former being blue-green, the latter yellow-green. This result is surprising in view of the fact that no two animals contain the same hæmoglobin, although one hæmatin is common to all, the globin (protein) component varying from species to species. Willstätter has further shown that, in the cell plastid, as indeed Sir G. G. Stokes first pointed out in 1864, the two chlorophylls are associated with two 'yellow' colouring matters, one the well-known hydrocarbon *carotene*, $C_{40}H_{56}$, the other a previously unisolated compound, *xanthophyll*, $C_{40}H_{56}O_2$, apparently a derivative of carotene. The Phæophyceæ alone also contain a third carotinoid, *fucoxanthin*, $C_{40}H_{56}O_6$.

The method of separating the chlorophyll compounds adopted by Willstätter is that originally proposed by Stokes and involves the use of more or less immiscible solvents, particularly petroleum spirit and aqueous alcohol. Being soluble in a mixture of petrol and alcohol but insoluble in petrol, α- and β-chlorophyll are precipitated when the alcohol is washed out of the solution. The method is one by means of which the pigments may be extracted from either dry or fresh leaves as easily as may an alkaloid or a sugar. The two chlorophylls are separated by fractional crystallisation from methylic alcohol and petrol. They are usually present in the proportion of about three molecules of the α- to one of the β-compound. Their composition is remarkable, that of the α-compound being represented by the formula

$$C_{32}H_{30}ON_4Mg(CO_2CH_3)(CO_2C_{20}H_{39}).$$

The β-compound differs only in containing an additional atom of oxygen. It will be seen that they are dicarboxylic derivatives. Significant constituents are magnesium and the radicle $C_{20}H_{39}$ of the complex alcohol, *phytol*, $C_{20}H_{39} . OH$, about one-third of the weight of the molecule consisting of this component. The condition of the magnesium is peculiar, as the metal is not displaced by the action of alkalies, though readily by that of acids. Its behaviour, therefore, is similar to that of the iron in hæmoglobin. The carboxyl-free mother substance of α-chlorophyll is a complex pyrrole derivative (*ætioporphyrin*) and the magnesium is probably associated with the nitrogen in this complex. This derivative is represented provisionally by the formula



Ætioporphyrin is a compound of outstanding interest as it is also obtainable from hæmoglobin. It is noteworthy that Fischer and Klarer have recently prepared a compound synthetically from 2 : 4-dimethyl-3-ethylpyrrole which appears to have the properties of Willstätter's product. That primary functions of life should be exercised, both in the plant and in the animal, by compounds of similar parentage is more than remarkable. The function of hæmoglobin, apparently, is that of a mere oxygen carrier—it is little more than a gas-holder. Chlorophyll plays a far more complex part, as it in some ways promotes the absorption of solar energy that is involved in the reduction of carbonic acid to formaldehydrol, $CH_2(OH)_2$, and the concurrent elimination of oxygen, in the primary process of assimilation.

Willstätter and his co-workers have shown that the chlorophylls remain unaltered in amount throughout the process and that they can enter into loose conjunction with carbonic acid : possibly the connexion is established through the magnesium and the carbonic acid thus made part of the energy-absorbing system. Once formaldehydrol is produced, passage to the sugars is a simple matter : yet this must be a directed operation, as the aldehydrol gives rise to only one of the two optically opposite forms of hexose. Those who talk glibly of the artificial imitation of the life process forget these little peculiarities and limitations—and so mislead the public into unjustifiable beliefs. Whatever the process, there is no reason to believe that carbonic acid is more than half reduced and the oxygen that is liberated is probably not derived from the carbon dioxide but is formed by the electrolysis of water. The operations are carried on within the chlorophyll plastid in presence of carotene and xanthophyll, both highly oxidisable substances; it is surprising that oxygen should be liberated within such a system and be without effect upon it, the more as various oxidisable materials are formed within the plastid. Elsewhere, I have ventured to suggest, that the yellows serve to inhibit oxidation and thus exercise a protecting effect upon the system—an effect such as Moureu and Dufraisse have shown to be often produced by the 'interference' of substances which are oxidisable separately but in admixture, apparently, are unaffected by oxygen.

