LII.—*Hydrolysis of Starch by Acids.*

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It has been generally accepted that the hydrolysis of starch, due to acid conversion, is similar in character to that brought about by the action of diastase; except, of course, in that the maltose, the final product of the diastase conversion, is transformed by acids into dextrose. The products of the hydrolysis by acids, should, therefore, consist of amyloins (maltodextrins), maltose, dextrose, and perhaps an unreducing dextrin $(C_{12}H_{20}O_{10})_n$. Brown, Morris and Millar (*Trans.*, 1896, 69, 121) evidently incline to this view, for they have shown that some fractions obtained by Lintner and Düll from conversions with dilute oxalic acid, after separation of the dextrose, would obey the laws of diastatic conversions, on the assumption that these fractions contained $2\frac{1}{2}$ per cent. of moisture. However, Soxhlet (*Zeitschrift Spirit. Industrie*, 1884, No. 11) stated that the dextrins produced by the action of acids on starch were quite different from those produced by the action of diastase. Rolfe and Defren (*J. Amer. Chem. Soc.*, 1896, 18, 869), in "An Analytical Investigation of the Hydrolysis of Starch by Acids," found that starch when hydrolysed by dilute acids, even under varying conditions, obeyed certain laws. The fall in the specific rotation is constant throughout the action, and bears a certain relation to the cupric-reducing power, so that, given the one, the other may be calculated. Rolfe and Defren also stated that there are only three carbohydrates present at any time during the action, namely, maltose, dextrose, and dextrin, existing possibly in molecular aggregates; these authors calculated the relative quantities of maltose, dextrin, and dextrose present at any time of the conversion by means of curves, the percentage of these carbohydrates being represented by ordinates, and the specific rotatory powers as abscissæ in the same ordinate system. It is apparent from this communication that Rolfe and Defren also suppose the conversions by acids to be similar in character to conversions by diastase, except that, of course, as before stated, the

maltose of the diastase conversion is transformed by acids into dextrose.

The object of the present paper is to show that these conclusions are erroneous, and that the intermediate products of acid hydrolysis are not identical with those of diastase hydrolysis. These differences probably form the starting point of the controversies relative to starch hydrolysis which have arisen between the English and the German school; Brown and Morris* maintain that the relation is constant between the cupric-reducing powers and specific rotations of the products of diastase hydrolysis, and can be expressed in terms of maltose and dextrin. Lintner and Düll have denied this relation, but as these authors (*Ber.*, 1895, 28, 1522) work indiscriminately on products from acid hydrolysis (after elimination of the dextrose), or from the products of diastase hydrolysis, it is not difficult to see how these differences may have arisen.

When the products of diastase conversions are fractionated by means of alcohol, the precipitated portions have specific rotations which may vary from about $[\alpha]_{D^{386}} 150^\circ$ to about 190° . These fractions present the following peculiarities: they are unfermentable by Saaz yeast, and their cupric reducing powers and specific rotations can be expressed in terms of dextrin and maltose. Dextrin has a specific rotation of $[\alpha]_{D^{386}} 195^\circ$, and maltose $[\alpha]_{D^{386}} 135.4^\circ$, so that no substance resulting from diastase hydrolysis can have a special rotation of less than 135.4° . When, however, we separate fractions from the products of acid hydrolysis, the specific rotations vary between about $[\alpha]_D 190^\circ$, and $[\alpha]_D 80^\circ$. These fractions contain no free dextrose, because they are unfermentable by Saaz yeast; moreover, they cannot be molecular aggregates of maltose and dextrin, since the specific rotation of a maltodextrin cannot fall much below $[\alpha]_D 150^\circ$, and we are in presence here of fractions whose rotations can fall as low as 80° ; we have, therefore, intermediate substances present which do not exist in diastase conversions.

Before beginning an account of the work which follows, it is necessary to say a few words concerning the methods employed in the investigation. The directions given by Brown, Morris, and Millar (*Trans.*, 1897, 71, 72) were followed closely. The polarimeter used was a half-shade instrument, the readings being very accurate to 0.1° . As regards the determination of the cupric-reducing powers, at first the Soxhlet tube was used, the precipitated Cu_2O being reduced to metallic copper. However, a series of duplicate experiments, in which the Cu_2O was collected simply on a strong, double filter paper, and then dried and ignited in a platinum dish, showed that the latter

* "Products of Starch Hydrolysis," Brown and Morris, *Trans.*, 1889, 55, 449—462; Brown, Morris and Millar, *Trans.*, 1897, 71, 73, 123.

method was the more accurate, and towards the end of the experiments this was alone used.

