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Nobel Prize in Chemistry 1915

Richard Martin Willstätter

The Nobel Prize in Chemistry 1915 was awarded to Richard Willstätter *"for his researches on plant pigments, especially chlorophyll"*.

RESEARCH INFORMATION:

By its property of making possible the assimilation of carbon dioxide under the influence of sunlight and hence introducing the synthesis of organic substances in the green parts of the plant, chlorophyll - as is well known possesses extraordinarily great biological significance and has an extremely important task to fulfil in the economy of Nature. The elucidation of the nature and the mode of operation of this substance is therefore a task which is of the highest degree of importance. The difficulties, however, which confront research scientists in this field have been so great that until very recently they have prevented a successful study of the problem of chlorophyll. Willstätter is the first, jointly with several of his students, to have been successful in overcoming these difficulties by working out new and very valuable methods and by extensive investigations carried out with masterly experimental skill. By the new and important discoveries resulting from these investigations he has been able to elucidate in all its essential parts the question of the chemical nature of chlorophyll.

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It is true that earlier investigators had observed that chlorophyll contains magnesium, besides other mineral substances. Willstätter, however, has the merit of having been the first to recognize and to prove with complete evidence the fact that magnesium is not an impurity, but is an integral part of the native, pure chlorophyll - a fact of high importance from the biological point of view. He has shown that magnesium is held within the chlorophyll molecule in a manner which is very similar to the way in which iron is held in haemoglobin; this bond is so firm that the magnesium is not liberated even by the action of a strong alkali. On the other hand, it can be removed by an acid without injury to the remainder of the chlorophyll molecule, and the magnesium-free chlorophyll which can be obtained in this way is well suited to certain investigations. Willstätter has made use of this circumstance to test to what extent chlorophyll can be the same in different kinds of plants. Investigations carried out on more than 200 different plants, both phanerogamia and cryptogamia, showed that the chlorophyll was the same in all the kinds so far examined. This chlorophyll is, nevertheless, not a chemically homogeneous substance. It is a mixture of two somewhat different but yet closely related chlorophylls, one of them being blue-green, the other yellowgreen, and the former occurring more richly in the leaves than the latter.

The fact that chlorophyll in the ordinary sense is a mixture of two green pigments had, it is true, already been shown to be probable by Stokes in 1864, and both Tsvett and Marchlevski had brought forward important support for this view. It is Willstätter, however, who has here produced the certain and conclusive proof.

To prepare chlorophyll in an unchanged, pure state and in such large quantities that it can be the subject of complete chemical analysis has of course been one of the most important tasks of chlorophyll research; at the same time, it was one of the most difficult of all. By the successful solution of this task Willstätter has also been able to prepare the two above-mentioned different types of chlorophyll in a pure state and so supply exact proof of their existence. In doing so he has been able to carry out a thorough investigation of the large amount of the various derivatives which can be produced from these two different

chlorophylls, and as a result of this means he has brought a desirable clarity and lucidity into a field of chlorophyll chemistry, which was previously very complicated and confused. By elaborating methods for the preparation of pure chlorophyll in rather large quantities he has also created new and rich possibilities for further fruitful research in this field.

The most important part of Willstätter's investigations is, nevertheless, that relating to the detection of the chemical structure of chlorophyll. He has shown that chlorophyll is an ester, which on saponification with alkali can be split up into a previously unknown alcohol called "phytol", which represents about one third of the molecule, and a colour component called "chlorophyllin", containing magnesium, which forms the remaining part. He has more closely investigated these two components both individually and for their transformation and decomposition products. Furthermore, he has found that this splitting-up of chlorophyll into the two mentioned main components can also take place as a result of the action of an enzyme occurring in the leaves, which he has called "chlorophyllase", and hence he has been able to elucidate the nature of the crystallized chlorophyll. He has established that this is not, as some investigators have assumed, the pure, unchanged natural pigment in the leaves. The crystallized chlorophyll is a laboratory product, an alkyl ester, which lacks phytol. The amorphous chlorophyll, containing phytol, is the unchanged natural pigment in the green parts of the plant.

A very important section of Willstätter's work on the chemical structure of chlorophyll is represented by his investigations into the colour components, the "chlorophyllin", and other "phyllins" and derivatives formed from it. These investigations are of particular interest with regard to the question of the relationship between blood pigment and chlorophyll.

From the iron-containing red blood pigment, haemoglobin, substances can be prepared, purple in colour and free from iron, which are known as porphyrins, and the one which has been known longest of these is haematoporphyrin. A substance very closely related to this, with regard to optical properties, has been prepared from a chlorophyll derivative by Hoppe-Seyler, who called this chlorophyll pigment phylloporphyrin on

account of the similarity between the two substances. Schunck and Marchlevski have shown later that a chemical relationship does exist between blood pigment and chlorophyll, but in this case, too, it is Willstätter who has conducted the completely conclusive investigations.

In these investigations, which concerned the pigment nucleus both in chlorophyll and in haemoglobin, he has made several new and important observations regarding the pyrroles and their position in this nucleus; in particular, however, he has shown that from these two pigments the same parent porphyrin, "aetioporphyrin", can be prepared, whose molecule has retained the essential characteristics of the pigment nucleus. By doing this he has produced the most interesting and decisive proof of the relationship between the two most biologically important pigments in Nature - haemoglobin and chlorophyll.

He has also prepared in a pure state and studied exhaustively the yellow pigments, the so-called carotenoids, which occur together with chlorophyll in the leaves of plants. By means of the results obtained regarding both these yellow pigments and the chlorophylls he has paved the way for new biological researches into the part played by the different leaf pigments in the assimilation of carbonic acid.

He has also studied with great success another group of plant pigments, namely: the blue and red pigments of flowers, the so-called "anthocyanins". He has isolated the characteristic pigment and investigated its chemical nature from a rather large number of flowers, such as cornflower, roses, pelargonia, larkspur, hollyhock, etc., as well as from some fruits, such as bilberries, black grapes and cranberries. As a result, the anthocyanins have been shown to be glycosides, which can be split up into a kind of sugar - in most cases glucose - and a colour component, a "cyanidin". Willstätter has elucidated the chemical structure of these cyanidins; he has proved in what their difference consists in the various flowers or fruits, and has also proved their close relationship with the yellow pigments, occurring in Nature, of the flavone or flavonol group. By the reduction of one such yellow pigment, quercetin, he has obtained the cyanidin which occurs in roses and cornflowers, and by chemical synthesis he has succeeded in preparing the cyanidin of the pelargonia,

pelargonidin. He has shown the dependence of the flower pigments upon the reaction of the plant sap and has thus explained how one and the same anthocyanin can have a different colour in different flowers, as is the case with roses and cornflowers. The anthocyanin is in both cases the same, but in the rose it is bound to a plant acid and is therefore red, whereas in the cornflower it is bound to an alkali and is therefore blue.

By extending his investigations to the yellow pigments of flowers as well, and by quantitative determination of the anthocyanins in certain kinds he has shown that the difference in the colour which the flowers assume in Nature or under the care of the grower depend upon several different circumstances, such as the appearance of several different anthocyanins in the same kind, great variations in anthocyanin content, different reaction of the cell sap and the simultaneous presence of different quantities of yellow pigments, which latter can again differ from one another in types.

In this field of plant-pigment chemistry, Willstätter's investigations can also be regarded as pioneering; the most comprehensive and the most important are, however, his investigations on chlorophyll, by which he has not only succeeded in unravelling the chemical structure of this substance, but also laid the sound scientific foundation for continued successful research into this extremely important field of plant chemistry.

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