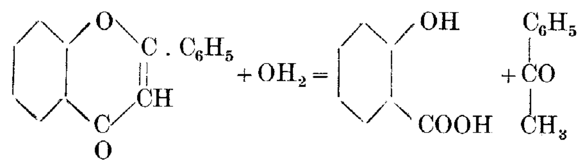
The statement is made in Sir Frederick Keeble's recent work on "The Life of Plants" that

"The wheat plant alone, producing as it does a world crop containing some 70 million tons of carbohydrate, 'handles' each year about 114 million tons of carbon dioxide and liberates to the atmosphere over 80 million tons of oxygen. The energy-value to the plant of the carbohydrate produced during photosynthesis may be computed on the basis of the amount of heat found by experiment to be liberated when a given amount of starch is caused to undergo combustion. The combustion of one ounce of starch liberates 116 calories and it is, therefore, only a matter of calculation to discover the energy value in terms of calories of the carbohydrates of the world's wheat-crop. The heat which would be produced by the combustion of the 70 million tons of carbohydrate would suffice to raise to boiling-point all the water of an ice-cold lake four miles long, four broad and of an average depth of forty fathoms."

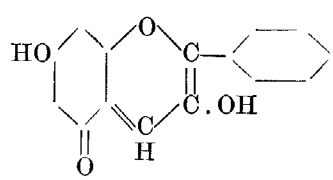
As all plants, through their leaves, exercise a similar activity, chlorophyll does some work in the world—we, therefore, might well learn to look upon it with respect, even take some little interest in its character and functions.

Of what value, however, is colour in the flower? Who shall say what the significance of colour may be? We are most of us alive to its æsthetic charm and value—what of insects: are they? If attracted by it and the fertilisation process be in large measure an outcome of such attraction, then indeed it is of utmost consequence to life.

The patterns of the colours in flowers have been deciphered with surprising skill and surprising swiftness by Willstätter and he has shown, moreover, that they are of remarkable simplicity. He has dealt with the reds and blues, which he has termed anthocyans; the yellows have been fairly well studied by others. In many plants, yellow and orange are due to xanthophyll and carotene: in other cases, they are mostly traceable to the presence of hydroxy-derivatives of flavone, present as a white meal upon the leaves and flower stalks of many of the Primulaceæ. Flavone, as shown by Hugo Müller, may be resolved into acetophenone and salicylic acid—two simple substances:



The anthocyans are mostly glucosides, yielding on hydrolysis either glucose or galactose or rhamnose together with the coloured component or *anthocyanidin*, which in some cases is a methylated derivative. They are resolved by the action of alkali into the trihydroxybenzene, phloroglucinol, either parahydroxybenzoic, protocatechuic acid or gallic acid or maybe a methylated derivative of one of these. The parent substance may be formulated as an orthoquinonoid derivative, thus:



In many respects their properties are peculiar but it is impossible to discuss them here. The reds are but acid forms of the blues. As in the flavones, the intensity of the colour increases with the number of hydroxy groups in the lateral phenyl group. Much might be said on the relation of colour to structure in these compounds were space available—no more fascinating subject could be entered upon.

Willstätter's work has of course been followed by a synthetic repercussion. In recent years, Prof. Robinson, in Manchester, has most skilfully developed methods with the aid of which it is possible to prepare anthocyanidins in the laboratory in any desired quantity: so to-day we can paint the lily with its own pigments.

Passing now to Willstätter's most recent work, that on enzymes, we are brought into a troubled field, one which, however, we must contemplate with wonder, as their activities lie behind the mysteries of life.

