THE RIDDLE OF CELLULOSE[1]

BY PROFESSOR DOCTOR EBNER

No other substance is receiving so much attention from the physical chemist today as cellulose. This is not only the chief structural material in all plants, but it is also the raw material of new and important industries. Notwithstanding the patient study that has been devoted to it, however, its chemical structure and composition still present many puzzles.

Cellulose has two qualities that render the investigation of its physical and chemical constitution especially difficult: it is insoluble in water or other ordinary solvents, and it is extremely sensitive to the action of acids and saline solutions. These qualities make it almost impossible to determine from the products of its decomposition what the form of its original constituents was. To be sure, cellulose shares this incapacity for molecular dispersion with several other organic substances, like albumin, starch, and certain pigments, which are classified together under the collective name of colloids.

The first investigator whose patient studies gave him some insight into the spacial structure of the colloids and their so-called solutions was Karl von Nägeli, whose researches into the constitution of starch in the late fifties of the last century convinced him that all colloids were made up of minute crystalloid bodies which he called micellæ, or 'little crumbs.' These he assumed to be extremely diminutive groups of molecules, too small to be visible under the most powerful microscope, arranged in symmetrical patterns so that their internal structure resembled that of crystals, although they might assume various outward shapes. While most chemical substances, like salt, sugar, and the like, separate into their individual molecules in water, the colloids cannot do this, but simply separate into these tiny molecular aggregations, or micellæ, which are the lowest subdivisions of which they are capable while retaining their collodial identity.

Nägeli's researches, however, could be pursued only to a certain point for lack of the technical instrumentalities necessary for further investigation. The next advance had to wait upon later discoveries, and only within the past few years has the nature of these molecular groups, or primary particles, of the cellulose structure been fully established. The first step forward followed the discovery that cellulose refracted light in the same way that crystals do — for instance, the cell walls of a flax fibre produced a refraction six times that produced by quartz. It was shown further, by saturating the cellulose with water, that this double refraction was not due to the fact that the tiny rod-groups, or micellæ, were embedded in a medium of different refractivity from itself, but that the micellæ themselves had a distinct refractive index, such as had hitherto been assumed to be peculiar to microscopic crystals.

This led to the conclusion that cellulose must consist of minute rodlike

[1] From *Kölnische Zeitung* (Conservative daily), *April* 22

crystals connected in series, and that this stringing together of the minute rods, and the parallel grouping of the strings, persisted even throughout a great number of chemical changes in the cellulose itself. For example, the rodlike structure of the micellæ was not affected when cellulose was treated with nitric acid and thus converted into guncotton.

These conclusions were brilliantly confirmed when the X-ray was applied to the investigation of fibres. In 1920 ramie, an almost pure form of cellulose, was discovered to produce an X-ray photograph of a kind previously observed only in case of crystals. For example, while noncrystallized, or so-called amorphous, substances produce simply a black blur on a Röntgen plate, crystals and crystalline bodies produce a number of alternating bright and dark curved lines called interference lines. The appearance and strength of these lines bear an intimate relation to the inner structure of the crystal — the so-called crystal grating. In case of ramie fibres, these interference rings were not, to be sure, complete, but fell into definite symmetrically arranged points or short segments of circles. Polanyi, who in 1921 made an exhaustive investigation of these Röntgen, four-point patterns, or fibre diagrams, showed that they appear only when the innumerable tiny crystals that form a crystalline substance all lie with their axes in the same direction, instead of in different directions. Such an arrangement of these crystalloids in parallels is characteristic of the structure of all fibres — not only of ramie, but cotton, silk, wood fibre, and all similar substances of vegetable or animal origin, including hair, muscles, and nerves.

But while natural cellulose in the form of ramie, cotton, flax, and other similar fibres, has all its crystallized micellæ lying with their axes parallel to the axis of the fibre itself, that is not true of artificial cellulose, mercerized cotton, and most kinds of artificial silk. The latter have their crystals lying pell-mell in all directions, and an X-ray photograph of them shows alternating dark and light lines in closed circles.