The Soxhlet tube presents the following inconveniences. The asbestos is extremely hygroscopic, holding water with the greatest tenacity, and even when dried in an oil bath at 150° , still retains water. This is a first cause of error; of course it may be reduced to a minimum by careful manipulation, but, when many determinations have to be made, it is impossible to devote all the time necessary to ensure accurate results. Secondly, the asbestos invariably loses weight during the collection of the Cu_2O , however carefully it may have been previously washed with acids and alkalis; perhaps this is due to the decomposition of the asbestos, or perhaps small portions of it are carried away in the washing. I had some tubes made expressly for me, with platinum cones fitting them exactly, but found that, however carefully the apparatus may be constructed, small difficulties will invariably present themselves. In dealing with the difficult problem of determining cupric-reducing powers, it is useless to complicate the apparatus; the simplest and most practical methods give the best results.

When the Cu_2O is collected on a filter paper, the following conditions must be observed to ensure accuracy. The filter with the precipitate, when completely washed, should be transferred to a wide, open platinum capsule, and dried in a water bath, the capsule being then heated over a low flame, preferably an argand burner, until the filter is completely burned, after which the contents of the dish are pounded with a small platinum pestle, which can be left in the capsule and weighed with it. The capsule is then placed over a Bunsen burner, heated to a dull red heat, and, when cold, the contents are again pounded. Finally, the capsule and contents are heated to a bright red heat, either over a very powerful Bunsen or in a muffle. The capsule is then cooled, and the contents weighed as CuO . The object of these manipulations is to ensure a thorough oxidation of the Cu_2O , which is incomplete if the heating is too vigorous at first.

If the two methods are carried out with all the care necessary, the results coincide very closely, but of the two the method of weighing as CuO is the simplest to perform, and open to less error than the process carried out in the Soxhlet tubes. It will be found impossible to wash the filter paper entirely free from the Fehling solution; this error should always be allowed for, and it differs with the kind of paper employed; the quantity was 0.003 gram for the paper which was used in these experiments. I have accepted as the cupric-reducing powers of dextrose the figures given by Brown, Morris and Millar (Trans., 1897, 71, 279); that these figures may be regarded as sufficiently accurate, is proved incidentally from the work which follows.

All values are expressed in terms of the factor 3.86 (for explanation see papers, Brown, Millar and Morris, already referred to). The specific rotation of soluble starch or dextrin has been taken as $[\alpha]_{D^{3.86}} 195^\circ$, and that of dextrose as $[\alpha]_{D^{3.86}} 52.8^\circ$. The starch was hydrolysed by means of dilute sulphuric or oxalic acid, and neutralised, after the conversion, respectively by barium or calcium carbonate; here there is another source of error which needs correction, and I have not anywhere observed that reference has been made to it. Barium and calcium carbonate are relatively very soluble in the saccharine solution resulting from the inversion, especially if the solution is fairly concentrated.

The calcium carbonate must be got rid of by careful precipitation with a weak solution of oxalic acid, and the barium carbonate by means of sulphuric acid. The solubility of these carbonates is in no way due to the presence of the carbonic acid resulting from the neutralisation of the acids, for after boiling a solution neutralised by barium carbonate, and leaving it for a week (of course, under aseptic conditions), a copious precipitate was produced on the addition of a few drops of sulphuric acid. In effecting this precipitation, it is, of course, necessary to carefully avoid the slightest excess of acid. The solubility of the calcium carbonate is even greater than that of barium carbonate, and leads to gross errors in the calculation of the solid matter, unless got rid of in the manner indicated. A pure starch is, of course, also necessary; this was obtained by washing good potato starch, first with 0.5 per cent. caustic soda to remove traces of proteid matter, and then with 3 per cent. HCl, finally washing with distilled water. The starch was saccharified at the boiling point of water, no pressure being exerted. The conversions were carried out in open beakers placed in a large water bath, the quantity of starch per 100 c.c. of water varying in the different trials from about 5 to 25 grams at the commencement of the hydrolysis, and the acid from about 3 to 8 grams per 100 c.c. As the beakers were not covered, the solutions became more concentrated as the hydrolysis proceeded, owing to the evaporation of the water, the solutions in some cases being reduced to one-half, or even one-third of their original volume; if any darkening of the solution was observed (this was the case when the sulphuric acid became too concentrated), a little distilled water was added. 50 to 80 grams of starch were taken for each experiment, and hydrolysed under varying degrees of concentration. Table A (p. 494) gives the results obtained from the hydrolysis of 16 different lots of starch.

