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CHEMICAL AND PHYSICO-CHEMICAL STUDIES ON THE STARCHES

By

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Introduction

The manufacture of starch from cereal grains has been practiced from very early times. In 184 B.C., Marcus Parcuis Cato described the fact. According to Pliny the Elder, the method for the extraction of starch from cereal grains was said to have been found by the inhabitants of the Island of Cios. From that time to the latter half of the 18th century, the source material practically used for the purpose of manufacturing starch was limited to wheat.

In the middle ages, the manufacture of wheat starch resulted in an important industry in Holland and the Dutch were famous for the quality of their starch. At that time, starch was used mainly in laundries. In the 16th century, it became the custom in France to powder the hair with starch and the custom continued till the end of the 18th century consuming an immense quantity of starch. Leonald da Vinci had intended to stiffen the wings of his flying machine with starch.

In the 18th century, the search for materials for starch manufacture cheaper than the wheat was carried out. In 1732, Sieur de Guife proposed to the French Government to use potatoes. In 1765, the manufacture of potato starch was carried on with the encouragement of Frederick the Great in Germany. In 1772, Duhamel de Monceàu had made clear that the arrowroot, potato and arum could be used instead of the cereal grains. At that time, starch was used for the preparation of cosmetic powder, in colour printing, in tablets, in some mixture of soap, etc. In 1796, Murray proposed to use the horsechestnut, and in 1799, Gibbs proposed to use the root of Arum maculatum as the materials for starch manufacture.

In the 19th century, starch was used in the textile, colour printing and paper industries. It was discovered that starch could change easily into glucose and dextrin, the demand for it became very large. The starch industry showed an enormous expansion. From the beginning of the 19th century potatoes were largely used for starch manufacture chiefly in Germany, then followed maize which was the principal raw material in the United States. From the middle of the 19th century rice also has been employed on a large scale.

In this country, the arrowroot starch has been used from early times. Also bracken powder and other sources were employed. About 1835 (in the 5th year of Tempo), the manufacture of sweet potato starch began in the province of Shimoosa. About 1870 (in the beginning of Meiji), the potato starch was produced accompanying the import of the potato. The sale of starch as a foodstuff began in about 1870 (in the 3rd year of Meiji). At the present time, potato starch is produced mainly from Hokkaido and sweet potato starch is produced mainly from the province of Chiba.

As starch was used very widely for many purposes, there was need to know its characteristics and its general properties. Thus chemical and physico-chemical studies were carried out from very old time and a great many authors had reported the colloid chemical, physico-chemical and chemical properties of the starch up to the recent days.

According to the idea of AME PICTET(111_1), starch is made up by the binding of groups which will produce the d-glucose when the starch is treated by thermal depolymerisation; the formula of the starch is expressed by $C_6H_{10}O_5$ or $(C_6H_{10}O_5)_n$, the half of the binding of the $C_6H_{10}O_5$-group is at least in the α-linkage forming whole molecule with the β-linkage. Similar to KARRER's opinion is the opinion of PRINGSHEIM, IRVINE, HESS, KUHN and BERGMANN, who considered that the $C_6H_{10}O_5$-group is combined to some extent by polymerisation, but the starch molecule is made up by the association of such relatively simple polymerisation products. The formation of hexahexosan results from the polymerisation of $C_6H_{10}O_5$-molecule and the formation of starch results from the association of hexahexosans, so that the starch is not considered as a molecule of certain magnitude, but as a polyhexosan. Considering from the results of the methylation of starch and the physiological phenomena, J. IRVINE(111_2) concluded that starch is not a homogeneous chemical individual, but a combined product of molecular units which vary their content of inorganic acid residue. The simplest possible formula has considered the molecular unit as an anhydrohexaglucose. Standing on the results of an enzymic hydrolysis of the starch, A. R. LING(111_3) discussed the structure of the starch molecule. He concluded that starch had contained two basal units i.e. α-hexaamylose and αβ-hexaamylose and that these were polymerised to a particular degree according to the kind of starch. α-amylose and amylopectin were produced by the mentioned polymerisation; a third substance, amylohemicellulose, was also produced in cereal starch by such polymerisation. H. PRINGSHEIM(111_4) observed that in the course of the bacterial degradation of starch, dihexosan was produced from the amylose and the trihexosan from the amylopectin. Though these hexosans were not considered as structural units of starch, it was proper in his opinion to conclude that the starch, lichenin, cellulose, inulin and salepmannan were complex hexose anhydrides. MAX SAMEC(111_5) stated regarding the relations between the colloid chemical properties and the chemical structure of starch, that the P_2O_5-content of the amylopectin was 0.185% and that of the amylose was 0.007%; the amylopectin was seen as the starch phosphoric acid ester. Studying the X-ray spectrography of starch, J. R. KATZ(111_6) stated that starch produced a crystalline X-ray spectrum, that the spectra of the starches showed different figure according to their kinds and that those of the swollen starch were all equal, that the spectra of the extremely dried starch and that of the gelatinized starch were different, that the latter had combined with the water, and that the elementary cell of the starch should be very small. KARRER(42) had considered that the elementary molecule of starch should be maltoseanhydride.

The author (62) has reported the results of the differences of chemical and physico-chemical properties of the starches of the brewing barleys according to their species. By the further studies and the comparison of the results of many starches, the author desired to make clear the different properties and the constitution of the starches and for that purpose has carried out the following investigations.

In the whole course of the investigations, Prof. TETSUTARO TADOKORO, Nogakuhakushi, Rigakuhakushi has given the author constant leadings and kind advices for which he is deeply grateful. He wishes to express his hearty thanks to him.

Experiments and Discussions

MATERIALS

The materials used in the present investigations comprise 14 samples of starch from 11 different plant species viz., the potato, dog-tooth violet, wheat, barley, common rice, common Italian millet, common sorghum, corn, cassava, buckwheat and arrowroot. The potato, dog-tooth violet and wheat starches were manufactured by KOJIMA and Co. Tokyo; the common rice, common Italian millet and common sorghum starches were prepared in the Laboratory of Professor TADOKORO in the Department of Agricultural Chemistry of the Faculty of Agriculture, Hokkaido Imperial University. The corn starch was purified by the author by the extraction with 0.2% natrium hydroxide solution of the commercial corn starch manufactured by T. KINGSFORD and Son Co. U.S.A. The potato, cassava, wheat, buckwheat, corn and arrowroot starches were prepared by Professor ITO in the Gifu Koto Norin Gakko.

Chapter I

Studies on the Original Starches

§ 1. Water and ash content of the starches

According to the usual method the water and the ash content of the 14 starches were determined as the following table shows.

TABLE 1.

Water and ash content of the starches.

Starch	Water	Ash (Water free)
Potato (Kojima)	17.30	0.264
Dog-tooth violet	12.88	0.112
Wheat (Kojima)	12.85	0.449
Sorghum	10.16	0.118
Rice	12.48	0.144
Italian millet	7.43	0.182
Barley	11.36	0.075
Corn (Kingsford)	18.47	0.076
Potato (Ito)	16.54	0.170
Cassava	10.51	0.075
Wheat (Ito)	12.44	0.063
Buckwheat	13.20	0.088
Corn (Ito)	11.40	0.046
Arrowroot	10.37	0.068

The ash content of the starches was counted between 0.5% to 0.05% of their dry matter. It seemed to be usual for the ash content of the starches to range 0.2–0.05%. By the comparison of the starches of the cereal plants and the starches of the tubers, it was observed that the ash content of the starches of the latter was higher than that of the starches of the former. The ash content was seen to differ markedly according to the difference of the method of manufacturing as may be seen from the fact that the ash contents of the potato starches were 0.264% and 0.170%, of the wheat starches 0.449% and 0.063%, of the corn starches 0.076% and 0.046% respectively. The same relation was observed in the phosphorus content of the starches as described later.

§ 2. Phosphorus content of the starches

Because of the fact that phosphorus is one component of the starch molecule, its content in starch and its chemical form in the starch molecule have been studied and reported by many authors, amongst whom are FERNBACH (29), FORD (30), MALFITANO (55), FOUARD (32), FRANCIS (34), SAMEC (82), SAMEC and HOEFFT (90), THOMAS (107), SAMEC and JENCIC (91), NORTHRUP and NELSON (64), KERB (45), TRYLLER (110), SAMEC and MAYER (92), EULER and MYRBÄCK (28), TIEBACKX (108), SAMEC and SSAJEVIC (95), MALFITANO and CATOIRE (56), and ROSENTHALER (80). The results of so many authors may be summarized as follows, that is, there is phosphorus in starch, it was said either to be combined with the organic compound of starch forming amylophosphoric acid or to be uncombined but simply adsorbed to the starch molecule, the viscosity of the starch solution is changed proportionately with the phosphorus content of the starch, the saponification of starch is caused by amylopectin which is the ester of the phosphorus, the phosphorus content of starch ranges 0.032–0.169%.

The author determined the phosphorus content of the starches of his investigation as follows. One g of the starch was taken into a Kjeldahl flask to which was added 10 c.c. of the mixture of concentrated sulphuric acid and concentrated nitric acid according to NEUMANN's procedure. The mixture was heated for 1 hour whereupon 2 c.c. of concentrated nitric acid were added and the whole was heated for one hour more. The main part of the acid of the solution was neutralized by the addition of 40% natrium hydroxide solution. With the resulting slightly acidic solution, colorimetric determination of the phosphorus content was carried out according to BELL-DOISY's method modified by BRIGGS (20). The slightly acidic solution was taken into a 100 c.c. measuring flask, to the solution was added water to make the volume up to about 80 c.c. then to the solution were added 5 c.c. of sulphuric acid—ammonium molybdate solution and 1 c.c. of newly prepared 20% natrium sulphite solution and 1 c.c. of 0.5% hydrochinone solution. The mixture was made up to 100 c.c. by the addition of water. After 30 minutes, the colour was compared by means of a Dubosque colorimeter with the standard solution prepared in the same way using a standard kalium phosphate solution. The results are shown in the following table.

TABLE 2.

Phosphorus content of the starches.

Starch	P (Water free)	P_2O_5 (Water free)
Potato (Kojima)	0.053	0.122
Dog-tooth violet	0.025	0.057
Wheat (Kojima)	0.059	0.134
Sorghum	0.020	0.045
Rice	0.022	0.051
Italian millet	0.021	0.049
Barley	0.025	0.058
Corn (Kingsford)	0.021	0.049
Potato (Ito)	0.047	0.108
Cassava	0.021	0.049
Wheat (Ito)	0.015	0.035
Buckwheat	0.017	0.038
Corn (Ito)	0.019	0.043
Arrowroot	0.021	0.049

The table shows that the phosphorus content of the starches was 0.134–0.035% and that the content was always great in the potato starches. Generally speaking, the phosphorus content of the starches ranged 0.058–0.035%. The results coincide very well with those reported by many other investigators. The phosphorus content of the starches differed very markedly according to the method of preparation of the starches. This may be seen in the potato starches containing respectively 0.122% and 0.108%, and also in the wheat starches showing 0.134% and 0.035%. The phosphorus content of the corn starches was 0.049% and 0.043% which resembled each other. The reason for this fact was considered to be that the purification of the starches were carried out by the use of natrium hydroxide solution in both cases and that the same treatment affected the two substances similarly. Treatment with natrium hydroxide solution seemed to diminish the phosphorus content of the starch. It seems that natrium hydroxide has some effect upon the separation of the phosphorus of the starches as in the case of the separation of the phosphorus of protein.

The difference between the ash content of the starches and their P_2O_5 content; the ratio of that difference to the ash content and the ratio of the P_2O_5 content to the ash content were calculated as follows.

TABLE 3.

Difference between the ash content and the P_2O_5-content; the ratio of the P_2O_5 to the ash content and of the difference to the ash content in terms of percentage.

