for this correction, it is better to establish for one's self just what it should be for each material operated upon, by check gravimetric determinations; for while within limits this may be taken as a constant factor, yet it is more or less affected by the character of the salts present. And further, this table was not carried far enough to cover the large volumes of gas evolved from the charges that my apparatus enables one to employ.

With this apparatus it is possible to make a determination of carbon dioxide in from ten to fifteen minutes, and that with extreme accuracy. Indeed with the large charges one may employ, and with careful weighings, repeated results obtained from the same sample, will never vary more than one-tenth per cent. and scarcely more in most instances than two or three one-hundredths per cent.

## ARE PENTOSES FORMED BY THE ASSIMILATION PROCESS?<sup>1</sup>

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IN recent years the chemistry of the sugars having been revolutionized by the investigations of Kiliani, Fischer, Tollens, and others, the study of the assimilation process, by which the carbohydrates in the plants are originally formed, has also received a new interest.

The theory of Bayer, according to which the first product of the assimilation is formaldehyde, has recently received a very strong support by the results which Bokorny obtained.<sup>2</sup>

Fischer observed some years ago that glyceric aldehyde was probably an intermediate product in the assimilation process, since it most readily unites with itself, yielding hexoses, when placed under proper circumstances.<sup>3</sup>

Pentosans, substances which yield pentoses by hydrolysis, are most widely distributed in plants and form often a large part of their dry matter.<sup>4</sup> The pentoses, xylose, and arabinose, belong to the laevo series (of Fischer) in contrast with the more

2 Ber. d. bot. Ges., g, 4, 103.

8 Ber. d. chem. Ges., 23, 2238.

4 Am. Chem. J., 15, 21, note.

<sup>1</sup> Read before the World's Congress of Chemists, August 23, 1893.

widely spread hexoses, glucose, and laevulose, which belong to the dextro series.

From a chemical point of view it is more likely that the laevo-pentoses and dextro-hexoses are formed beside each other by the assimilation process, than that they are formed out of each other. The theory of Bayer thereby admits just as well the formation of pentoses as that of hexoses. On the other hand, strong support will be given to Fischer's theory that glyceric aldehyde is an intermediate product, if it be proved that the pentoses in plants are not formed by the assimilation process. I have, therefore, investigated this subject, and I have reached results which prove that pentoses are not formed by the assimilation process unless in imperceptible quantities. Let us see how this result was obtained.

Of the methods used for the quantitative analysis of the pentoses I can only say a few words. Pentoses yield, as is well known, about fifty per cent. of furfurol when heated under proper circumstances with dilute hydrochloric acid. Upon this property the methods for determining pentoses are based, since they vary only in the way in which the furfurol is estimated.

Two different methods were used. When larger quantities of pentoses are present. I used the method of Tollens and myself with the alterations recently proposed by Tollens and Flint. By this method the furfurol is precipitated and weighed in the form of hydrazon. This method when properly executed gives very accurate results. If only very small quantities of pentoses are present in solutions, the furfurol is determined by a colorimetric method making use of its property of yielding a red dyestuff when mixed in an acetic acid solution with an alcoholic solution of anilin oil in the absence of free mineral acid. This method was published in the American Chemical Journal of this year.' Since hexoses also yield small quantities of furfurol when heated with hydrochloric acid, for examples, fructose (0.2 per cent.), glucose, and galactose (0.04 per cent.) it is necessary to determine also the total amount of sugars if only very small quantities of furfurol are obtained, in order to be sure that pentoses are present. I considered that the pentosans known

1 Ibid. 15, 25 and 277.

to exist in plants are insoluble in water and can not, therefore, be removed as such. As it is a matter of course that if the pentoses are formed in the leaves they must migrate to other parts of the plants, since we find them there. I looked for easily soluble pentoses. I therefore made extracts of the parts to be investigated by immersing them in water, and was able to trace in the leaves of thirty-five plants belonging to widely different families and also in the colorless bark soluble pentoses. I concluded that soluble pentoses occur universally in green higher plants.