The time taken for the hydrolysis varied according to the conditions of concentration and the point to which the hydrolysis was carried. A high percentage of starch retards the conversion, whilst a high percentage of acid has the opposite effect. As extremes for the times

taken to effect the conversions described in Table A, 12 minutes and 5 hours may be mentioned. The progress of the hydrolysis was followed by withdrawing the beaker from the water bath from time to time and determining the specific rotation of the solution. When the hydrolysis had reached the point desired, the acid was carefully eliminated, and the cupric-reducing power, the specific rotation, and the solids (by the factor 3.86) were carefully estimated.

Table A gives the results found for a series of conversions carried to different degrees. These results record the striking fact which seems to have escaped most observers up to the present, that the cupric-reducing powers and specific rotations of the products resulting from the action of acids on starch can be estimated in terms of dextrose and dextrin or soluble starch. (This is a verification of a statement made by M. Pellet (*Compt. rend.*, 2, 450) in a communication on commercial glucose read before the International Congress of Chemistry at Paris in 1896; M. Pellet, however, brought forward no experimental evidence to prove his assertion.) To render the results, as tabulated below, quite clear, a few explanations are necessary.

Column A gives the cupric-reducing power expressed as dextrose on 100 grams of 3.86 solids.

Column B, the dextrin by difference.

Column C, the specific rotation calculated from these percentages of dextrose and dextrin.

Column D gives the specific rotation found.

Column E, the difference between the specific rotation found and calculated.

TABLE A.

A.	B.	C.	D.	E.
13.90	86.10	175.2	174.4	+0.8
20.38	79.62	166.0	166.6	-0.6
20.72	79.28	165.5	165.5	0
32.44	67.56	148.9	148.2	+0.7
33.70	66.30	147.1	147.7	-0.6
40.03	59.97	138.1	137.9	+0.2
40.24	59.76	137.8	138.4	-0.6
42.61	57.39	134.4	134.9	-0.5
53.50	46.50	118.9	118.5	+0.4
57.55	42.45	113.1	112.6	+0.5
66.44	33.56	100.5	100.4	+0.1
70.18	29.82	95.2	95.4	-0.2
79.14	20.86	82.4	81.9	-0.5
80.43	19.57	80.6	80.3	+0.3
85.40	14.60	73.5	73.8	-0.3
95.52	4.48	59.2	59.7	-0.5

The figures of this table need little comment, being sufficiently striking in themselves. It will be seen that the differences between the specific rotations, found and calculated, do not exceed in any case more than 0.8° . If we take the mean of the differences, we find it only 0.05° , the *plus* differences and the *minus* differences being about equal; we can therefore consider them as errors of experiment.

Before proceeding farther, however, let us see what would be the error involved supposing there was a small amount of maltose present which had been calculated in terms of dextrose. Let us consider a case where we find in this manner 50 per cent. of dextrose and 50 per cent. of dextrin. The specific rotation of this conversion would be 123.9 . Supposing 6.2 parts of the dextrose should be in reality calculated in terms of maltose, we should have 10 per cent. of maltose to substitute in its place; (maltose having a K of 62). We should then have a mixture containing 43.8 per cent. of dextrose, 10 per cent. of maltose, and 46.2 per cent. of dextrin, the specific rotation of which would be 126.75 in place of 123.9 as formerly. From this we see that, supposing there should be 10 per cent. of maltose present, and it has been estimated as dextrose, the rotation calculated would fall 2.85° short of the rotation found. An examination of the above table shows that the calculated rotation in no case falls below more than 0.6° that of the rotation found, and as we have pointed out, this small difference can be safely put down to experimental error. Rolfe and Defren (in the paper already referred to) asserted that a specific rotation of $[\alpha]_D 129^\circ$ corresponded with the maximum percentage of maltose, namely, 44.1 per cent., the dextrin and the dextrose being present in equal quantities at this stage of the conversion. The conversion in the above table nearest to $[\alpha] 129^\circ$ is one with a rotation of $[\alpha] 134.9$, and should contain about 40 per cent. of maltose according to Rolfe and Defren. If this were so, the rotation calculated as above would fall about 11° lower than that found. The rotations found and calculated agree, however, almost exactly, and, therefore, there can be no ground for the supposition that any maltose is present.

A number of fractions precipitated by alcohol from the products of acid conversion were next carefully examined. The cupric-reducing powers and specific rotations of these fractions, in a similar manner to the total products of conversion, can be expressed exactly in terms of dextrose and dextrin. These results are set out in Table B.