Starch	Ash$-P_2O_5$	$\frac{\text{Ash}-P_2O_5}{\text{Ash}}\times 100$	$\frac{P_2O_5}{\text{Ash}}\times 100$
Potato (Kojima)	0.142	53.78	46.22
Dog-tooth violet	0·055	49.10	50.90
Wheat (Kojima)	0.315	70.15	29.85
Sorghum	0.069	58.47	41.53
Rice	0.093	64.58	35.42
Italian millet	0.137	75.27	24.73
Barley	0.017	22.68	77.32
Corn (Kingsford)	0.028	36.84	63.16
Potato (Ito)	0.062	36.47	63.53
Cassava	0.026	34.67	65.33
Wheat (Ito)	0.028	44.44	55.56
Buckwheat	0.050	56.82	43.18
Corn (Ito)	0.003	6.52	93.48
Arrowroot	0.021	30.89	69.11

Comparing the ash content and the P_2O_5 content of the starches and the differences between the content of ash and the P_2O_5 content, the author was able to divide the starches into two groups, one of which had increasing P_2O_5 content with increasing ash content and the other had decreasing P_2O_5 content with increasing ash content. The percentage of P_2O_5 in the ash of the starches from the tubers was greater than those of the starches from the cereal plants. The method of preparation of the starches had no influence upon the percentage, since almost equal percentages were found notwithstanding the difference in methods of preparation. Accordingly in the course of the preparation of the starch, the constituents of the ash of the starches other than P_2O_5 were also lost in the same proportion as in the case of the P_2O_5. It was generally found that the ash constituents of the starch had to play an important role in the construction of the starch and that the proportion of the ash constituents other than P_2O_5 to the P_2O_5 was almost constant to each starch.

§ 3. Nitrogen content of the starches

J. M. NORTHRUP and J. M. NELSON (64) reported that starch contained less than 0.1% of nitrogen in the granule. L. MOESER (58) observed that the commercial starches contain 0.03–0.7% of nitrogen and that for the purpose of removing it the starch has to be treated with alcoholic potassium hydroxide or natrium hydroxide solution. J. C. IRVINE with J. MACDONALD (40), however, reported that nitrogen is absent from the starch. O. S. RASK and C. L. ALSBERG (75) reported that wheat starch contains 0.039% of nitrogen. Recently, SAMEC and BENIGER (87) confirmed the existence of nitrogen in the starches of the wheat and the potato amounting to 0.076–0.0049% and they also reported that nitrogen was present in starch as the form of phytovitellin which combined with the polysaccharide in the phosphorus.

The author digested 1 g each of the starches with 1 g of copper sulphate, 1 g of potassium sulphate and 15 c.c. of concentrated sulphuric acid, then the nitrogen was determined by the micro Kjeldahl method as follows.

TABLE 4.

Nitrogen content of the starches.

Starch	N (Water free) %	Starch	N (Water free) %
Potato (Kojima)	0.0198	Corn (Kingsford)	0.0227
Dog-tooth violet	0.0481	Potato (Ito)	0.0070
Wheat (Kojima)	0.0176	Cassava	0.0041
Sorghum	0.0254	Wheat (Ito)	0.0111
Rice	0.0184	Buckwheat	0.0467
Italian millet	0.0332	Corn (Ito)	0.0236
Barley	0.0169	Arrowroot	0.0048

The table shows that the nitrogen content of the starches runs 0.004–0.05%, mainly 0.02% or so.

To compare the content of the phosphorus and the content of the nitrogen, the author calculated their molecular number. The ratio of the two components was calculated and tabulated as follows.

TABLE 5.

Molecular numbers of the phosphorus and the nitrogen contained in 100 g of the starches and their ratio to each other.

Starch	Phosphorus	Nitrogen	P : N
Potato (Kojima)	0.001708	0.001414	1 : 0.828
Dog-tooth violet	0.000806	0.003434	1 : 4.262
Wheat (Kojima)	0.001902	0.001257	1 : 0.661
Sorghum	0.000677	0.001813	1 : 2.679
Rice	0.000709	0.001314	1 : 1.852
Italian millet	0.000642	0.002370	1 : 3.677
Barley	0.000806	0.001207	1 : 1.497
Corn (Kingsford)	0.000677	0.001619	1 : 2.394
Potato (Ito)	0.001515	0.000500	1 : 0.330
Cassava	0.000677	0.000293	1 : 0.433
Wheat (Ito)	0.000484	0.000793	1 : 1.643
Buckwheat	0.000548	0.003334	1 : 6.085
Corn (Ito)	0.000613	0.001685	1 : 2.751
Arrowroot	0.000677	0.000343	1 : 0.506

It may be seen from the table that the ratio between the phosphorus and the nitrogen was 0.3–6.0. This ratio in the case of the tuber starches, with the exception of the dog-tooth violet starch, was 0.3–0.8 while that of the cereal plant starches was 0.6–6.0. The former was markedly small compared to the latter. Thus, it is possible to say that the starches could be divided into two groups, that is those of the tubers and those of the cereal plants.

§ 4. Acetylation of the starches

The acetylation of the starch was carried out by SCHUETZENBERGER (97) for the first time in the year 1865. From that time, the acetylation of starch and soluble starch has been carried out by many authors as follows: SCHUETZENBERGER and NAUDIN (99), SCHUETZENBERGER (98), MICHAEL (57), SKRAUP (102), PREGL (69), CROSS, BEVAN and TRAQUAIR (25), SKRAUP, GEINSPERGER, KNAFFL-LENZ, MENTER and SIRK (103), LAW (49), TRAQUAIR (109), PRINGSHEIM and LANGHAUS (71), PRINGSHEIM and EISSLER (70), BÖESEKEN, BERG and KERSTJENS (17), KARRER (44), BERGMANN and BECK (8), KARRER and SMIRNOFF (43), PRINGSHEIM and LASSMAN (72), ZECHMEISTER (114), ESCALES and LEVY (27), PRINGSHEIM and WOLFSOHN (74), SJÖBERG (101), BERGMANN and LUDEWIG (9), PEISER (67), BERGMANN, KNEHE and LIPPMANN (10), HAWORTH, HIRST and WEBB (36), FRIESE and SMITH (35), BRIGLE and SCHINLE (21). Summarizing the results of these authors, it may be reported that the reagents used were acetic acid, glacial acetic acid, acetic acid anhydride and acetyl bromide, the catalyser was either used or not used, when the catalyser was used it was either sulphuric acid, hydrochloric acid, hydrobromic acid, zinc chloride or pyridine, the temperature of the reaction was either the room temperature, lower than 80°C., 100–105°C., 140°C. or 150°C., and the time of the reaction was more than one hour to many days. The acetyl compounds resulting from the above various treatments were very different respectively. The content of the acetyl group of the compound was 2.8–17.4%, 45–48% or the reaction products were starch triacetate, starch hexaacetate and starch nonaacetate. In the course of the reaction, there were produced soluble starch, dextrine or substances which possessed the reducing power by hydrolysis or saponification. TRAQUAIR gave the name feculose to the acetic ester of starch. KARRER considered that the acetylation of the starch did not change the degree of polymerisation. ESCALES and LEVY reported that the starch did not produce any destructive depolymerisation by the process of the acetylation.

(a) *Acetylation of the starch at high temperature*

In an earlier paper, the author has already reported the results of the acetylation of the starch of barley and rice by means of acetic acid anhydride and zinc chloride. The author treated the starches of the present investigation by the same method as follows. To ten g of the starch were added 0.5 g of zinc chloride and 100 g of acetic acid anhydride (Merck) and the mixture was heated on a sand bath with a reflux condenser for 3 hours. At the end of that time, the clear solution obtained was poured into cold water in a fine stream. The precipitate thus obtained was washed carefully with water until no acid reaction was observed in the washings. The precipitate was then dried in a water oven at 100°C. for 5 hours and was stored in a desiccator of sulphuric acid. The content of the acetyl group of the product was estimated by WENZEL's method, the rotatory power of the product was measured by means of a GOELTZ-LIPPICH polariscope, the melting point of the product was estimated using THIEL's apparatus making the necessary corrections and the refractive index of the product was measured by means of a GOELTZ refractometer. The rotatory power and the refractive index were estimated with the solution of 0.2 g of the product dissolved in 15 c.c. of pyridine 5 hours after the time of solution.

TABLE 6.

Acetyl content of the acetyl starches. Two tenths g of the sample was used. One c.c. of sulphuric acid corresponded to 0.01293 g of CH_3CO.

Starch		H_2SO_4 (c.c.)	Acetyl group (g)	Acetyl content (%)
Potato (Kojima)	(1) (2)	6.95 6.95	0.089863	44.93
Dog-tooth violet	(1) (2)	7.0 7.0	0.09051	45.26
Wheat (Kojima)	(1) (2)	7.05 7.05	0.09156	45.58
Sorghum	(1) (2)	7.15 7.15	0.0924495	46.22
Rice	(1) (2)	6.9 6.9	0.089217	44.61
Italian millet	(1) (2)	7.2 7.15	0.09277	46.38
Barley	(1) (2)	7.3 7.3	0.094389	47.19
Corn (Kingsford)	(1) (2)	7.0 7.0	0.09051	45.26

TABLE 7.

Melting point, rotatory power and refractive index of the acetyl starches.

Starch	M.P.	α	$[\alpha]$	n
Potato (Kojima)	151.0	3.56	133.50	1.536
Dog-tooth violet	136.5	3.50	131.25	1.542
Wheat (Kojima)	150.0	3.54	132.75	1.552
Sorghum	150.0	3.77	141.38	1.548
Rice	149.0	3.62	135.75	1.550
Italian millet	146.0	3.60	135.00	1.538
Barley	148.0	3.54	132.75	1.556
Corn (Kingsford)	157.0	3.80	142.50	1.543

The acetyl starches were easily soluble in pyridin, aceton and chloroform, soluble in benzol and soluble with difficulty in carbon tetrachloride. The elementary analysis of the compounds was carried out by PREGL's micro-method with the following results.

TABLE 8.

Elementary analysis of the acetyl starches.

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Potato (Kojima)	3.830 3.740	2.290 2.160	7.230 6.990	6.688 6.462	51.47 50.97
				6.58	51.22
Dog-tooth violet	5.250 4.210	2.800 2.390	10.250 8.200	5.967 6.351	53.23 53.11
				6.16	53.17
Wheat (Kojima)	4.110 4.300	2.540 2.540	7.880 8.270	6.913 6.607	52.29 52.43
				6.76	52.36
Sorghum	5.920 3.320	3.470 1.825	10.430 5.980	6.557 6.151	48.03 48.39
				6.35	48.21

TABLE 8. (*Continued*)

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Rice	3.890	2.150	7.890	6.183	55.33
	4.550	2.460	9.300	6.047	55.75
				6.12	55.54
Italian millet	3.840	2.150	7.750	6.236	53.76
	5.085	2.830	10.050	6.226	53.89
				6.24	53.83
Barley	4.285	2.380	8.015	6.215	51.01
	5.010	2.990	9.260	6.677	50.41
				6.45	50.71
Corn (Kingsford)	3.520	1.910	6.620	6.070	51.30
	4.640	2.590	8.730	6.244	51.31
				6.16	51.31

The results have been summarised in the following table.

TABLE 9.

Elementary composition of the acetyl starches.

Starch	C	H	O
Potato (Kojima)	51.22	6.58	42.20
Dog-tooth violet	53.17	6.16	40.77
Wheat (Kojima)	52.36	6.76	40.88
Sorghum	48.21	6.35	45.44
Rice	55.54	6.12	38.34
Italian millet	53.83	6.24	39.93
Barley	50.71	6.45	42.84
Corn (Kingsford)	51.31	6.16	42.53

From the above table, it was observed that the higher the content of the acetyl groups of the acetyl starch, the lower were the melting point and the rotatory power and the higher was the refractive index of the compound, and vice versa.

With the assumption that the hydroxyl group in the glucose residue of the molecule of the starch was replaced by the acetyl group when the acetylation of the starch was carried out, the theoretical content of the acetyl groups of the acetyl starch was calculated as shown in the next table.

TABLE 10.

Theoretical content of the acetyl groups of acetyl starch.

Glucose residue	CH_3CO group	Ratio	Content %
1	1	1	19.37
1	2	2	32.58
1	3	3	42.16
6	19	3.16	43.40
5	16	3.20	43.74
4	13	3.25	44.16
3	10	3.33	44.79
5	17	3.40	45.30
2	7	3.50	46.03
5	18	3.60	46.73
3	11	3.66	47.21
4	15	3.75	47.78
5	19	3.80	48.10
6	23	3.83	48.35
1	4	4	49.43

The content of the acetyl group in the author's acetyl starches was 44.93–47.19%. If these numbers were compared with the calculated numbers shown in the above table, it may be seen that the ratio of the author's acetyl starches lie between 3.33 to 3.66. The mean of the values approximated to 3.50. It may be seen, therefore, that the author's acetyl starches are compounds which were built up with 2 glucose residues and 7 acetyl groups, that is, mixtures of equal quantity of triacetyl glucose and tetraacetyl glucose. In other words it may be said that the compounds are aggregates of heptaacetyl maltose.