The colouring matters of plants appear to be without functional significance—they seem to be mere dress effects. Chlorophyll, however, is life at its outset, as by its agency the bricks are shapen which Nature hands to the plant : not only so, for with its aid energy is captured from the sun, which the plant not only uses to its own ends but also passes on to us. What of the enzymes, Willstätter's latest subject of study ? Life, we know, in the main involves only two processes—on one hand, that of hydrolysis and its reverse ; on the other, that of oxidation (hydroxylation) and its reverse. Oxidation, apparently, is determined and controlled by agents which are limited in their range of action but not specifically selective and, therefore, are not to be counted with the enzymes. The enzymes are the agents in charge of the hydrolytic process, whether this be downgrade or upgrade. They apparently are the templates which regulate constructive metabolism, both in plants and animals, for they are strictly selective agents. Hitherto they have been elusive entities, only characterised by their effects. Willstätter's efforts have been to prepare them in the individual state, so that they may be further characterised and their nature determined. The task is one of extraordinary difficulty. He has shown that they may be handled with far greater impunity than had been supposed and has devised methods of purifying them whereby he has greatly raised their activity but without arriving at any definite result. The final picture he has drawn for us of the enzyme is that of a colloid carrier of a group which is the active component : a picture drawn by my son and myself in 1913 ; indeed, we went further, in showing the colloid in attachment with a directing group, in addition.

I perhaps more than any one can appreciate the value of work so varied yet always in logical connexion—can wonder at the genius displayed and the self-sacrificing devotion of the worker to his task. Only the few among us can be aware what such inquiry means, what it involves —what are its joys—what its pains. Perhaps, some day, these matters will come home, in some slight measure, to those who in the arrogance of their ignorance pretend to rule the world—I say this because I should like to think that " the flag of my disposition [is] out of hopeful green stuff woven" and that the moral value of inquiries such as have been referred to may not always remain unknown to the public. HENRY E. ARMSTRONG.

Corrosion—Some Causes and Remedies.

The Corrosion of Metals. By Ulick R. Evans. Second edition. Pp. xvi + 259. (London : Edward Arnold and Co., 1926.) 15*s*. net.

TWO years ago (May 23, 1925, p. 793) the first edition of Mr. Evans's book was reviewed by the present writer in the columns of NATURE. Its good qualities have evidently been widely recognised, since a second edition has recently been published. The author states in his preface to this that progress made during this period in the understanding of the processes of corrosion has made so many additions necessary, that it has taken him longer to write the second edition than the first. The same general arrangement has been preserved, and he has adhered to the policy of giving a concise statement of the subject in the text accompanied by numerous references in the foot-notes to papers where further details can be sought on any particular point of interest. The net result is the production of a book some forty pages longer than the original volume and the published price has been slightly increased.

We learn from the chapter on the corrosion of copper and copper alloys, that an interesting protection process has recently been adopted by the Cunard Steamship Company, Ltd., which consists in spraying the interior of the condenser tubes with a bituminous composition. Austin, who has described the process in detail (*Trans. Liverpool Eng. Soc.*, **46**, 1925), states that the vacuum is reduced by $\frac{1}{4}$ to $\frac{1}{2}$ inch (owing to the decrease in the thermal conductivity of the coated tubes) but the over-all efficiency is not affected. Mr. Evans suggests as the reason for this, the increased cleanliness of the boiler heating surfaces and turbine blades. So far the experiment has proved very successful, only 21 tubes out of 28,500 having failed since its installation. As yet the process has not been tested in ships sailing in warm waters. The electrochemical process for protecting condenser tubes is stated to be somewhat of a disappointment, and the latest reports from many trustworthy sources indicate that in many cases little or no benefit has been obtained where it had been installed. Dr. Honegger states that in some cases the process has failed completely, while in other cases it has proved very useful. It seems quite possible that in the latter cases this has been achieved by the deposition on the tubes of a film of iron compounds derived from the anode rather than by true cathodic protection. Bengough and Stuart have pointed out that the weak feature of the method