Column A contains the cupric-reducing powers expressed as dextrose on 100 grams of 3.86 solids.

Column B, the dextrin by difference.

Column C, the specific rotation calculated.

Column D, the specific rotation found.

Column E, fermentative action of Saaz yeast on the fraction.

Column F, Fermentative action of *Saccharomyces apiculatus*.

A.	B.	C.	D.	E.	F.
19.50	80.50	167.2	167.5	Nil.	Nil.
36.41	63.59	143.2	144.0	Nil.	Nil.
56.63	43.37	114.5	114.0	Nil.	Nil.
62.27	37.73	106.4	106.9	Nil.	Nil.
63.41	36.59	104.8	104.3	Nil.	Nil.
70.24	29.76	95.1	95.4	Nil.	Nil.
73.36	26.64	90.7	90.2	Nil.	Nil.
79.60	20.40	81.8	82.2	Nil.	Nil.

In order to show that these fractions were not merely mixtures of dextrose and other carbohydrates, they were put to ferment with Saaz yeast and *S. apiculatus*, some carefully prepared yeast water or a small portion of a nutrient solution containing asparagine and all the salts necessary for yeast development being added to afford nutriment for the yeast cells. All the necessary aseptic conditions were, of course, observed in carrying out these experiments. Nevertheless, as will be seen from Table B, these yeasts were quite powerless to set up the smallest fermentation. However, the type of yeast known as "logos," with which experiments were also made, produced a *partial* fermentation of the fractions, those with the lowest rotations yielding most readily to the action of this yeast.

Another proof that these fractions are definite compounds and not mixtures of dextrose and other carbohydrates is to be found in their behaviour when submitted to dialysis, the purified fractions, after being several times redissolved in water and again precipitated by alcohol, dialysing without undergoing material change in specific rotation. When a mixed fraction (that is to say, the precipitates resulting from a conversion thrown down by alcohol of increasing strength) is submitted to dialysis, the products that pass through the dialyser possess rotations lower than those of the substances remaining in the dialyser; however, the substances which pass through contain no free dextrose, as may be ascertained by putting them in presence of Saaz yeast, which will be found to fail to set up any fermentation.

The fractions, when submitted to a further treatment by acids, are completely transformed into dextrose, which is the final and only product of the conversion; the specific rotation remaining stationary at about $[\alpha]_{D_{3-86}} 52^\circ$ to 53° , the dextrose is not affected by the acid, even when the concentration of the latter is as high as 15 per cent.

A point worthy of interest with regard to these fractions is the large range presented by their specific rotations, which vary from $[\alpha]_{D_{3-86}} 80^\circ$ to $[\alpha]_{D_{3-86}} 170^\circ$. No attempt has been made to separate fractions with rotations higher than 170° , since they present no interest here, but that it is possible to separate them with higher rotations is shown by Lintner (*Ber.*, 1895, 28, 1522). It will be observed that the

lowest rotation presented by a fraction was 82.2 ; this corresponds very closely with 20 per cent. of dextrin and 80 per cent. of dextrose. This fraction dialysed without change. A substance of the same composition was also obtained by fermenting a conversion with a rotation of $[\alpha]_{D^{25}} 60^\circ$ with Saaz yeast. The residue, after fermentation, contained 79.80 per cent. of dextrose and 20.2 per cent. of dextrin, and was evidently identical in composition with the fraction obtained by precipitation with alcohol.

A further proof that the substances from starch conversion by acids intermediate between starch and dextrose are *not* identical with those produced by diastase, is to be found in their behaviour towards diastase or malt extract. Soxhlet, as already mentioned, stated that diastase had no action on the dextrins from acid conversion. A careful examination has shown, however, that diastase *does* possess a slight action, but that, even on high conversions, its degrading power is very limited. This will be apparent on looking at Table C, where the results obtained by the action of malt extract on a number of conversions are tabulated.

Column A gives original rotation of the conversion.

Column B, the rotation after one hour's digestion with malt extract.

Column C, the rotation after two hours' digestion.

Column E, the fall in rotation.

The malt extract, obtained by digesting malt at 30° with distilled water, was added in quantities varying from 10 to 25 c.c. to each 10 grams of solids. The temperature employed was 60° .

TABLE C.

A.	B.	C.	E.
177.5°	165.9°	165.4°	12.1°
166.6	159.8	159.4	7.2
147.0	142.1	142.1	4.9
138.4	134.6	134.6	3.8
134.1	127.8	127.8	6.3
112.6	112.4	112.4	0.2
94.5	94.5	94.5	0

FRACTIONS FROM ALCOHOL.