(b) *Acetylation of starch in room temperature*

The above mentioned acetylation was carried out at the boiling point of the acid used and it may be that more or less changes of the starches occur such as hydrolysis or depolymerisation. The acetylation of the starches was therefore repeated according to the method reported by H. FRIESE and F. A. SMITH (35). Three g of the starches were soaked in 8 c.c. of 80% pyridin for one night, to the mixture were added 20 c.c. of pyridin and 20 c.c. of acetic acid anhydride. The mixture was stood at room temperature with an occasional shaking. The viscous liquid thus obtained was poured into a large quantity of cold water and the product was precipitated from the solution. The precipitate was carefully washed with water and dried in a desiccator of diminished pressure of sulphuric acid as described above.

The content of the acetyl group of the product was estimated as follows. A given quantity of the sample was taken in a given quantity of natrium hydroxide solution, the mixture was heated in a boiling water bath for 30 minutes under a reflux condenser. At the end of the time and after the saponification of the substance was completed, the remaining natrium hydroxide was titrated by sulphuric acid using phenolphthalein as an indicator. From the results of the titration, the quantities of the acetic acid liberated were determined. The elementary analysis of the compound was carried out by means of the micro-method as described above. The results of the analysis have been enumerated as in the following table.

TABLE 11.

Acetyl content of the acetyl starches. One tenth g of the sample was used. One c.c. of the sulphuric acid corresponded to 0.01291 g of CH_3CO.

Starch		H_2SO_4 (c.c.)	Acetyl group (g)	Its content (%)
Sorghum	(1)	2.6	0.033566	33.57
	(2)	2.6		
Rice	(1)	3.2	0.043571	43.57
	(2)	3.35		
Italian millet	(1)	3.15	0.040344	40.34
	(2)	3.10		
Barley	(1)	1.75	0.022269	22.27
	(2)	1.70		
Corn (Kingsford)	(1)	3.5	0.045185	45.19
	(2)	3.5		

TABLE 11. (*Continued*)

Starch		H_2SO_4 (c.c.)	Acetyl group (g)	Its content (%)
Cassava	(1)	3.4	0.043894	43.89
	(2)	3.4		
Wheat (Ito)	(1)	3.1	0.040021	40.02
	(2)	3.1		
Buckwheat	(1)	3.2	0.041312	41.32
	(2)	3.2		
Corn (Ito)	(1)	3.5	0.045185	45.19
	(2)	3.5		
Arrowroot	(1)	3.3	0.042603	42.60
	(2)	3.3		

TABLE 12.

Elementary analysis of the acetyl starches.

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Sorghum	3.595	2.075	6.370	6.292	47.08
	3.615	2.200	6.340	6.808	47.82
				6.65	47.84
Rice	2.905	1.785	5.250	6.874	49.29
	3.260	1.990	5.925	6.829	49.57
				6.85	49.43
Italian millet	3.160	1.860	5.530	6.585	47.72
	4.035	2.340	7.030	6.488	47.52
				6.54	47.62
Barley	3.890	2.475	6.400	7.119	44.86
	5.010	3.280	8.195	7.324	44.62
				7.22	44.75
Corn (Kingsford)	3.755	2.260	6.700	6.733	48.66
	4.395	2.640	7.780	6.719	48.27
				6.73	48.47
Cassava	6.105	3.445	10.890	6.313	47.56
	4.870	2.800	8.565	6.433	47.97
				6.37	47.77
Wheat (Ito)	3.690	2.085	6.370	6.292	47.08
	4.450	2.430	7.710	6.108	47.25
				6.20	47.17
Buckwheat	4.815	2.635	8.400	6.124	47.58
	4.440	2.420	7.775	6.096	47.75
				6.11	47.66

Table 12. *(Continued)*

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Corn (Ito)	3.765	2.275	6.670	6.759	48.31
				6.76	48.31
Arrowroot	5.820	3.145	10.250	6.045	48.05
	6.030	3.185	10.560	5.909	47.76
				5.98	47.91

The results were summarised in the following table.

Table 13.

Elementary composition of the acetyl starches.

Starch	C	H	O
Sorghum	47.84	6.65	45.51
Rice	49.43	6.85	43.72
Italian millet	47.62	6.54	45.84
Barley	44.75	7.22	48.03
Corn (Kingsford)	48.47	6.73	44.80
Cassava	47.77	6.37	45.86
Wheat (Ito)	47.17	6.20	46.63
Buckwheat	47.66	6.11	46.23
Corn (Ito)	48.31	6.76	44.93
Arrowroot	47.91	5.98	46.11

The present acetyl starches were insoluble in ethyl, methyl and amylalcohol, swollen in aceton and ethyl acetate, soluble in benzol, chloroform and carbon tetrachloride, easily soluble in pyridin. The content of acetyl group in the compounds was 40.02–45.19% excepting those of the barley and the sorghum. If these values were compared with the theoretical values, the results correspond to the ratio 2–3–3.40. The mean value was nearly 3 and it is possible to say that the compounds were aggregates of triacetyl glucose.

From the two series of results of the acetylation of the starches above described, it was observed that the acetylation by heating combined more acetyl groups with the starches than the acetylation at the room temperature using pyridin with the exception of the cases of the rice and corn starches which showed almost equal contents of the acetyl group by the two different treatments. The treatment of the starches at the boiling point of the acetic acid anhydride seemed to cause the reaction of the difficultly reacting part of the starches to occur. The heating, therefore, had accelerated the acetylation of the starches. The acetyl content in the acetyl starches and the content of phosphorus in the starches showed some relation; it is possible to say that the acetylation of the starches progressed in inverse proportion to their content of phosphorus. According to SAMEC's consideration that a higher phosphorus content was observed in amylopectin than in amylose, the starches containing much phosphorus or these containing much amylopectin should be less acetylated without heating. The acetylation was influenced seriously by heating in the case of the starches of the cereal plants excepting those of rice and corn. This fact caused the author to consider that amylopectin is contained in the starches of the cereal plants which were more unstable to the action of the heating than the starches of the tubers. The starches of potato and dog-tooth violet did not undergo acetylation without heating, or they produced acetyl starches with very little acetyl groups. The author believes that the starches of the tubers differed markedly from those of the cereal plants in their constitution. From the consideration, the author ventures to say that there were two sorts of starches at least, those of the cereal plants and those of the tubers and that one might classify the starches into the starches of the cereal plant and those of the tubers.

Among the starches of the cereal plants, the starches of rice and corn were relatively stable and the molecular combinations were firm, the starches of barley and sorghum were the most unstable and the molecules were combined loosely. The other cereal starches were between these two extremes. Among the starches of the tubers those of potato and dog-tooth violet were the most stable and that of cassava the most unstable.

§ 5. Benzoylation of the starches

CROSS, BEVAN and BEADLE (26) benzoylated the soluble starch with alkali and benzoyl chloride, SYNIEWSKI (104) obtained the benzoyl derivatives of the soluble starch. Benzoylation replaces the free hydroxyl groups of the organic substances as in the case of acetylation. Therefore, benzoylation should also yield something in the investigation of the constitution of the starches.

The author carried out benzoylation of his starches with the following processes. Five g of the starch were suspended in 15 c.c. of water. To the suspension were added very slowly 210 c.c. of 10% natrium hydroxide and the starch was thoroughly dissolved. Then as fast as possible, 30 c.c. of benzoyl chloride were added to the solution and the mixture was stirred up very well. In the course of the reaction, heat was liberated and at the end of the reaction, the product of the reaction separated into an white mass. This separated product was washed well on filter paper and was dried at 100°C. in a water oven for 5 hours, then stored in a sulphuric acid desiccator.

The content of the benzoyl group of the product was estimated freeing the benzoyl group as benzoic acid by heating the product with hydrochloric acid in a sealed tube.

TABLE 14.

Benzoyl content of the benzoyl starches.
Two tenths g of each sample was used.

Starch	N/10 NaOH (c.c.)	Benzoyl group (g)	Its content (%)
Potato (Kojima)	8.10	0.08505	42.53
Dog-tooth violet	10.55	0.110775	55.39
Wheat (Kojima)	8.95	0.093975	46.99
Sorghum	9.60	0.10080	50.40
Rice	11.00	0.1155	57.75
Italian millet	10.60	0.1113	55.65
Barley	6.90	0.07245	36.23
Corn (Kingsford)	8.90	0.09345	46.73

The elementary analysis of the benzoyl starches was carried out as described before with the following results.

TABLE 15.

Elementary analysis of the benzoyl starches.

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Potato (Kojima)	4.155	1.965	9.530	5.290	62.56
	3.560	1.640	8.070	5.153	61.83
				5.22	62.20
Dog-tooth violet	4.440	2.275	9.300	5.732	57.12
	5.025	2.410	10.550	5.365	57.27
				5.55	57.20
Wheat (Kojima)	3.060	1.530	7.215	5.594	64.30
	3.315	1.555	7.820	5.248	64.34
				5.42	64.32
Sorghum	3.780	2.250	8.210	6.643	59.23
	3.515	2.000	7.705	6.365	59.78
				6.50	59.51
Rice	3.115	2.190	7.340	7.863	64.25
	4.640	3.185	10.960	7.679	64.43
				7.77	64.34
Italian millet	3.725	1.945	8.080	5.841	59.16
	3.510	1.705	7.745	5.433	60.17
				5.64	59.66
Barley	3.970	2.580	8.870	7.269	60.92
	5.475	3.410	12.190	7.131	60.70
				7.20	60.81
Corn (Kingsford)	4.505	2.585	10.310	6.419	62.40
	3.070	1.810	7.000	6.597	62.17
				6.51	62.29

The results have been summarised in the following table.

TABLE 16.

Elementary composition of the benzoyl starches.

Starch	C	H	O
Potato (Kojima)	62.20	5.22	32.58
Dog-tooth violet	57.20	5.55	37.25
Wheat (Kojima)	64.32	5.42	30.26
Sorghum	59.51	6.50	33.99

TABLE 16. (*Continued*)

Starch	C	H	O
Rice	64.34	7.77	27.89
Italian millet	59.66	5.64	34.70
Barley	60.81	7.20	31.99
Corn (Kingsford)	62.29	6.51	31.20

The benzoylation also seemed to replace the hydroxyl groups of the glucose residues of the starch as in the case of the acetylation. The author calculated the theoretical content of the benzoyl groups of the compound.

TABLE 17.

Theoretical content of the benzoyl groups of the benzoyl starches.

Glucose residue	Benzoyl group	Ratio	Content (%)
1	1	1	37.84
2	3	1.5	46.87
1	2	2	54.14
2	5	2.5	59.68
1	3	3	64.00

Comparing the numbers in Table 14 and Table 17, it is evident that a monobenzoyl compound had been obtained by the benzoylation of the barley starch; an equal mixture of monobenzoyl and dibenzoyl compounds or a compound containing 3 benzoyl groups to 2 glucose residues, was obtained by the benzoylation of the potato, wheat, sorghum and corn starches; a dibenzoyl compound was obtained by the benzoylation of the rice, dog-tooth violet and Italian millet starches. The compound which contained 3 benzoyl groups to 2 glucose residues or the compound whose ratio was 1.5 was the most easily obtained. The results of the acetylation and the benzoylation of the starches had showed the same tendency that the starches which were easily acetylated without heating were also easily benzoylatable. The relation that the acetylation and the content of phosphorus were inversely proportional was again recognised between the benzoylation and the content of the phosphorus of the starches, excepting the rice starch.

The starches of the tubers, especially the potato starch, were benzoylated with relatively more difficulty than the starches of the cereal plants. Therefore, the starches of the tubers and the starches of the cereal plants seem to be different in constitution and in other points as was seen when the acetylation was carried out, described above in the former part of the investigation.