Very recently it has proved possible, by employing certain methods of drawing and tension when the cellulose is leaving the copper-ammoniac solution, to produce an artificial silk whose crystalline structure as shown by its X-ray photograph is the same as that of natural cellulose. In other words, its rodlike, crystalloid micellæ all have their axes lying in the same direction. The displacement, or jumbling-up out of their normal parallel order, of the crystals in ordinary artificial silk explains why this substance reacts so much more readily to chemicals, and absorbs water and colors so much more quickly, than natural fibres. Its component crystals lie in all directions, leaving interstices and exposing a larger surface to foreign ingredients like pigments and moisture. On the other hand, the end-to-end arrangement of the micellæ in parallel lines that exists in natural fibres is easy to understand, for it is necessary, not only for the upward growth of the plant, but in order to give the plant greater resistance to wind, weather, and other external influences.

While the origin of the crystalloid structures now assumed to make up every fibre is not definitely known, it is very probable that they do not exist in the young plant or animal from the beginning, but are developed from an amorphous jelly. Young asparagus, for example, and the chitin of insects in the chrysalis state, are still structureless, and consist of an incompact, watery substance that is later converted

into a firm crystalline composition. We may infer that drawing and tension play the same part in the formation of the fibre here that they do in the latest processes of producing artificial silk. Drawn-metal wire, which likewise consists of minute crystalline rods and consequently produces the same Röntgen diagrams as natural cellulose, gives us a hint to this effect, and confirms the inference that vegetable fibres are crystallized from some amorphous material.

This assumption has been strengthened by the results of recent investigations in natural silk-fibrine and chitin, which play the same part in the animal structure that cellulose does in the vegetable structure. In all these different organic compounds, both vegetable and animal, an identical crystalline substance has been discovered embedded in certain adhesive materials which chemists have for a long time designated as mucilages, or semicellulose, without knowing their exact constitution. Unless there were some such intermediate substance, cellulose itself would not possess sufficient resistance to wind-pressure and similar forces to perform its functions in plant and animal existence. For if the tiny crystalline rods were in direct contact, their size and shape would be easily modified by external accident and the strength of the cellulose fibre would be seriously weakened.

This binder or cement in cellulose is much more easily attacked by chemicals than the crystals themselves. Every laundryman knows how quickly textile fibres are affected by mineral acids, which weaken them so that they will rub to pieces between the fingers. Chemists have hitherto called the product resulting from the action of such acids upon cellulose hydrocellulose, without being able to describe exactly what the chemical reaction producing it was. Investigations show that this product consists mostly of unchanged or very slightly changed cellulose. X-ray photographs show that hydrocellulose has practically the same Röntgen diagram as ordinary cellulose. We are thus led to infer that acids do not affect the tiny crystalline rods or micellæ themselves, but only the binder between them, and that their effect is simply to allow these rods to fall apart.

This isolation of the crystalline bodies is important in its bearing upon other chemical transformations. We have already mentioned that when cotton is converted into guncotton, or nitrocellulose, the outer form of the fibres is not changed. All that occurs is an internal transformation, or pseudomorphosis, of the tiny crystalloids. That is, the chemical reaction occurs in each of these crystalloids individually, while it is kept in its original position by the binding substance. Very recent researches show that when cellulose absorbs water the latter is taken up by the binder between the micellæ, and not by the crystalloids themselves.

What we have said of the structural character of fibres, as consisting of minute micellæ, or rodlike crystalloids arranged parallel and end-to-end, which we can now assume to have been definitely demonstrated by the X-ray, fully explains two characteristics which distinguish cellulose from other organic substances — its tensile strength and its chemical inertness. But when we extend our inquiries to the ultimate component of these crystalloid formations, to the primary parts of the micella, we immediately encounter new difficulties which have not yet been solved. We are practically certain that the ultimate constituents of the micella must be a grape-sugar residuum consisting of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen. The presence of these grape-sugar or

glucose residua is inferred from the well-known fact that both plant cellulose and starch, which is closely related to it, can be produced out of grape sugar and can again be converted into grape sugar. Cellulose and starch are easily converted into grape sugars with acids and ferments, by a process which we call hydrolysis, because it is associated with the incorporation of water in the cellulose molecule.