A.	B.	C.	E.
167.5°	158.8°	158.8°	8.7°
144.0	142.8	142.8	1.2
114.0	114.0	114.0	0
95.4	95.4	95.4	0
82.2	82.2	82.2	0

It is rather difficult to account for this slight action which diastase has on the products of starch conversion by acids. The explanation that seems the most feasible is that the diastase attacks only the starch which has not been touched by the acid. As a rule the last traces of the blue colour* produced by iodine do not disappear until the specific rotation has fallen to about $[\alpha]_D 140^\circ$ or even lower. The point at which the blue coloration disappears depends a good deal on the concentrations of the acid and the starch; when the latter exists in concentrations of about 25 per cent. and the acid is very dilute (2 per cent.) a blue coloration will still be produced with iodine at a rotation of $[\alpha]_D 115^\circ$. The stronger the acid, the more quickly does the blue coloration disappear, thus, with a solution of starch at 5 per cent. and acid at 12 per cent., the blue coloration will disappear at a rotation of $[\alpha]_D 150^\circ$.

However, it must be stated that diastase has a slight action on conversions which give no blue coloration with iodine; perhaps in the splitting up of the molecule of starch there may be produced, as Brown and Morris have suggested, an unreducing dextrin, $(C_{12}H_{20}O_{10})_n$; the slight fall in the rotation under the influence of diastase would then be due to degradation of this dextrin. It is, however, impossible to say anything for certain, except that diastase does possess a slight action on the products of starch hydrolysis by acids. It will be noticed that diastase has no action on fractions with rotations of 114° and lower; this is another proof that these are not mixtures of dextrose and amyloins.

From the above data, we can now resume as follows the properties of the substances intermediate between starch and dextrose, produced by the action of dilute acids on starch; the specific rotations of these substances vary between $[\alpha]_{D_{3.86}} 80^\circ$ and 190° ; their cupric-reducing powers and specific rotations can be expressed in values of dextrose and the amylin group $(C_{12}H_{20}O_{10})_n$. This relation is shown by the following equation, in which $K_{3.86}$ = the cupric-reducing power in terms of dextrose on 100 parts of the substance, and $[\alpha]_{D_{3.86}} X^\circ$ = specific rotation. Then, given one of these values, the other can be calculated.

$$[\alpha]_{D_{3.86}} X^\circ = 195 - \frac{195 - 52.8}{100} K_{3.86}$$

* With regard to the various colours such as red, brown, &c., produced by iodine at varying stages of the conversion, the author finds that they are of no value whatever, being produced by an intimate mixture of starch with other substances. This may be shown by taking a drop of the mixture giving the cherry red colour with iodine, and leaving it to dry for 24 hours on a white porcelain tile; at the end of this time, the starch will have separated out in the form of a number of little blue specks and the rest of the mass will be yellow, the red colour having quite disappeared. A microscopical examination of a drop left to dry on a glass slide will render this phenomenon still more apparent.

(The values given in this equation, of course, hold good for the total products of conversion, as well as the intermediate compounds.)

On simplification of the equation, we have

$$[\alpha]_{D_3^{86}} X^\circ = 195^\circ - 1.422 K_{3^{86}}.$$

When further treated by acids, these substances are completely transformed into dextrose. When treated by diastase, they undergo a slight fall in rotation when this value is not lower than about $[\alpha]_{D_3^{86}} 120^\circ$. They are unfermentable by Saaz and *apiculatus* yeasts, being partially fermented by logos. On purification, they dialyse without change. A precipitate thrown down by alcohol contains a mixture of these substances, whose solubility in alcohol decreases in proportion as their specific rotations rise. It should also be added that, when treated with phenylhydrazine acetate, they yield gummy precipitates. These precipitates were not further examined, owing to the difficulty experienced in attempting their purification; moreover, phenylhydrazine, as the history of starch hydrolysis has shown, is not a reagent on which much reliance can be placed for isolating the divers products of conversion. It is thus apparent from their character that these intermediate compounds are molecular aggregates of dextrose and the amylin group, $(C_{12}H_{20}O_{10})_n$, and, therefore, the author ventures to call them glucoamylin, which name accurately describes their composition. Moreover, in starch conversion by acids, there is no ground for supposing that at any time during the reaction is there formation of maltose or amyloins (molecular aggregates of maltose and the amylin group, $C_{12}H_{20}O_{10}$), the sole products of the hydrolysis being dextrose and glucoamylin.†