§ 6. Nitration of the starches

In 1833, BRACONNOT (18) studied the reaction between starch and nitric acid and obtained a nitric acid compound which he named xyloidin. PELOUZE (68), BALLOT (3), KINDT (47), PAYEN (66), REINSCH (77), BÉCHAMP (4), RITTER (78), LIEBEN and REICHARDT (50), BERTHELOT (12), MÜHLHÄUSER (59), WILL and LENZE (113), BROWN and MILLAR (23), SAPOZHNIKOV (96), BERL and SMITH (6), TRAQUAIR (109), BERE and BÜTLER (11), COPE and BARAB (24), SADTLER (81), KESSELER and RÖHM (46), PRINGSHEIM, LEIBOWITZ and SILMANN (73), H. OKADA (65) carried out the nitration of starch. By the action of nitric acid or the mixture of nitric acid and sulphuric acid with the starch, a nitro compound of starch was obtained. The heat of the formation of the compound was estimated. The compound had an explosive power and it decomposed explosively at 194°C. The product was the nitric acid ester of starch and by treatment with a ferrous salt or ferrous chloride, the compound produced starch or soluble starch. The nitrogen content of the compound differed very markedly, according to the investigators, ranging between 6.7% and 14.08%. The form of the combination of the nitro groups with the starch molecule was reported as the mono-, tetra- or the hexanitrate of the starch.

The author proposed the nitration of the starches and carried out the following experiments. To 2 g of the starch were added 20 c.c. of nitric acid of specific gravity 1.5 and 40 c.c. of concentrated sulphuric acid. The mixture was kept still for 2 days. The reaction product was poured into ice water with the greatest care when it was precipitated and was next washed well with water. The material was dried in the desiccator of diminished pressure over sulphuric acid. The product obtained was a white amorphous mass of markedly explosive power.

The nitrogen content of the product was measured by digestion after GUNNING's modified method, the distillation of the ammonia by the micro KJELDAHL method, and the elementary analysis was carried out by the micro method.

TABLE 18.

Nitrogen content of the nitro-starches.

Starch	Sample (mg)	N/100 HCl (c.c.)	Nitrogen (%)	Mean
Potato (Kojima)	4.530 5.300	3.09 3.59	9.55 9.48	9.52
Dog-tooth violet	3.685 4.480	2.74 3.39	10.41 10.59	10.50
Wheat (Kojima)	3.675 3.120	2.96 2.44	11.27 10.95	11.11
Sorghum	3.870 5.350	2.65 3.66	9.59 9.58	9.58
Rice	3.860 3.230	2.69 2.25	9·76 9.75	9.76
Italian millet	4.970 3.470	3.47 2.37	9.77 9,56	9.67
Barley	2.170 2.150	1.54 1.54	9.93 10.02	9.98
Corn (Kingsford)	4.670 3.690	2.79 2.19	8.36 8.31	8.34

Elementary analysis of the nitro-starches.

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Potato (Kojima)	3.280 3.110	1.550 1.535	3.580 3.360	5.285 5.521	29.77 29.45
				5.40	29.61
Dog-tooth violet	3.400 2.970	1.300 1.135	3.700 3.205	4.277 4.275	29.68 29.43
				4.28	29.55
Wheat (Kojima)	3.650 2.410	1.470 0.920	4.080 2.680	4.505 4.271	30.49 30.33
				4.39	30.41

TABLE 18. (*Continued*)

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Sorghum	3.600	1.370	4.055	4.257	30.72
	3.180	1.220	3.550	4.292	30.45
				4.27	30.58
Rice	2.155	0.855	2.295	4.437	29.73
	4.505	1.780	4.885	4.420	29.56
				4.43	29.64
Italian millet	3.910	1.680	4.250	4.806	29.64
	3.140	1.295	3.490	4.614	30.32
				4.71	29.98
Barley	4.490	1.775	4.850	4.326	28.82
	3.960	1.500	4.175	4.237	28.75
				4.28	28.78
Corn (Kingsford)	3.400	1.380	3.810	4.540	30.56
	3.155	1.220	3.555	4.326	30.73
				4.43	30.65

The results have been summarised in the following table.

TABLE 19.

Elementary composition of the nitro-starches.

Starch	C	H	N	O
Potato (Kojima)	29.61	5.40	9.52	55.47
Dog-tooth violet	29.55	4.28	10.50	55.67
Wheat (Kojima)	30.41	4.39	11.11	54.09
Sorghum	30.58	4.27	9.58	55.57
Rice	29.64	4.43	9.76	56.17
Italian millet	29.98	4.71	9.67	55.64
Barley	28.78	4.28	9.98	56.96
Corn (Kingsford)	30.65	4.43	8.34	56.58

The nitrogen content of the nitro-starches lay between 8.34–11.11% and the results were analogous to those reported formerly. The theoretical content of the nitrogen of the compound was calculated by the author as follows.

TABLE 20.

Theoretical content of the nitrogen of the nitro-starches.

Glucose residue	Nitrogen	Ratio	Content (%)
1	1	1	6.23
2	3	1.5	8.89
3	5	1.67	9.54
1	2	2	10.37

Comparing Table 19 and Table 20, the following facts were observed: that the starches of wheat and dog-tooth violet produced dinitro-glucose; that the starch of corn produced a nitro compound of the ratio of 1.5, i.e., a compound containing 3 nitro groups to 2 glucose residues or the mixture of equal quantities of dinitroglucose and mononitroglucose; and that the other starches produced nitro compounds of the ratio of 1.67, i.e., compounds containing 5 nitro groups to 3 glucose residues or mixtures of 2 dinitroglucose and 1 mononitroglucose.

These nitro-starches were insoluble in benzol, chloroform, carbon tetrachloride, amylalcohol and ether, soluble in ethylalcohol, methylalcohol, aceton and pyridin. Two tenhts g of the sample were dissolved in 15 c.c. of pyridin. After 3 hours the rotatory power of the solution was measured by the GOELTZ' LIPPICH polariscope using a natrium lamp as the light source at 18°C.

TABLE 21.

Rotatory powers of the nitro-starches dissolved in pyridin.

Starch	α	$[\alpha]_D^{18^\circ}$
Potato (Kojima)	3.68	138.0
Dog-tooth violet	3.62	135.7
Wheat (Kojima)	3.38	126.8
Sorghum	3.62	135.7
Rice	3.08	115.5
Italian millet	3.43	128.6
Barley	3.14	117.7
Corn (Kingsford)	3.60	135.0

No relations were observed between the rotatory powers and the nitrogen content of the nitro-starches.

When the results of the acetylation and the benzoylation were compared with the results of the nitration of the starches, there were observed no significant relations among them. It could be said, however, that the starches easily acetylated by heating seemed to produce nitro compounds of high nitrogen content. Accordingly it is possible to say that the treatment of the starches with acid, either hot or cold, had effected some changes upon the constitution of the starch molecules. Therefore, full attention had to be paid to the use of acid when the study of the starch molecules was intended.

§ 7. Mechanism of the hydrolysis of the starches by the action of the diastase

By the action of the diastase, the starch is hydrolysed and forms maltose. The mechanism of this hydrolysis of the starch was studied by BROWN and GLENDINNING (22) for the first time. They concluded that the hydrolysis progressed according to the linear function of the reaction time until 36% of the substrate was hydrolysed, then the hydrolysis progressed according to the logarithmic law. LING (51) denied KJELDAHL's "law of proportionality" when the hydrolysis of the starch was carried out with the diastase of dried malt, but FORD (31) observed that the hydrolysis progressed precisely according to the same law. LAER (48) reported that hydrolysis was controlled by the logarithmic law of unimolecular reaction when the initial concentration of the starch was below 4.5%. He observed that the velocity coefficient decreased when the time of the reaction was lengthened. HEYL (38) confirmed that hydrolysis obeyed the logarithmic law, BIEDERMANN (14) experienced that the time required for the hydrolysis of the starch was inversely proportional to the quantity of the enzyme used. SHERMAN, WALKER and CALDWELL (100) reported that the velocity coefficient of the hydrolysis of the potato starch was slightly greater than that of the starch of the cereal plants. LÜERS and WASMUND (54) observed that the hydrolysis obeyed KJELDAHL's "law of proportionality". SYNIEWSKI (104) denied that hydrolysis was a monomolecular reaction. AMBARD (2) reported that the amylolysis did not obey the simple kineitic formula derived from the law of mass action. The present author stated in his former report (61) that the hydrolysis of the proteins by the action of the enzyme progresses according to the equation

$$\frac{1}{t^{k'}} \cdot \frac{x}{a(a-x)} = k .$$

Intending to study the law of the hydrolysis of starch by the action of the diastase, the authors performed the following experiments.

In a thermostat at 40°C., a mixture of the following composition was kept for 5, 10, 20, 40, 80, 160 minutes and for 3–4 days. The last mentioned time was taken as the end of the hydrolysis.

0.5% diastase solution	5 c.c.
1% starch solution	50 c.c.
Buffer solution of pH 5.2 (Phosphate mixture) .	35 c.c.
Water	10 c.c.

At the end of each time, the quantity of the reducing sugar 10 c.c. of each mixture was estimated by BERTLAND's method. One c.c. of the potassium permanganate solution used for the titration was equivalent to 0.00854 mg of copper. The following numbers are the mean of 3–5 determinations.

TABLE 22.

Hydrolysis of the starches by the action of the diastase.

Time (min.)	5	10	20	40	80	160	End
			Potato starch (Kojima)				
$KMnO_4$ (c.c.)	1.1	1.9	3.2	4.0	4.3	4.5	4.85
Cu (mg)	9.39	16.13	27.33	34.16	36.72	38.43	41.42
Maltose (mg)	6.64	13.02	23.55	29.96	32.38	34.00	36.82
%	18.04	35.36	63.97	81.39	87.96	92.37	100.00
			Dog-tooth violet starch				
$KMnO_4$ (c.c.)	1.1	1.9	3.1	3.6	3.85	4.1	4.6
Cu (mg)	9.39	16.13	26.59	30.76	32.88	35.01	39.28
Maltose (mg)	6.64	13.02	22.89	26.76	28.68	30.81	34.76
%	19.10	37.44	65.85	76.98	82.50	88.65	100.00

TABLE 22. (*Continued*)

Time (min.)	5	10	20	40	80	160	End
Wheat starch (Kojima)							
$KMnO_4$ (c.c.)	1.1	1.8	3.1	3.6	3.9	4.0	4.7
Cu (mg)	9.39	15.37	26.59	30.76	33.31	34.16	40.14
Maltose (mg)	6.64	12.27	22.89	26.76	29.11	29.96	35.54
%	18.68	34.52	64.40	75.30	81.91	84.31	100.00
Sorghum starch							
$KMnO_4$ (c.c.)	1.1	1.9	2.9	3.4	3.6	3.8	4.4
Cu (mg)	9.39	16.13	24.77	29.04	30.76	32.45	37.58
Maltose (mg)	6.64	13.02	21.08	25.17	26.76	28.30	33.18
%	20.02	39.23	63.53	75.88	80.67	85.31	100.00
Rice starch							
$KMnO_4$ (c.c.)	1.1	2.0	2.9	3.3	3.5	3.7	4.65
Cu (mg)	9.39	17.08	24.77	28.18	29.89	30.74	39.71
Maltose (mg)	6.64	13.88	21.08	24.38	25.93	26.74	35.15
%	18.89	39.50	59.96	69.36	73.77	76.08	100.00
Italian millet starch							
$KMnO_4$ (c.c.)	0.4	0.7	1.3	2.4	3.1	3.45	4.2
Cu (mg)	3.42	6.18	11.10	20.50	26.59	29.56	35.87
Maltose (mg)	2.38	4.31	8.30	17.19	22.89	25.63	31.67
%	7.51	13.61	26.20	54.26	72.26	80.91	100.00
Barley starch							
$KMnO_4$ (c.c.)	1.2	1.8	3.1	3.5	3.8	3.85	5.0
Cu (mg)	10.25	15.37	26.59	29.89	32.45	32.88	42.70
Maltose (mg)	7.45	12.27	22.89	25.93	28.30	28.68	38.00
%	19.61	32.28	60.23	68.23	74.47	75.48	100.00
Corn starch (Kingsford)							
$KMnO_4$ (c.c.)	1.3	1.9	2.9	3.4	3.7	3.8	4.8
Cu (mg)	11.10	16.13	24.77	29.04	30.74	32.45	40.99
Maltose (mg)	8.30	13.02	21.08	25.17	26.74	28.30	36.39
%	22.81	35.77	57.92	69.16	73.48	77.76	100.00
Potato starch (Ito)							
$KMnO_4$ (c.c.)	1.1	1.95	3.18	3.5	3.8	3.9	4.6
Cu (mg)	9.39	16.65	27.16	28.89	32.45	33.31	39.28
Maltose (mg)	6.64	13.75	23.33	25.93	28.30	29.11	34.76
%	19.10	39.56	67.13	74.59	81.41	83.73	100.00

