oxygen was tested. The experiment involving the feeding and starving of corals in light and darkness was continued, and gave results confirming those recorded in previous statements. Corals kept for four months in a light-tight box on the reef flat showed no ill effects other than those caused by the heavy deposition of sediment which smothered some; the survivors were pale, almost all the algæ being dead, but otherwise healthy. Further evidence has done nothing but confirm the view previously expressed that the algæ are useless as food for the coral, but may be of vital importance as the source of an accessory supply of oxygen.

Less detailed work on the algæ in *Tridacna* showed that the algæ here are probably of great importance as food. They form the bulk of the contents of the stomach (here modified in structure) and are found in process of digestion in phagocytes and in the digestive diverticula. There is no evidence that they provide any appreciable amount of oxygen, but they may serve to maintain the hydrogen ion concentration in the mantle cavity. The feeding of *Tridacna*, *Pteroceras*, and *Vermetus* was examined in the light of previous work on the feeding of mollusca.

Mr. Nicholls did special work on the calcium metabolism. He was unable to find any evidence of enzyme agency in the formation of the skeleton in corals. He also did further work on the variation in calcium and excess base in coral pools during low tides by day and by night, and on the calcium content of the fluid in the gut and body cavity of Holothurians. A second spawning period for the pearl oyster (*Pinctada margaratifera*) was found in May, and data as to the rate of growth obtained.

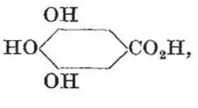
Mr. Spender, who worked for the most part in conjunction with the shore party, completed his detailed survey of Low Island, including soundings outside the anchorage and also at various positions to give characteristic profiles to the reef edge. He also made several level traverses across the flat, along the rampart and over the strips which were being surveyed ecologically. He also surveyed Three Isles, and made general surveys of outer barrier reefs near Lizard Island and around Papuan Pass.

In conclusion, it is particularly gratifying to be able to state that the work of the Expedition, especially on the economic side, will be continued by the Queensland Government, to whom the huts on Low Island and the bulk of the equipment have been given.

The Vegetable Tannins.[1]

By Prof. K. FREUDENBERG, University of Heidelberg.

THE subject of the vegetable tannins [2] is a small field in organic chemistry. Although the subject has been considerably developed and extended in recent years, its beginnings date back to the rise of modern chemistry. One hundred and fifty years ago, Carl Wilhelm Scheele, one of the discoverers of oxygen, in his dark apothecary's shop at Køping in Sweden, allowed an aqueous infusion of Turkish oak galls to be fermented by moulds, doubtless not the first occasion that such a fermentation took place in a pharmaceutical laboratory. But Scheele was one of the best observers chemistry ever had. He noticed that a crystalline substance settled down below the layer of the mould and he was able to recrystallise this substance from water. He called it *sal essentiale gallarum*, and it became known in the literature as gallic acid, having the formula



that is, a trioxybenzoic acid.

In Scheele's opinion, the action of the mould on the extract consisted in the removal of impurities, which might prevent the crystallisation of the *preformed* substance. Some years later, French chemists, however, pointed out that crystalline gallic acid and the amorphous gallotannic acid are not identical. A Flemish botanist, van Tieghem, made a detailed investigation of the fermentation of gallotannin. In the course of his work he discovered a mould specially suited for the fermentation of gallotannin, namely, the well known *Aspergillus Niger*. He was able to show that a mould mycelium, weighing only a few milligrams, was able to decompose some fifty grams of gallotannic acid. He therefore ascribed the action of the mould to an enzyme, named tannase, and further showed that at the same time an alcoholic fermentation sets in, a fact already mentioned by Liebig and attributed to the presence of sugar in the gallotanic acid molecule.

Previously, in 1834, it had been found by Liebig and Pelouze that gallotannin acted upon by dilute acids splits off the same gallic acid obtained earlier by fermentation. In 1850, Strecker published an account of a fundamental investigation on the subject. With hot dilute acid, he obtained in addition to a large amount of gallic acid, a small but definite quantity of glucose.

Unfortunately, at about the same time, theoretical speculations began to obscure clear-cut experimental results. Under the influence of Gerhardt's work on acid anhydrides, Mulder interpreted gallotannin as an anhydride of gallic acid, the sugar content being ascribed to the adventitious presence of an admixed glucoside. Curiously enough, the more analytical methods were improved, the less could Strecker's results concerning glucose be confirmed. His yield of fifteen and more

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[1] A lecture given to Section B (Chemistry) of the British Association at Cape Town on July 26, 1929.