These soluble pentoses diffuse readily through membranes permeable to water, as parchment paper and parchment. They furthermore do not diminish perceptibly in dying leaves. For these reasons the soluble pentoses are true transport substances. They are, however, present in much smaller quantities than the soluble hexoses. The largest amount found was 0.4 per cent. in the leaves of Tecoma radicans. In many instances the amount does not exceed 0.05 per cent.

If the pentoses are formed by the assimilation process, they are either removed as soon as they are formed or they are temporarily stored, probably in an insoluble form and gradually removed. If the pentoses are removed as soon as they are formed, there ought to be much more soluble pentoses in the leaves during the time of the assimilation than after that time. I therefore collected of the sycamore and the oak the same surface of leaves at half-past four and ten o'clock in the morning and at five and nine in the afternoon. The oak leaves contained at sunrise slightly less soluble pentoses than at other times of the day. In the sycamore leaves I could not perceive any difference. The pentoses are therefore not us quickly removed as they are formed, a fact which was probable from the beginning. I made nine investigations of oak leaves and found in seven instances slightly more soluble pentoses in the evening than at sunrise. In one instance the leaves contained less soluble pentoses in the evening, but then the specimens of morning and evening leaves did not exactly agree. A small difference seems therefore evident, a

1 Ibud, 15, 21.

difference amounting to from 0.01 to 0.02 per cent. of the weight of the fresh leaves. In leaves of other plants I have not been able thus far to detect the same difference. I therefore concluded that the pentoses are temporarily precipitated in the chlorophyl grains and gradually removed. In the oak leaves the pentoses assimilated during the previous day should be nearly or fully removed at sunrise.

The idea that the pentoses are temporarily precipitated mixed with hexoses as starch of assimilation is not so improbable since Winterstein found pentosans which are soluble in boiling water and give a blue color with iodine.<sup>1</sup> Moreover, I was able to prove that the insoluble pentosans in seeds are resolved during the germination and removed into the germs. Notwithstanding all this, this hypothesis is wrong, as I have proved beyond doubt that no such accumulation of pentoses in the leaves takes place.

If pentosans are transported to any extent out of the leaves during the night we will find that a certain surface of leaves collected in the evening contains more pentosans than a closely similar surface of exactly the same size collected in the morning. If, on the contrary, no such transportation takes place we will find no difference, and since a certain amount of dry matter is transported out of the leaves during the night we will find that the dry matter in the leaves contains a smaller percentage of pentosans in the evening than in the morning.

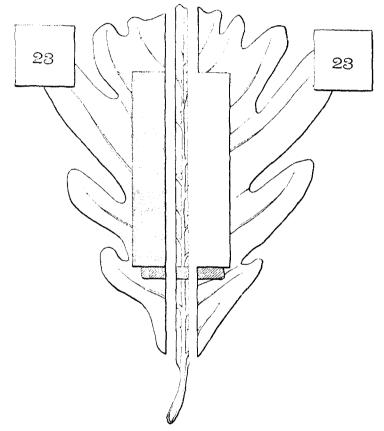
For these investigations I used the method of leaf halves of the German physiologist, Sachs,<sup>2</sup> and collected my specimens as indicated in the drawing. I number from 70 to 100 leaves, attaching with varnish on both halves the same number. I make on the lower part of each leaf also with varnish a little mark across the mid-rib. At seven o'clock in the evening I sever a piece from every leaf by cutting close to and paralell with the mid-rib. Out of each of these pieces I cut with a razor a strip the form of which is given by a piece of iron plate. This is applied with one of its long sides along the cut, and with its lower end touching the mark. Each strip receives the

1 Ber. d. chem. Ges., 25, 1237.

<sup>2</sup> Vorlesungen über Pflanzenphysiologie, 304.