TABLE 22. (*Continued*)

Time (min.)	5	10	20	40	80	160	End
Cassava starch							
$KMnO_4$ (c.c.)	1.4	2.0	3.28	3.6	3.75	3.95	4.9
Cu (mg)	11.96	17.08	28.01	30.76	32.03	33.75	41.85
Maltose (mg)	9.11	13.88	24.28	26.76	28.73	29.53	37.23
%	24.47	37.30	65.22	71.90	77.20	79.32	100.00
Wheat starch (Ito)							
$KMnO_4$ (c.c.)	1.0	1.8	2.7	3.1	3.5	3.8	4.7
Cu (mg)	8.54	15.37	23.06	26.59	29.89	32.45	40.14
Maltose (mg)	7.80	12.27	19.54	22.89	25.93	28.30	35.54
%	21.95	34.52	54.98	64.40	72.97	79.64	100.00
Buckwheat starch							
$KMnO_4$ (c.c.)	1.18	2.05	3.1	3.2	3.5	3.65	4.6
Cu (mg)	10.08	17.51	26.59	27.33	29.89	31.17	39.28
Maltose (mg)	7.28	14.31	22.89	23.55	25.93	27.16	34.76
%	20.94	41.16	65.85	67.75	74.59	78.12	100.00
Corn starch (Ito)							
$KMnO_4$ (c.c.)	1.05	1.78	2.9	3.23	3.5	3.75	4.7
Cu (mg)	8.97	15.20	24.77	27.58	29.89	32.03	40.14
Maltose (mg)	6.26	12.10	21.08	23.78	25.93	28.73	35.54
%	17.62	34.05	59.30	66.91	72.97	80.85	100.00
Arrowroot starch							
$KMnO_4$ (c.c.)	1.1	1.9	3.19	3.55	3.8	4.0	4.9
Cu (mg)	9.39	16.13	27.18	30.32	32.45	34.16	41.85
Maltose (mg)	6.64	13.02	23.42	26.32	28.30	29.96	37.23
%	17.84	34.97	62.92	70.71	76.03	80.50	100.00

Taking the logarithms of the author's equation, the following equation was obtained.

$$-k'\log t+\log\frac{x}{a(a-x)}=\log k\ ,$$

or

$$\log k+k'\log t-\log\frac{x}{100(100-x)}=0\ .$$

Taking the hydrolysis of the starch of the potato (KOJIMA) as the example, the observation equations were formed as follows.

$$\log k + k' \, 0.6990 + 2.6574 = 0$$
$$\log k + k' \, 1.0000 + 2.2620 = 0$$
$$\log k + k' \, 1.3010 + 1.7507 = 0$$
$$\log k + k' \, 1.6021 + 1.3591 = 0$$
$$\log k + k' \, 1.9031 + 1.1363 = 0$$
$$\log k + k' \, 2.2041 + 0.9170 = 0$$

The normal equations were formed and they were solved in the usual way with the following results.

$$6 \log k + 8.7093 \, k' + 10.0825 = 0$$
$$8.7093 \log k + 14.2277 \, k' + 12.7582 = 0$$
$$k' = 1.1837$$
$$\log k = -3.3986 = \bar{4}.6014$$
$$k = 0.0003994$$

Similar calculations according to the method of least squares were carried out upon the other experimental results showed in Table 22.

TABLE 23.

The two constants of the equation calculated from the numbers of Table 22.

Starch	*k*	*k'*	Starch	*k*	*k'*
Potato (Kojima)	0.0003994	1.1837	Corn (Kingsford)	0.0004222	1.0260
Dog-tooth violet	0.0006369	0.9991	Potato (Ito)	0.0008612	0.8853
Wheat (Kojima)	0.0006969	0.9362	Cassava	0.001289	0.7368
Sorghum	0.0008145	0.9032	Wheat (Ito)	0.0009672	0.7608
Rice	0.001101	0.7365	Buckwheat	0.001283	0.7171
Italian millet	0.00009645	1.2593	Corn (Ito)	0.0007695	0.8327
Barley	0.0009654	0.7606	Arrowroot	0.0008170	0.8409

The percentages of the hydrolysis of the starch were calculated by the use of the obtained constants. They were compared with those obtained by the experiments and arranged in the following table.

TABLE 24.

Percentages of the hydrolysis of the starches calculated and observed.

Time (min.)	5	10	20	40	80	160
Potato starch (Kojima)						
Observed	18.04	35.36	63.97	81.39	87.96	92.37
Calculated	21.16	37.87	58.07	75.89	87.72	94.20
Difference	−3.12	−2.51	5.90	5.50	0.24	−1.83
Dog-tooth violet starch						
Observed	19.10	37.44	65.85	76.98	82.50	88.65
Calculated	24.13	38.86	55.97	71.74	83.54	91.02
Difference	−5.03	−1.42	9.88	5.24	−1.04	−2.37
Wheat starch (Kojima)						
Observed	18.68	34.52	64.40	75.30	81.91	84.31
Calculated	23.93	37.57	53.53	68.80	80.83	88.97
Difference	−5.25	−3.05	10.87	6.50	1.08	−4.66
Sorghum starch						
Observed	20.02	39.23	63.53	75.88	80.67	85.31
Calculated	25.84	39.46	54.93	69.51	81.00	88.85
Difference	−5.82	−0.23	8.60	6.37	−0.33	−3.54
Rice starch						
Observed	18.89	39.50	59.96	69.36	73.77	76.08
Calculated	26.47	37.50	40.99	62.48	73.50	82.21
Difference	−7.58	2.00	9.97	5.99	0.27	−6.13
Italian millet starch						
Observed	7.51	13.61	26.20	54.26	72.26	80.91
Calculated	6.82	14.91	29.55	50.12	70.63	85.19
Difference	0.69	−1.30	−3.35	4.14	1.63	−4.28
Barley starch						
Observed	19.61	32.28	60.23	68.23	74.47	75.48
Calculated	24.71	35.74	48.51	61.49	73.01	82.08
Difference	−5.10	−3.46	11.72	6.74	1.46	−6.60

TABLE 24. (*Continued*)

Time (min.)	5	10	20	40	80	160
			Corn starch (Kingsford)			
Observed	22.81	35.77	57.92	69.16	73.48	77.76
Calculated	18.05	30.95	47.72	65.02	79.10	88.51
Difference	4.76	4.76	10.20	4.14	−5.62	−10.75
			Potato starch (Ito)			
Observed	19.10	39.56	67.13	74.59	81.41	83.73
Calculated	26.36	39.80	55.00	69.29	80.65	88.50
Difference	−7.26	−0.24	12.13	5.30	0.76	−4.77
			Cassava starch			
Observed	24.47	37.30	65.22	71.90	77.20	79.32
Calculated	29.67	41.28	53.94	66.14	77.31	84.43
Difference	5.20	−3.98	11.28	4.76	−0.11	−5.11
			Wheat starch (Ito)			
Observed	21.95	34.52	54.98	64.40	72.98	79.64
Calculated	24.76	35.80	48.58	61.15	73.07	82.13
Difference	−2.81	−1.28	6.40	2.85	−0.10	−2.49
			Buckwheat starch			
Observed	20.94	41.16	65.85	67.75	74.59	78.12
Calculated	28.92	40.09	50.25	64.39	74.83	83.01
Difference	−7.98	1.07	15.60	3.36	−0.24	−4.89
			Corn starch (Ito)			
Observed	17.62	34.05	59.30	66.91	72.97	80.85
Calculated	22.71	34.36	48.25	62.42	74.73	84.04
Difference	−5.09	−0.31	11.05	4.49	−1.74	−3.19
			Arrowroot starch			
Observed	17.84	34.97	62.92	70.71	76.03	80.50
Calculated	24.02	36.15	50.35	64.51	76.50	85.35
Difference	−6.18	−1.18	12.57	6.20	−0.47	−4.85

The values of k of the equation were between 0.0006 and 0.0013, with the exceptionally small value of 0.000096 for the Italian millet starch. This starch seemed to have a great resistance to the action of the diastase, but the cause of such a great resistance could not be made clear by the present investigations.

Taking the values of log k as ordinates and the values of k′ as abscissae, the author obtained a straight line in graph. This fact coincides with the results when the proteins are hydrolysed. In the case of the hydrolysis of the proteins, the values of log k and k′ of the 10% natrium chloride solution soluble proteins, those of the 70% alcohol soluble proteins and those of the 0.2% natrium hydroxide solution soluble proteins were determined all to graph as straight lines. With the exception of the values of the Italian millet starch, the author calculated the two constants of the equation

$$y = ax + b,$$

by means of the method of least squares as follows.

Observation equations.

$$\begin{array}{lcl}
-3.3986 = a\,1.1837 + b & \text{or} & b + 1.1837\,a + 3.3986 = 0 \\
-3.1959 = a\,0.9991 + b & & b + 0.9991\,a + 3.1959 = 0 \\
-3.1567 = a\,0.9362 + b & & b + 0.9362\,a + 3.1567 = 0 \\
-3.0981 = a\,0.9032 + b & & b + 0.9032\,a + 3.0891 = 0 \\
-2.9584 = a\,0.7365 + b & & b + 0.7365\,a + 2.9584 = 0 \\
-3.0153 = a\,0.7606 + b & & b + 0.7606\,a + 3.0153 = 0 \\
-3.3745 = a\,1.0260 + b & & b + 1.0260\,a + 3.3745 = 0 \\
-3.0649 = a\,0.8853 + b & & b + 0.8853\,a + 3.0649 = 0 \\
-3.1138 = a\,0.8327 + b & & b + 0.8327\,a + 3.1138 = 0 \\
-3.0878 = a\,0.8409 + b & & b + 0.8409\,a + 3.0878 = 0 \\
-2.8898 = a\,0.7368 + b & & b + 0.7368\,a + 2.8898 = 0 \\
-3.0145 = a\,0.7608 + b & & b + 0.7608\,a + 3.0145 = 0 \\
-2.8916 = a\,0.7171 + b & & b + 0.7171\,a + 2.8916 = 0
\end{array}$$

Normal equations

$$13\,b + 11.3189\,a + 40.2509 = 0$$

$$11.3189\,b + 10.0951\,a + 35.2948 = 0.$$

Solving

$$a = -1.0378$$

$$b = -2.1989.$$

Therefore

$$\log k = -1.0378\,k' - 2.1989.$$

Generally speaking, if the mechanism of the hydrolysis by the enzyme were expressed by the equation

$$\frac{1}{t^{k'}} \cdot \frac{x}{a(a-x)} = k,$$

it is possible to deduce that the relations between log k and k′ could be expressed by an equation of a straight line.

§ 8. Viscosities of the solutions of the starches

The viscosities of the solutions of the starches have been investigated by many authors. SAMEC reported his detailed studies in his book "Kolloidchemie der Stärke" (83). In that book were described the relations between the viscosity and the concentrations of the solution of the starch, the influences of temperature and time of heating in the preparation of the solution of the starch upon the viscosity, the changes in the viscosity of the solution of the starch when it was stood for a long period at room temperature, the influences of the acids, the alkalies and the salts upon the viscosity of the solution of the starch and the viscosities as characteristics of the starches of various kinds of plants.

Studying the viscosities of the solutions of his starches, the author obtained the following results. To given quantities of the starch were added 40 c.c. of water; the mixture was heated for 2 hours in an autoclave at the pressure of 2½ kg/cm^2; after 1 hour's standing the mixture was taken out and cooled to room temperature. The solution was made up to 50 c.c. and the flowing time of the solution using an Ostwald's viscosimeter was measured at 20°C. The flowing time of water was taken as 1 and the specific viscosity of the solution of the starch was calculated. The following are the mean values of more than 2 experiments.

TABLE 25.

Specific viscosities of the solutions of the starches.

Starches	Concentrations of solution			
	0.5%	1.0%	2.0%	4.0%
Potato (Kojima)	1.054	1.236	2.218	6.363
Dog-tooth violet	1.127	1.400	2.509	7.000

TABLE 25. (*Continued*)

Starches	Concentrations of solution			
	0.5%	1.0%	2.0%	4.0%
Wheat (Kojima)	1.091	1.327	2.636	13.600
Sorghum	1.327	2.090	7.654	53.390
Rice	1.273	1.963	6.908	—
Italian millet	1.309	2.018	6.527	—
Barley	1.109	1.309	1.781	9.745
Corn (Kingsford)	1.181	1.545	3.545	26.080
Potato (Ito)	1.115	1.231	1.481	1.788
Cassava	1.212	1.442	1.981	3.770
Wheat (Ito)	1.134	1.231	1.461	2.231
Buckwheat	1.134	1.269	1.577	2.615
Corn (Ito)	1.173	1.326	1.923	4.134
Arrowroot	1.115	1.231	1.423	1.942

By the same method described before, 2% solution of the starch was prepared and the viscosities of the solution were measured at various intervals of time. The same calculations were performed; the results have been arranged in Table 26.