How many of these glucose residua are contained in the crystalloid cell, or micella, and how they are arranged with reference to each other, are not yet definitely known. To be sure, Polanyi has attempted to determine the constitution of the micella from X-ray photographs of cellulose. He has estimated the length of the three edges of these tiny, rodlike, orthorhombic, or possibly monoclinic crystals, and from that their cubical content, and has reached the conclusion that each micella has a volume of about six hundred and eighty quadrillionths of a cubic centimetre, which indicates that a small thimble would hold about fifteen hundred trillions of these little rods. Since we know how much space a single atom of carbon, hydrogen, or oxygen occupies, we can easily figure out how many grape-sugar residua, with the chemical formula $C_6H_{10}O_5$, a single micella can contain. It works out practically four glucose groups to one cellulose crystal.

Unfortunately this astonishingly simple chemical solution, as derived from the X-ray photographs, is subject to some doubt. We are not perfectly certain whether the length of the edges of the rodlike micellæ may not be some multiple of the figure at which Polanyi arrived. If so, the number of glucose groups each one contains would be correspondingly increased. In any case, the Röntgen method has not shown us definitely the molecular weight and the molecular size of the cellulose micella. The only way in which we can solve that problem beyond question will be by chemical analysis, probably by a procedure similar to that through which the constitution of albumin was so cleverly determined.

Provisionally, however, we are in possession of one interesting fact. Cellulose and other fibre materials do not consist, as chemists have hitherto assumed, of large and complex molecular combinations, but of relatively small and simple molecular groups.

MY CHINESE SERVANTS[1]

BY ANI PFISTER

To-day I met upon the street my former 'German boy,' the pearl of boys. One day, shortly after I first came to China, he suddenly turned up in my kitchen. My old boy told me that he himself had been suddenly called back to Shantung by the death of his father. As a matter of fact, he had got a better job, for I saw him two days later washing the windows of a neighbor's house, and he gave me a cheerful bow. He explained that his friend Lu, who had been called Fritz by his former master, had come to take his place. I was a greenhorn and did not know that this was the invariable procedure in China, and was doubtful as to what I should do.

In the Celestial Kingdom death is a servant's conventional excuse for leaving a place or taking a vacation. Whenever a boy wants a little time off he kills his father or his mother. My present boy is not quite such a chronic mourner as most of them, especially since the first time he reported a new baby in his family as an excuse for a short absence and I gave him some of my husband's discarded linen to make clothes for it. Since then he has always reported new arrivals instead of departures when he wants a short vacation. I have figured out that these occur every three or four months, and wonder if he is a polygamist.

My husband's Chinese laboratory assistant has had a regular epidemic in his family. Death has followed death with appalling frequency. But after every funeral the young man turns up at the Institute as blithe and merry as ever. The Chinese stenographer has had equally impressive reasons for pondering on our common mortality. He recently informed my husband, in great distress, that his last child had just died and that he must go to Tientsin to the funeral. I'll wager, though, that inside of a few months another child of his will need to be conducted to its last resting-place. Since death and funeral rites do not occur at the same time in China, but the latter ceremonies are held by the priests several months after the soul has left the body, these events have the advantage of making an excuse for two distinct holidays.

But to come back to Lu. I had no reason to regret the exchange. He had learned to cook at Tsingtau, where he had worked for a long time in the family of a first lieutenant. He never tired of singing the praises of the good man and his wife, and spoke German with remarkable fluency. It is a striking fact that the average Chinese servant here learns Russian and German perfectly, but never gets beyond pidgin in speaking English.

Lu had copied his etiquette from the lieutenant's orderlies. His '*Zu Befehl, Herr Doktor,*' and his '*Weiss schon Bescheid, gnädige Frau,*' with his hands precisely where his trouser-seams would have been if there were any in Chinese trousers, were impeccable.

One day when I went out into the

[1] From *Vossische Zeitung* (Berlin Liberal daily), *April* 16