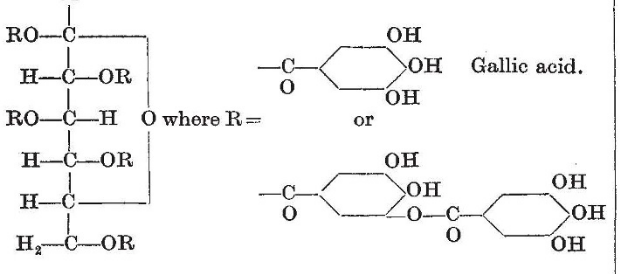
[2] There is some confusion in the nomenclature owing to the fact that 'tannins' (*Gerbstoffe*) in general and 'gallotannin' have been termed simply 'tannins' by Emil Fischer.

per cent was never again obtained; there seemed to exist samples containing not more than a few per cent of sugar, or even none at all. To-day we know that, presupposing exact laboratory methods, no gallotannin exists yielding less than seven to eight per cent of glucose. I may add that the view that sugar-free gallotannin exists has been abandoned by everyone except Dr. Nierenstein. Some years ago, Dr. Mitchell and, afterwards, Dr. Nierenstein described a gallotannin which was stated to be nearly free from sugar. Through the kindness of Prof. A. G. Perkin, I was able to obtain a sample of their original material. This has been shown by Dr. O. Schmidt (unpublished results) to yield seven per cent of glucose when E. Fischer's method is closely followed. It may be mentioned that Prof. P. Karrer has confirmed E. Fischer's formula quite independently. We know further that the failure to confirm Strecker's work was due to the employment of different specimens of gallotannin.

Strecker's gallotannin originated from Turkish oak galls which do actually contain 15 per cent of glucose, as Strecker has stated. Subsequent investigators were furnished with Chinese gallotannin resulting from galls in the leaves of *Rhus semialata*. This Chinese product, on hydrolysis by dilute acids, does indeed only furnish seven per cent of glucose, as mentioned above.

I have laid some stress on the above results, because they are typical of investigations dealing with amorphous substances. When crystalline material is worked up no discussion about identity or purity need arise.

It is no mere accident that the task of solving the problem fell to Emil Fischer. His experience in handling amorphous proteins and carbohydrates, backed by an exceptional knowledge of analytical and synthetical methods, which he had previously applied to crystalline substances, enabled him to attempt the solution of the problem. At the outset he showed that the glucose does not result from an accidental admixture, but is an essential constituent of the gallotannin molecule. In a manner which was so far as possible quantitative, he studied both the amount of glucose present and the manner in which it is linked to the gallic acid. As a result he proposed the following formula:



Digallic acid.

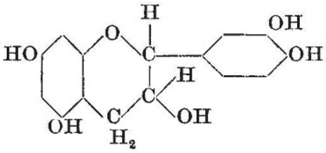
R is the residue of gallic acid, and five such residues are attached to a glucose molecule which is here represented according to Haworth's amylene oxide formula, which I venture to think has been conclusively established. We thus get a five-fold ester of gallic acid with glucose, the latter playing the part of a pentahydric alcohol. This is the scheme given by Emil Fischer for the Turkish gallotannin studied by Strecker. Joining two molecules of gallic acid we obtain a digallic acid, likewise able to function as *R*; this is the scheme given for Chinese gallotannin where ten gallic acid residues are accumulated on one glucose molecule by esterification.

These formulæ are not to be taken as a strict expression of any single chemical individual, but rather as a type. There is no doubt that both varieties of gallotannin, Turkish and Chinese, are a mixture of substances of the same type but differing to a minor extent (P. Karrer). The Turkish gallotannin, composed on the average of five gallic acids and one glucose, may quite well be mixed with similar molecules containing four or six gallic acids. In Chinese gallotannin, the possibility of variations is even greater and it can only be said that the number of gallic acid residues lies between eight and twelve. At the time of Fischer's researches, this kind of structural problem was new, for he only attempted to give a general scheme for the kind of chemical bodies in question. I have already referred to his special fitness for this task due to his experience with amorphous substances.

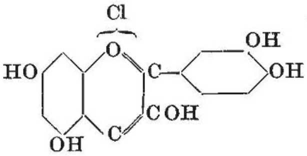
There is another trait in Fischer's tannin work, characteristic of this master of organic synthesis. We may distinguish two kinds of organic biochemical research. In the first kind, for example, that of indigo or other chemical individual, the goal lies open in front of the investigator like the summit of a mountain. He can measure it and survey it from below and at last venture to attack the summit by undertaking a synthesis. The other kind is that inaugurated by Fischer, my venerated teacher. He explored the large tracts of amorphous substances where marsh land prevents access and primeval forest obscures the view, so that no fixed points are available on which to base a survey. There the master penetrates into the unknown field with a band of his apprentices and obtains a view not only by cutting down some giants of the forest, but also by building up artificial structures from which to survey the surrounding country. Thus the synthesis of a five-fold gallic and digallic ester of glucose was intended to provide an artificial object of comparison for the amorphous substances given to us by Nature.