TABLE 26.

Changes of the viscosity of the solution of the starches by aging.

Starch	Time of aging (day)							
	0	1	2	3	4	5	6	7
Potato (Kojima)	2.218	2.218	2.000	1.690	1.454	1.454	1.363	1.363
Dog-tooth violet	2.509	2.491	2.400	2.072	1.891	1.746	1.618	1.600
Wheat (Kojima)	2.636	2.273	1.636	1.327	1.254	1.218	1.199	1.181
Sorghum	7.654	7.308	7.199	6.853	6.853	6.053	5.418	4.782
Rice	6.908	6.689	7.399	7.872	7.800	6.145	4.544	3.854
Italian millet	6.527	6.307	9.036	12.220	10.580	8.762	8.035	6.853
Barley	1.781	1.836	1.927	2.018	2.109	2.145	2.200	2.254
Corn (Kingsford)	3.545	3.510	3.545	3.470	4.490	3.363	3.309	3.309

TABLE 26. (*Continued*)

Starch	Time of aging (day)							
	0	1	2	3	4	5	6	7
Potato (Ito)	1.481	1.500	1.481	1.481	1.481	1.442	—	—
Cassava	1.981	2.019	2.000	1.981	1.981	1.981	—	—
Wheat (Ito)	1.462	1.500	1.481	1.481	1.462	1.500	—	—
Buckwheat	1.577	1.596	1.577	1.577	1.577	1.596	—	—
Corn (Ito)	1.923	1.942	1.846	1.904	1.923	1.942	—	—
Arrowroot	1.423	1.423	1.423	1.404	1.404	1.423	—	—

According to the two tables, it may be seen that the highest viscosity was observed in the case of the sorghum starch instead of the potato. After the sorghum followed the starches of rice and Italian millet. As to the potato starch it could not be said that its viscosity was a higher one. By aging of the solution of the starch, the viscosity reached its maximum in 1–4 days, whereafter a decrease of the viscosity was observed. The barley starch alone showed increasing viscosity as a result of aging, within the limits of the present investigation.

§ 9. Electrical conductivity of the solution of the starches

FOUARD(33) reported that the solution of the starch polymerised to granular starch particles and the electrical conductivity of the solution increased when the solution was kept for a long period. SAMEC(82), SAMEC and VON HOEFFT(90), also SAMEC and HAERDTL (89) reported that the electrical conductivity of the solution of the starch was increased by the aging of the solution, a phenomena opposite to the viscosity of the solution, that by the electrodialysis of the solution of the starch the electric conducting fraction of the solution had precipitated and that there was no direct relation between the conductivity and the phosphorus content of the starch. TIEBACKX(108) proposed that the heating and the aging of the solution of the starch made the amylopectin decompose increasing the electrical conductivity of the solution.

The author carried out the following experiments. One g of the starch and 40 c.c. of water were taken into an Erlenmeyer flask of hard glass, the material was heated for one hour in an autoclave at 120°C. (or 1.3 kg/cm^2), after cooling of the matter, the mixture was made up to 50 c.c. with water. The electrical conductivity of the obtained 2% solution of the starch was measured at 18°C. using a cell whose cell constant was 0.6329.

TABLE 27.

Electrical conductivity of the solutions of the starches.

Starch	R	x	K	Mean
Potato (Kojima)	13000	41.4	3.440×10^{-5}	3.429×10^{-5}
	13300	41.8	3.417	
Dog-tooth violet	13000	38.1	2.997	2.988
	13300	38.5	2.979	
Wheat (Kojima)	13000	41.7	3.482	3.492
	13300	42.4	3.502	
Sorghum	13000	35.9	2.727	2.730
	13300	36.5	2.733	
Rice	13000	34.9	2.610	2 615
	13300	35.5	2·619	
Italian millet	13000	30.3	2.115	2.102
	13300	30.5	2.088	
Barley	13000	15.4	0.886	0.893
	13300	15.9	0.900	
Corn (Kingsford)	13000	19.2	1.157	1.159
	13300	19.6	1.160	
Potato (Ito)	13000	31.0	2.189	2.193
	13300	31.6	2.198	
Cassava	13000	11.5	0.633	0.641
	13300	12.0	0.649	
Wheat (Ito)	13000	11.4	0.627	0.632
	13300	11.8	0.637	
Buckwheat	13000	16.0	0.927	0.934
	13300	16.5	0.940	
Corn (Ito)	13000	11.8	0.652	0.650
	13300	12.0	0.649	
Arrowroot	13000	20.0	1.217	1.215
	13300	20.3	1.212	

No direct relation was observed between the electrical conductivity of the solution of the starch and the phosphorus content as had been already reported by HAERDTL. Also no direct relations were observed between the conductivity and the ash content, nor between the conductivity and the nitrogen content of the starch.

On the whole, however, the conductivity of the solution of the starch seemed to be increased when the content of ash, phosphorus or nitrogen of the starch was increased.

§ 10. Influence of salts added to the solutions of the starches upon the viscosity of the solutions

M. SAMEC (83) summarised in his book the results of many investigations concerning the influence of the salts added to the solutions of the starches upon their viscosity. The viscosity of the starch solutions was diminished by the addition of salts to the solution when the quantities of the salts were small. However, there was observed a tendency for the viscosity of a starch solution to increase when the quantity of the salts added was increased.

As one of the reasons for this phenomena, SAMEC had stated that the amylopectin of the starch was destroyed by the addition of the salt and therefore the separation of the phosphoric acid from the starch which combined in the form of an ester was observed by the action of the salt. According to SAMEC's view, the amylopectin of the starch was the sole factor influencing the viscosity of the starch solutions.

To 1 g of the starch were added 25 c.c. of salt solution of given concentration and 15 c.c. of water. The mixture was heated for 1 hour at 120°C. in an autoclave. When the solution was cooled, it was made up to 50 c.c. by the addition of water. The viscosity of the obtained solution was measured at 20°C. by means of an OSTWALD's viscosimeter. The following table shows the relative viscosity of the various starch salt solutions when the viscosity of water was taken as unit.

TABLE 28.

Influence of the salts upon the viscosity of the solutions of the starches.

Concentration of salt (N)	Potato (Kojima)	Dog-tooth violet	Wheat (Kojima)	Sorghum	Rice	Italian millet	Barley	Corn (Kingsford)
				NaCl				
0	6.759	5.999	8.352	6.222	6.296	6.778	4.130	4.167
2.10^{-4}	7.482	6.296	8.519	6.094	6.074	6.463	3.925	4.222
1.10^{-3}	5.981	6.037	6.612	5.964	5.481	6.092	3.833	4.352
5.10^{-3}	5.204	5.630	5.852	5.463	5.759	7.241	3.722	4.370
$1\ 10^{-2}$	5.000	5.463	5.723	5.389	5.815	7.389	3.611	4.278
2.10^{-2}	5.075	5.500	5.555	5.222	6.537	6.688	3.462	4.148
4.10^{-2}	5.147	5.186	5.538	5.204	6.037	7.166	3.426	4.200
1.10^{-1}	5.222	5.723	6.074	5.518	6.074	7.052	3.334	4.095
				KCl				
0	—	5.694	8.555	6.981	—	6.037	—	4.130
2.10^{-4}	—	5.630	8.056	6.852	—	7.092	—	4.204
1.10^{-3}	—	5.888	6.759	6.371	—	7.685	—	4.296
5.10^{-3}	—	5.684	5.944	6.648	—	14.570	—	4.352
1.10^{-2}	—	5.352	5.833	5.277	—	8.500	—	4.148
2.10^{-2}	—	5.093	5.852	5.705	—	8.389	—	4.000
4.10^{-2}	—	4.777	5.852	5.888	—	6.944	—	4.095
1.10^{-1}	—	4.612	5.759	5.630	—	7.148	—	4.037
				$CaCl_2$				
0	—	5.500	8.796	5.999	—	6.240	—	4.130
2.10^{-4}	—	5.852	8.592	6.889	—	6.110	—	4.000
1.10^{-3}	—	5.408	6.371	6.889	—	7.759	—	4.111
5.10^{-3}	—	4.315	5.630	6.704	—	6.685	—	3.870
1.10^{-2}	—	4.148	5.593	5.964	—	5.759	—	3.833
2.10^{-2}	—	3.778	5.075	5.666	—	5.726	—	3.759
4.10^{-2}	—	3.649	4.815	5.500	—	5.723	—	3.519
1.10^{-1}	—	3.389	4.205	3.963	—	5.241	—	3.037
				$BaCl_2$				
0	—	5.538	8.537	6.037	—	5.075	—	4.278
2.10^{-4}	—	4.648	6.907	6.054	—	6.054	—	4.426
1.10^{-3}	—	4.648	6.317	6.555	—	6.482	—	4.333
5.10^{-3}	—	4.204	6.110	7.131	—	6.352	—	4.148
1.10^{-2}	—	4.037	5.779	6.573	—	8.426	—	4.037
2.10^{-2}	—	3.537	5.259	6.832	—	7.111	—	3.759
4.10^{-2}	—	3.833	5.222	6.092	—	6.537	—	3.778
1.10^{-1}	—	2.648	4.852	5.518	—	6.630	—	3.555

The values when the concentration of the salts added was zero were taken as 100 and the relative values of each concentration of the salts added were calculated as shown in the following table.

TABLE 29.

Relative values of the viscosities of the starch solutions taking as 100 the values obtained when the concentration of the salt added was zero.

Concentration of salt (N)	Potato (Kojima)	Dog-tooth violet	Wheat (Kojima)	Sorghum	Rice	Italian millet	Barley	Corn (Kingsford)
				NaCl				
0	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
2.10^{-4}	110.69	104.95	102.00	97.91	96.47	95.35	95.04	101.32
1.10^{-3}	88.49	100.63	97.17	95.85	87.05	89.88	92.81	104.44
5.10^{-3}	76.99	93.85	70.07	87.80	91.47	106.83	90.12	104.87
1.10^{-2}	73.98	91.06	68.52	86.61	92.36	109.01	87.43	102.66
2.10^{-2}	75.08	91.68	66.51	83.93	103.83	98.67	83.83	99.54
4.10^{-2}	76.15	86.45	66.31	83.64	95.64	105.72	82.95	100.79
1.10^{-1}	77.26	95.40	72.72	88.69	96.47	104.04	80.73	98.27
				KCl				
0	—	100.00	100.00	100.00	—	100.00	—	100.00
2.10^{-4}	—	99.05	94.17	98.15	—	117.47	—	101.79
1.10^{-3}	—	103.59	79.01	91.26	—	127.30	—	104.02
5.10^{-3}	—	100.00	69.48	95.23	—	241.34	—	105.38
1.10^{-2}	—	94.16	68.18	75.59	—	140.80	—	100.43
2.10^{-2}	—	89.60	68.40	81.72	—	138.96	—	96.85
4.10^{-2}	—	84.04	68.40	84.34	—	115.02	—	99.15
1.10^{-1}	—	81.14	67.32	80.65	—	118.40	—	97.75
				$CaCl_2$				
0	—	100.00	100.00	100.00	—	100.00	—	100.00
2.10^{-4}	—	106.40	97.68	114.84	—	97.92	—	96.85
1.10^{-3}	—	98.33	72.43	114.84	—	124.34	—	99.54
5.10^{-3}	—	78.45	64.01	111.75	—	107.13	—	93.70
1.10^{-2}	—	75.42	63.59	99.42	—	92.29	—	92.81
2.10^{-2}	—	68.69	57.70	94.45	—	94.97	—	91.02
4.10^{-2}	—	66.34	54.74	91.68	—	91.71	—	85.21
1.10^{-1}	—	61.62	47.79	66.06	—	83.99	—	73.54

TABLE 29. (*Continued*)

Concentration of salt (N)	Potato (Kojima)	Dog-tooth violet	Wheat (Kojima)	Sorghum	Rice	Italian millet	Barley	Corn (Kingsford)
				$BaCl_2$				
0	—	100.00	100.00	100.00	—	100.00	—	100.00
2.10^{-4}	—	83.93	80.91	100.28	—	106.12	—	103.46
1.10^{-3}	—	83.93	73.98	108.58	—	113.62	—	101.28
5.10^{-3}	—	75.91	71.57	118.12	—	111.34	—	96.96
1.10^{-2}	—	72.90	67.69	108.88	—	147.69	—	94.37
2.10^{-2}	—	63.87	61.60	113.17	—	124.64	—	87.87
4.10^{-2}	—	69.21	61.17	100.91	—	114.58	—	88.31
1.10^{-1}	—	47.82	56.83	91.40	—	116.21	—	83.10

Considering from the values of the table, it is to be observed that the effects of the addition of salts to the solution of the starches were in two directions, one of which was that when the concentration of the salt added was low, the viscosity of the solutions of the starches was increased by the addition and the other was that when the concentration of the salt added became high, the viscosity of the solution was decreased generally. The former effect was observed in the case of the starches of potato, dog-tooth violet, wheat and corn by the addition of NaCl, in the cases of sorghum, Italian millet and corn with KCl, in those of dog-tooth violet, Italian millet and corn with $CaCl_2$ and in those of sorghum, Italian millet and corn with $BaCl_2$. In the case of the Italian millet starch by the addition of NaCl, KCl $BaCl_2$, the viscosity of the solutions became greater with the increase in the concentration of the salts added. These were considered as exceptional and interesting cases by the author. The starches of the potato, dog-tooth violet, wheat, barley and corn had decreased their viscosity with the increasing addition of the salts and the decreases became greater, when the quantities of the salts added were increased.