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same number as the leaf from which it is derived on a strip of paper which is wrapped around it. The strips of leaves are then quickly dried at  $100^{\circ}$  C. The next morning at half past three I collect, number and dry the symmetrical strips of the other halves of the leaves. The numbers of strips of both series are then compared and those strips taken out of which the



counterpart fails, which will sometimes happen, since one of the times of collection is before sunrise. The difference in weight of both lots of dried strips gives very accurately the total amount of dry substance removed during the night or stored during the day in the case in which I collect the first lot before

sunrise and the second in the evening. The dried strips are then pulverized and exactly the same quantity of each taken for the estimation of the pentoses. Both analyses are made side by side and with the utmost care. I have put together in the following table the different results obtained:

	Evening.		Morning.		it of prod- 1 sq. ves.	the the	nto- the the
	Weight of I sq. meter of leaves.	Per cent. of pentosan.	Weight of I sq. meter of leaves.	Per cent, of pentosan.	Total amon assimilation ucts stored in meter of lea	Excess of pesan in 1 sq. m san in 1 sq. m of leaves in morning	Excess of pe san in 1 sq. n of leaves in evening.
	gnis.	gms.	gms.	gms.	gms.	gms.	gnis.
Corn (Zea Mays) I II	33.456 35.354	14.49 15.35	28.633 31.644	17.26 17.21	4.823 3.710	0.098 0.018	
Oak (Quercus alba) I II	70.343 57.906	6.77 7.86	66.977	7.16	3.366	0.030	
Tropaeolum majus	26.143	4.01	55.493 23.401	8.30 4.42	2.742	•••••	0.014

Corn promised to be a favorable subject as the leaves are thin and assimilate strongly. This plant contains large amounts of pentosans, 17 per cent. in the leaves and 11.5 in the stems. The first investigation showed that one square meter of leaves weighed in the evening 33.456 grams and in the morning 28.633 grams. During the night 4.823 grams were removed and still one square meter of leaves contained in the morning ninety-eight mgms. more pentosans than in the evening. As it seemed possible that a small amount of pentosan was formed during the night in the leaves I collected in my second investigation first in the morning and afterwards in the evening, I found that one square meter of leaves had stored during the day 3.710 grams of dry matter, but no pentosans, since eighteen nignis. more were found in the morning, which difference is well within the limits of experimental error. Oak leaves had also to be investigated, as little difference was found in the amount of soluble pentosans in morning and evening leaves. They offer a much less favorable subject than corn leaves, since they are thicker and do not assimilate as strongly. Oak plants are, however, also rich in pentosans. The leaves, it is true, contain only from seven to eight per cent., but the stems, which weigh far more, are also much richer in these substances. The stems of the shrubs which I used contained nineteen per cent. of pentosan.

In the experiments made I collected first in the evening and afterwards in the morning. The plants used for the two experiments belonged to two different localities. The results of both investigations showed slightly more pentosans in the morning, but the differences found do not exceed the limits of experimental error. The seeds of tropaeolum majus contain a pentosan that is soluble in boiling water and conducts itself also in other respects as starch. I therefore experimented also with this plant. The plants contain but little pentosan, the leaves 4 per cent., and the stems 6.5. The leaves are very thin, and therefore I was obliged to take 300 leaves in order to obtain enough substance for the estimation of the pentosans. These leaves were cut during several evenings and nights in succession. One square meter of leaves lost during the night 2.742 grams of dry matter, but only fourteen mgms. of pentosan.

All these investigations show that an accumulation of pentosans in the day time and transportation of the same during the night does not take place. The pentosans therefore are not formed by the assimilation process, unless in such imperceptible quantities as can not explain the large amounts that plants contain.

The theory of Fischer, according to which a formation of pentoses by the assimilation process is improbable, thus receives unexpected support.

## IMPROVEMENTS IN THE MANUFACTURE OF SULPHURIC ACID.

BY PETER S. GILCHRIST. Received September 17, 1893.

A NYTHING tending towards cheapening the cost of producing sulphuric acid has now become of vital importance to chemical manufacturers. The chief source of improvement lies in the reduction of the large chamber space necessary for condensation, owing to its cost and maintenance. This has been attained in several ways.

A simple but very effective method has been devised by Hacker and Gilchrist, which has been attended with very satis-