Apart from the gallotannins already dealt with, there exists only one other group of tannins the chemistry of which is based on a sure foundation. The chemistry of catechin and catechol-tannins was outlined only after the gallotannin class had been explored, and in this second group the biochemical relationships are of some interest. The widely distributed amorphous tannins of the catechol group seem to originate by polymerisation and condensation from crystalline primary substances called catechins.

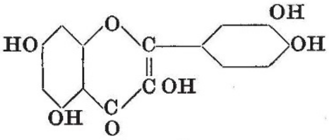
Catechin itself is not uncommon in the leaves and the wood of various tropical plants. Its constitution, first surmised by A. G. Perkin, shows a phloroglucinol and a pyrocatechol nucleus, and between them a heterocyclic ring containing an oxygen atom. The connexion between cyanidin and quercetin is evident. Quercetin belongs to the type of yellow colouring matters called flavonols. They are widely distributed throughout the plant kingdom. Cyanidin, in acid solution, is the colouring matter of the red rose and, in an alkaline medium, the blue pigment of the cornflower. On reduction of cyanidin, catechin was ultimately obtained, whereby the constitution of the latter substance was established. I say ultimately, because at first another catechin results, which I called epicatechin. Its presence in plants has likewise been realised. Epicatechin, as well as catechin, contains two asymmetric carbon atoms which cause the existence of two inactive and four optically active forms. They have all been prepared. In passing, it may be observed that the constitution of cyanidin, on which the constitution of catechin and epicatechin depend, has been completely established by synthesis, first by Willstätter and more recently by Robinson. Those botanists who consider that cyanidin and quercetin play a part in the respiratory process of plants should also take catechin into account.



Catechin.



Cyanidin hydrochloride.



Quercetin.

The most widely used of all vegetable tanning materials to-day is the extract of the wood of *Schinopsis*, called *quebracho*, and is produced in South America. Its resemblance to the amorphous tannin produced by condensation of tannin leads to the assumption that there exists likewise a primary substance of the quebracho-tannin which we could name quebracho-catechin. We can even predict its probable constitution. It seems to be distinguished from catechin by the lack of the phenolic hydroxyl group adjacent to the methylene group. Unfortunately, all attempts to isolate this presumed crystalline substance have failed. We know only the amorphous quebracho-tannin, which is recognised as a product of condensation and polymerisation of the hypothetical quebracho-catechin. As catechin is generally accompanied in the plant by the corresponding flavonol, in this case quercetin, so quebracho-tannin contains a flavonol of lower oxygen content, differing from quercetin by the absence of the corresponding hydroxyl group.

Most of the chemical facts we know about the other tannins suggest that these belong to one or other of the two groups described. There exist, indeed, some other types which are evidently quite distinct from these; but their constitution still requires elucidation. So the question is still open whether the tannins of the Cape sumach, *Colpoon compressum*, and of the wattle (*Acacia*) belong to the catechol group or not. The Sicilian tanning material generally called *sumach* is a member of the gallotannin group.

The only resemblance between gallotannin and catecholtannin lies in their high content of phenolic hydroxyl groups. To these they owe their ability to combine with proteins and to convert hide into leather. As a chemical concept the name tannin is without value. In spite of this, however, the group deserves further investigation, on one hand, because its members are widely distributed constituents of plants; on the other hand, because their investigation calls for novel methods which I have endeavoured to indicate.

Obituary.

DR. E. E. SLOSSON.

A WIDE circle of scientific workers and lay readers will learn with regret that Dr. Edwin E. Slosson, director of Science Service, Washington, died at his home there on Oct. 15. He had been suffering from cardiac trouble for some time, and an acute attack about a week previously hastened his end.

Dr. Slosson was born in Albany, Kansas, in 1865, and graduated in the University of Kansas. In 1891 he went to the University of Wyoming to take charge of the department of chemistry, and he also conducted chemical research for the Wyoming agricultural experiment station. He married Dr. May Preston, the first woman who ever received a Ph.D. degree from Cornell University.

In spite of his manifold teaching and research duties, Dr. Slosson found time to work towards his own doctor's degree during the summers, and received it in 1902 from the University of Chicago. He also found time to write numerous little essays on scientific subjects, which, because of their happy style and lucid presentation of ideas in ordinary English, rapidly won him a wide audience. In 1903 he was invited to become literary editor of the *Independent*, a position which he held until 1921, when he was asked to become director of Science Service, then newly organised as an agency for the dissemination of popular knowledge on scientific subjects. He held this latter post until his death.

The most successful of Dr. Slosson's books has