Comparing the effects of the cations added, the effects of the natrium ion were the smallest and the effects were increased in the order, kalium, barium and then calcium ion. These facts coincide well with HOFMEISTER's series for colloidal solution of gelatin.

In general, the influences of the salts upon the viscosities of the solutions of the starches may be summarised as follows. When the concentration of the salt was low, the viscosity of the solutions of some starches were increased, but when the concentration of the salt was increased, the viscosity of the solutions was decreased in all cases of the starches used.

§ 11. Gold value of the starches

Starch solution showed the properties of a hydrophile colloid as reported by many authors. Therefore, it was thought to effect the protective action in respect to the other colloid. The gold value of the starch as the protective colloid was reported as 5.00 for wheat starch and 25.00 for potato starch and 6.00–20.00 for dextrine by J. ALEXANDER (1). SAMEC (84) and ZSIGMONDY (115) had also reported similar values. W. BILTZ (15) reported that the gold value of dextrine increased according to the diminution of the molecular weight of the dextrines or in other words protective action of the dextrines decreased concordantly with the diminution of their molecular weight. However, M. SAMEC and M. MINAEFF (94) obtained opposite results. The reason for the two contradictory results was reported by SAMEC as lying in the difference of the methods of their investigations.

The author proposing to determine the gold values of his starches carried out the following experiments. Six g of gold chloride were dissolved in 1 L. of water. To 150 c.c. of water were added 2.5 c.c. of the gold solution and 0.9 c.c. of 0.2 N potassium carbonate solution. The mixture was boiled, the heating was stopped at once and 0.9 c.c. of the solution of formaline was added with vigorous stirring. After 2–3 minutes, rosa gold colloidal solution was obtained. The water used in the process was redistilled water obtained by the use of a pure tin tube. The formaline solution was prepared by mixing 100 c.c. of water and 1 c.c. of distilled formaline which was collected at 94–96.5°C. The solution of the starch was prepared with redistilled water as a 1% solution heating for 1 hour under the pressure of 1.3 kg per sq. cm. To 10 c.c. of the gold solution were added the given quantities of the starch solution. To the mixture was then added 1 c.c. of 10% natrium chloride solution and the changes in the colour of the solution were observed. The colour of the solution became violet when the quantity of the starch added was other than the values described in the following table. Thus the author was able to show that the protective action of the starch upon the gold solution had an optimum quantitative limit.

TABLE 30.

The gold value of the starch.

Potato starch (Kojima)	12	Rice starch	11–12
Dog-tooth violet starch	2–3	Italian millet starch	7
Wheat starch (Kojima)	8	Barley starch	4
Sorghum starch	13	Corn starch (Kingsford)	4

§ 12. Heat of combustion of the starches

The heat of combustion of the starch was reported by BLOEMENDAL (16) as 4000–4027 cal. and by BERTHELOT and VIEILLE (13) as 4228 cal. and 4183 cal. RECHENBERG (76) reported that it was 4448 cal. in rice starch. TADOKORO and collaborators (106) determined the heat of combustion of the starches of common and glutinous rice and reported them as 4262–3893 cal. They also reported that the values of the common rice starches were higher than those of the other.

Considering that the heat of combustion of the starch might differ according to differences in mode of formation of the starch and according to the differences of the plant, the author carried out the estimation of the heat of combustion using ATWATER's bomb calorimeter. The results obtained have been arranged in Table 31.

TABLE 31.

Heat of combustion of the starches.

Starch	Sample (g)	Heat evolved	Heat for 1 g	Dry matter	Mean
Potato (Kojima)	0.4522 0.6076	1569.79 2088.95	3472 3439	3911 3874	3892 cal.
Dog-tooth violet	0.4673 0.5439	1643.53 1890.45	3571 3476	3988 3942	3965

TABLE 31. *(Continued)*

Starch	Sample (g)	Heat evolved	Heat for 1 g	Dry matter	Mean
Sorghum	0.6781 0.5416	2405.84 1895.87	3548 3501	3897 3846	3872 cal.
Rice	0.8633 0.6704	2999.96 2328.77	3474 3472	3909 3908	3909
Italian millet	0.4393 0.4941	1640.13 1809.51	3733 3662	3993 3917	3955
Barley	0.7220 0.9800	2501.65 2366.98	3470 3481	3809 3821	3815
Corn (Kingsford)	0.5528 0.8275	1909.59 2830.83	3446 3421	3978 3949	3963
Wheat (Kojima)	0.4002 0.6499 0.5903	1344.49 2177.33 1973.83	3360 3351 3345	3942 3930 3922	3931

The heat of combustion of the starches averaged about 3900 calories. The author did not find any difference according to the method of the formation of the starches, i.e. any difference of the heat of combustion between the starches formed in the part of a plant of above the ground and those in the part of a plant underground. The heat of combustion was the greatest in the dog-tooth violet starch and followed those of corn, Italian millet, wheat, rice, potato, sorghum and barley.

§ 13. Adsorption of iodine by the starch granules

Studies of the chemical and physico-chemical reactions between iodine and the starch have been reported abundantly from the early time. SAMEC described in his book (85) the coloring and the decoloring of the starch by the action of iodine, the effects of heating and drying upon the starch-iodine reaction and the properties of the starch-iodine products. He discussed the quantitative relations between starch and iodine and observed that the starch-iodine products were thought to be one of the chemical compounds or the solid solution of iodine in starch or the adsorbed products of the two components, whose distinction he thought extremely difficult.

The author (61) has studied the adsorption of iodine by barley starch and calculated the values of the two constants of FREUNDLICH'S adsorption isotherms. In the present investigation, in order further to study the same matter and to calculate the same constants, the following experiments were carried out.

To each 0.5 g of the starches were added 20 c.c. of about N/10, N/25, N/50, N/75, N/100 and N/200 iodine potassium iodide solutions. The mixture was shaken for 30 minutes by means of the shaking machine. It was stood for more 30 minutes and the adsorption reached equilibrium. It was then centrifuged for the purpose of separating the starches; the quantities of iodine remaining in 10 c.c. of the supernatant solution were titrated with the standard solution of natrium thiosulphate. The results were converted to the basis of 1 g of the starch as follows.

TABLE 32.

Adsorption of iodine by the starches.

	Iodine remained C (mg)	Adsorbed x (mg)	log C	log x
Potato starch (Kojima)				
1 (About N/200)	0.49	23.95	$\bar{1}.69020$	1.37931
2 („ N/100)	5.74	40.70	0.75891	1.60959
3 („ N/75)	11.36	52.18	1.05538	1.71750
4 („ N/50)	28.96	68.80	1.46180	1.83759
5 („ N/25)	70.02	120.61	1.84522	2.08138
6 („ N/10)	271.77	214.59	2.43420	2.33161
Dog-tooth violet starch				
1 (About N/200)	0.61	23.83	$\bar{1}.78533$	1.37712
2 („ N/100)	6.11	40.33	0.78604	1.60563
3 („ N/75)	11.61	51.93	1.06483	1.71542
4 („ N/50)	32.26	65.50	1.50866	1.81624
5 („ N/25)	76.99	123.64	1.88643	2.09216
6 („ N/10)	273.24	213.12	2.43635	2.32862
Wheat starch (Kojima)				
1 (About N/200)	0.98	23.56	$\bar{1}.99123$	1.37033
2 („ N/100)	7.09	39.35	0.85065	1.59494
3 („ N/75)	13.08	50.46	1.11661	1.70295
4 („ N/50)	32.85	65.01	1.51521	1.81298
5 („ N/25)	78.70	111.93	1.89597	2.04895
6 („ N/10)	280.08	206.28	2.44728	2.31446

TABLE 32. (*Continued*)

	Iodine remained C (mg)	Adsorbed x (mg)	log C	log x
Sorghum starch				
1 (About N/200)	2.93	21.51	0.46687	1.33264
2 („ N/100)	10.87	35.57	1.03623	1.55108
3 („ N/75)	14.30	49.24	1.15534	1.69232
4 („ N/50)	23.58	74.18	1.37254	1.87029
5 („ N/25)	36.17	154.46	1.55835	2.18881
6 („ N/10)	252.83	233.53	2.40283	2.36834
Rice starch				
1 (About N/200)	1.22	23.22	0.08636	1.36586
2 („ N/100)	6.97	39.47	0.84323	1.59627
3 („ N/75)	12.22	51.32	1.08707	1.71029
4 („ N/50)	26.66	71.10	1.42586	1.85187
5 („ N/25)	67.94	122.69	1.83213	2.08880
6 („ N/10)	268.59	217.77	2.42909	2.33800
Italian millet starch				
1 (About N/200)	0.24	24.20	$\bar{1}.38021$	1.38382
2 („ N/100)	3.67	42.77	0.56467	1.63114
3 („ N/75)	6.97	56.57	0.84323	1.75259
4 („ N/50)	19.56	78.20	1.29137	1.89321
5 („ N/25)	56.95	133.68	1.75549	2.12607
6 („ N/10)	259.31	227.05	2.41382	2.35612
Barley starch				
1 (About N/200)	0.24	24.20	$\bar{1}.38021$	1.38382
2 („ N/100)	1.89	44.55	0.27646	1.64885
3 („ N/75)	5.87	57.67	0.76864	1.76095
4 („ N/50)	19.80	77.96	1.29667	1.89187
5 („ N/25)	53.77	136.86	1.73054	2.13627
6 („ N/10)	275.32	211.04	2.43984	2.32436
Corn starch (Kingsford)				
1 (About N/200)	0.73	23.71	$\bar{1}.86332$	1.37493
2 („ N/100)	6.11	40.33	0.78604	1.60563
3 („ N/75)	11.16	52.38	1.04766	1.71917
4 („ N/50)	31.77	65.99	1.50202	1.81948
5 („ N/25)	82.61	108.02	1.91703	2.03350
6 („ N/10)	277.88	208.48	2.44386	2.31907

By means of the method of least squares, the values of the two constants 1/n and k of FREUNDLICH's adsorption isotherms

$$x/m = k\,C^{1/n}$$

were calculated. According to the formula

$$\log k' = (\log k + 3 \times 1/n) - 3\ ,$$

the values of k' was calculated from the value of k, the latter being the constant when the calculation was carried out on the basis of mg and k' the constant which was calculated on the basis of g.

TABLE 33.

Values of the constants of FREUNDLICH's adsorption isotherms.