Glucoamylin with low rotations can be easily obtained by fermenting with Saaz yeast a commercial glucose or a conversion made in the laboratory whose rotation is about $[\alpha]_{D_3^{86}} 60-70^\circ$. The residue after fermentation will have a rotation of $[\alpha]_{D_3^{86}} 80-90^\circ$, and will consist of glucoamylin. The existence in commercial glucose of an unfermentable reducing substance with a rotation of about 80° to 90° has been known of for a long time, and has received the name of gallasin. If we examine the properties usually attributed to gallasin, we shall see that it is nothing but a mixture of glucoamylin. Thus according to the various authors, the specific rotation of gallasin varies from $[\alpha]_{D_3^{86}} 80^\circ$ to 100° , its cupric-reducing power is equal to about half that of dextrose, it is insoluble in strong alcohol, and on treatment with dilute acids is transformed completely into dextrose. These characters clearly show that gallasin is composed of a mixture of glucoamylin, but up to the present its real nature has escaped observation.

On first consideration, it seems strange that the intermediate compounds produced by the action of acids on starch should differ in

† The question of the existence of an unreducing dextrin, $(C_{12}H_{20}O_{10})_n$, is left aside.

character from those produced by diastase; however, on carefully looking into the matter we shall see that it is very easy to account for this difference. Dilute acids being able to hydrolyse free maltose, would also exercise this action on maltose combined in a molecular aggregate with the amylin group, $(C_{12}H_{20}O_{10})_n$, and therefore amyloins at the moment of their formation are transformed into glucoamylin and glucose (dextrose).

Maltose can be regarded as a simple anhydride of dextrose, being due to condensation of 2 molecules of the latter with loss of water. In the same way, starch may be regarded as an anhydride of maltose, being due to the condensation of at least 100 molecules of this carbohydrate, for, as Brown and Morris have shown, the molecular weight of soluble starch cannot be less than 32400, $5(C_{12}H_{20}O_{10})_{20}$. The anhydrous group in the amylin aggregates cannot, however, have the same structure as the anhydrous group in the maltose molecule, because diastase is only capable of hydrolysing one of these groups, with production of maltose and amyloins, whereas dilute acids hydrolyse both with production of dextrose and glucoamylin. The aldehyde groups of maltose and dextrose are probably formed at the moment of the hydration of the amylin aggregates by intramolecular rearrangement. Whether or not a dextrin with the formula $(C_{12}H_{20}O_{10})_n$ is formed in the splitting up of the starch molecule there is no evidence to show, excepting the fact that diastase has a slight action on the products of conversion whose specific rotations lie between $[\alpha]_D$ 135° and 115°, and which give no blue coloration with iodine.

As diastase has no action on the products of conversion whose rotations are less than 115°, the dextrin, if produced, does not offer much resistance to the hydrating action of acids, and must be modified at an early period of the reaction.

For the present, however, it will be better to leave aside the possible existence of an unreducing dextrin, and to consider the reaction in its simplest form, which can be expressed by the following equations.

As a $\sigma\chi\hat{\eta}\mu\alpha$ for the formula of starch, the following figure is suggested.

Starch σχηµα.

As will be seen on looking at the figure, each amylin group (between the large brackets) is composed of two maltose molecules (separated by the dotted lines) each of the latter being composed of two dextrose molecules. To show the points where the dextrose molecules condense to maltose and the latter to amylin groups, the H_2O molecules are inclosed in brackets. As is seen, the two dextrose molecules condense in a secondary group $(HC \cdot O \cdot \overline{H} \quad \overline{HO} \cdot CH)$, whilst the maltose molecules condense in the primary group $(H_2C \cdot O \cdot \overline{H} \quad \overline{HO} \cdot CH_2)$, the former becoming $HC \cdot O - CH$ and the latter $H_2C \cdot O - CH_2$. The two aldehyde groups of the original dextrose molecules condense in the amylin group as is shown above. This explains the non-reducing character of starch. According to the above σχηµα, the molecular weight of starch can be any multiple of $(C_6H_{10}O_5)_4$.

This figure is only intended to convey, in a figurative manner, the probable nature of the starch molecule, and is suggested by the behaviour of starch when submitted to the action of diastase or dilute acids. No claim is made that this represents the absolute formula of starch. The question of the possible formulæ of the glucoamylins presents too many difficulties to be dealt with here ; however, I hope to return to it in a subsequent communication to the Society.