Starch	The concentrations of iodine used were					
	Low			High		
	$1/n$	k	k'	$1/n$	k	k'
Potato (Kojima)	0.25111	28.176	0.15967	0.50085	13.336	0.42423
Dog-tooth violet	0.25695	26.705	0.15756	0.54344	10.536	0.44976
Wheat (Kojima)	0.29195	23.268	0.17482	0.53400	10.375	0.41495
Sorghum	0.56990	10.896	0.55843	0.40015	26.981	0.43805
Rice	0.35926	20.983	0.25100	0.41410	20.302	0.35470
Italian millet	0.27408	33.320	0.22128	0.40818	44.107	0.40429
Barley	0.26451	36.099	0.24441	1.36818	0.421	5.3547
Corn (Kingsford)	0.27545	25.675	0.17213	0.50851	11.577	0.38824

The values of the constants 1/n, k and k' were different when the concentrations of the solutions of iodine were different as has already been reported in the author's former investigation upon the starch of barley. The value of 1/n was lower, the value of k was higher and the value of k' was lower in the case of the low concentration of iodine than in the case of the high concentration. When the concentration of iodine was low, the values of 1/n, k and k' were smaller in the case of the starches of the tuber plants than in the case of the cereal plant starches and when the concentration of iodine was high the relation was the opposite.

For the purpose of examining the correlations between 1/n, *k* and *k′*, the author calculated the coefficients of correlation between 1/n and *k*, 1/n and *k′* as shown in the following table.

TABLE 34.

Coefficients of correlation between 1/n and *k*, 1/n and *k′*.

	The concentrations of iodine used were	
	Low	High
Between 1/*n* and *k*.	−0.8556	−0.9753
Between 1/*n* and *k′*.	0.9619	0.4260

In the calculation of the values when the concentrations of iodine used were high, the values for the barley starch were not used which were exceptionally different from the other values. From the results of Table 34, it is seen that there are close correlations between 1/n and *k*, 1/n and *k′* when the concentrations of iodine used were low. Between 1/n and *k*, a negative correlation was observed, but the coefficient of correlation between 1/n and *k′* was 0.4260 and the correlation was not sufficient when the concentration of iodine used were high.

The starch was treated with sufficient quantities of the solution of iodine potassium iodide. The jod-starch formed was separated from the solution by means of a centrifugal machine. The separated jod-starch was washed repeatedly with the solution of 1% potassium iodide until the washing was completely colorless. The substance was washed well with water and dried in a desiccator of diminished pressure containing phosphoric anhydride. The jod-starch was treated with potassium hydroxide and potassium permanganate, where the free iodine was oxidized to iodate. The solution was acidified by the addition of hydrochloric acid; to the solution was added potassium iodide solution and the solution was titrated with the solution of natrium thiosulphate. The content of iodine measured by the described treatment was as follows.

TABLE 35.

Iodine content of the jod-starch.

Starch	Quantities of iodine (g)	k'
Potato (Kojima)	0.01558	0.15967
Dog-tooth violet	0.01589	0.15756
Wheat (Kojima)	0.01273	0.17482
Sorghum	0.00468	0.55843
Rice	0.01548	0.25100
Italian millet	0.02118	0.22128
Barley	0.02851	0.24441
Corn (Kingsford)	0.01915	0.17213

The values of k' in the table were the values of the constants k' of the adsorption of iodine when the concentration of iodine used were low. The quantities of iodine measured were greatest in the starch of barley and diminished in the order the starches of Italian millet, corn, dog-tooth violet, potato, rice, wheat and sorghum. It could be seen that the quantities of iodine measured were about 1/10 of the values of k' when they were compared as shown in Table 35. In other words, definite quantities of iodine counting to about 1/10 of the constants k' were combined with the starch in a form that was not removed by the washing with the potassium iodide solution. The mode of the combination between the starch and the iodine was supposed to be either the formation of a solid solution or a chemical combination between them.

Chapter II

Electrodialysis of the Starches

The action of electric current upon the starch was studied from many decades ago. BRESTER(19) stated that the starch was not changed by the electric current, that the reaction was neutral, and that the sugar was not formed by the treatment continued for 5 days. ROSENTHAL(79) and HEIMROD(37) recognised that electromagnetic force decomposes starch just like an enzyme does, and NEUBERG(62) reported that the starch was scarcely effected by the action of 220 volts of direct current, and after 4–5 days there was formed a very slight amount of reducing sugar. LOEB (52), and LOEB and SATO (53) reported that an induction current decomposes starch and forms rapidly reducing substance.

On the dialysis of starch solution, BECKMANN (5), MÜLLER (60), BERCZLLER (7), SAMEC and HAERDTL (89), SAMEC and MAYER (93), HOLMBER (39), SAMEC and BLINC (88) have published reports. It was recognized that the dextrin did not pass the membrane.

Thus, on the effect of electric current upon the starch, the reported results vary widely amongst these authors; some reported that the starch was not decomposed but others reported that it was decomposed to form the reducing substance. Therefore, the present author attempted to ascertain clearly how the electric current effects the starch particle, and then to discover the difference between the original starch particle and the starch particle which was effected by the electric current. Accordingly the following experiments were carried out by him.

§ 1. Method

The electro-dialysis of starch particle was carried out with PAULI's electro-dialysator. For the dialysis membrane, the sulphuric paper of the best quality was used. Ten g of starch were suspended in water and put into the middle cell of the dialysator. Then, 110 volts direct current was passed through; every two hours the water in both sides of the dialysator was changed. At first the strength of current passed was 5–6 milliamperes, but by and by the ampherage was increased and at last is reached the maximum of 12 milliamperes, then again it decreased, and after 8 hours' electro-dialysis the current decreased to 5–6 milliamperes. Therefore, this time was considered as the end point of the experiment. The water in both sides of the dialysator and the solution in the middle cell which was separated from the starch were evaporated till they became 100 c.c. respectively. With 25 c.c. of these solutions respectively and also with 25 c.c. of these solutions respectively which had been boiled for 1 minute after the addition of 2 c.c. of concentrated hydrochloric acid, the reducing substances which reduced FEHLING's solution by BERTLANDT's method were measured. These results were taken as the amount of potassium permanganate solution titrated.

TABLE 36.

Amount of reducing substance formed by electro-dialysis.
c.c. of $KMnO_4$ titrated for 10 g of starch.

Starch	Hydrolysed by conc. HCl					
	Before			After		
	Anode	Cathode	Middle	Anode	Cathode	Middle
Potato (Kojima)	1.80	4.40	1.60	3.60	3.60	5.80
Dog-tooth violet	0.80	0.60	0.60	1.80	2.20	2.20
Wheat (Kojima)	0.80	0.48	1.80	1.60	1.20	6.40
Sorghum	0.60	1.00	1.00	2.00	1.60	2.40
Rice	0.40	0.80	0.60	1.60	1.80	3.00
Italian millet	0.40	0.40	0.40	2.00	1.60	2.00
Barley	1.00	0.80	0.80	2.00	2.00	3.00
Corn (Kingsford)	0.60	0.40	1.20	1.60	1.60	2.40

The effect of the electric current was to separate the reducing substance from the starch also substance which showed reducing power after hydrolysis by acid. It was not distinctly determined, however, in which part of the dialysator this substance was abundant, but it was separated from both sides. The amount of this substance in the middle cell was the greatest, which suggests that from the starch had separated mostly a particle of such size that it could not pass through the dialysis membrane.

From the starch also was separated large amounts of the substance which showed the reducing power after hydrolysis by acid. This substance was of two kinds, the one consisted of too great particles to pass through the membrane, but the other of so little particles that it could pass through the membrane.

From these results, it was observed that the electric current had decomposed the starch though the degree of decomposition was slight. In this case from the starch were separated the reducing substance and the other substances which showed reducing power after hydrolysis by acid, both in particles of widely differing size, from great ones which could not pass through the membrane to little ones which could.

The phosphorus content of the same solution which was used for the measurement of the reducing substance was measured by BELL-DOISY's colorimetric method modified by BRIGGS. But the phosphorus was not obtained in the solution from the anode, but only in the solution from the cathode was the phosphorus content measured as follows:—

TABLE 37.

Phosphorus content of the solution from the cathode after electro-dialysis.

Starch	mg for 1 g of starch	% for phosphorus content of original starch
Potato (Kojima)	0.0492	9.23
Dog-tooth violet	0.0397	15.92
Wheat (Kojima)	0.1016	17.32
Sorghum	0.0421	19.72
Rice	0.0594	26.67
Italian millet	0.0748	38.00
Barley	0.0516	20.44
Corn (Kingsford)	0.0603	29.00

Phosphorus had migrated to the cathode by the electro-dialysis of starch, and in this case the phosphorus seemed to be charged as cation but not as anion such as PO_4''' ion. It must be a complex organic compound of phosphorus and was charged as cation by electro-dialysis. But this organic compound of phosphorus seemed to have not the least reducing power, because it was observed that the amounts of reducing substances which were separated in both sides of the dialysator were about the same and that there was no quantitative relation between the reducing substance and the substance containing the phosphorus.

§ 2. Water, phosphorus and nitrogen content of electro-dialysed starch

The water, phosphorus and nitrogen content of starch separated by electro-dialysis as described above were measured respectively.

TABLE 38.

Water, phosphorus and nitrogen content of electro-dialysed starch.

Starch	Water (%)	Nitrogen (% for dry subs.)	Phosphorus (mg in 1 g of starch)
Potato (Kojima)	13.81	0.0137	0.4226
Dog-tooth violet	14.80	0.0389	0.1970
Wheat (Kojima)	16.69	0.0129	0.4325
Sorghum	15.11	0.0188	0.1450
Rice	13.93	0.0145	0.1400
Italian millet	14.91	0.0312	0.1525
Barley	14.64	0.0147	0.1880
Corn (Kingsford)	14.69	0.0221	0.1643

To ascertain how much the phosphorus and nitrogen content of starch was decreased or increased after electro-dialysis, the phosphorus and nitrogen content of the original starch was taken as 100 and the ratios of the above values were calculated as follows.

TABLE 39.

Phosphorus and nitrogen content of starch before and after electro-dialysis.

Starch	Original starch (%)	Electro-dialysed starch (%)	%
	Nitrogen		
Potato (Kojima)	0.0198	0.0137	69.18
Dog-tooth violet	0.0481	0.0389	80.87
Wheat (Kojima)	0.0176	0.0129	73.30
Sorghum	0.0254	0.0188	74.03
Rice	0.0184	0.0145	78.81
Italian millet	0.0332	0.0312	93.99
Barley	0.0169	0.0147	86.98
Corn (Kingsford)	0.0227	0.0221	97.36

TABLE 39. (*Continued*)

Starch	Original starch (%)	Electro-dialysed starch (%)	%
	Phosphorus		
Potato (Kojima)	0.5333	0.4226	79.25
Dog-tooth violet	0.2495	0.1970	78.96
Wheat (Kojima)	0.5865	0.4325	73.74
Sorghum	0.2131	0.1450	68.05
Rice	0.2228	0.1400	62.84
Italian millet	0.1968	0.1525	77.47
Barley	0.2524	0.1880	74.49
Corn (Kingsford)	0.2078	0.1643	79.05

The phosphorus and nitrogen content of starch were both decreased by electro-dialysis. The degree of decrease was 70% to 97% of the content of the original starch in the case of nitrogen. In the case of phosphorus it was 62% to 80%. Thus it was observed that the degree of decrease of phosphorus was greater than that of nitrogen.

The phosphorus content of the solution which was obtained from the polar cell by the dialysis as described above was compared with the amount of phosphorus lost from the original starch.

TABLE 40.

Phosphorus content of the solution obtained from the polar cell by dialysis and the amount of phosphorus of starch lost by dialysis.

(% of the content of original starch)

Starch	In the polar solution	Lost by dialysis	Starch	In the polar solution	Lost by dialysis
Potato (Kojima)	9.23	20.75	Rice	26.67	37.16
Dog-tooth violet	15.92	21.04	Italian millet	38.00	22.53
Wheat (Kojima)	17.32	26.26	Barley	20.44	25.51
Sorghum	19.72	31.95	Corn (Kingsford)	29.00	20.95

According to this table, except in the case of corn and Italian millet starch, the phosphorus amount contained in the polar solution was smaller than that lost by dialysis. This suggested that the phosphorus contained in the polar solution had originated from the starch used. This agrees well with SAMEC's statement that the electro-dialysis of starch frees the phosphorus contained in starch.

From these results, that the phosphorus and nitrogen content of starch were decreased and the existence of phosphorus and reducing substance in the solution used for dialysis were observed as a result of electro-dialysis, it may be said that the starch particle is changed in its construction in some way as a result of electro-dialysis. This agrees well with ROSENTHAL's, NEUBERG's and LOEB's reports.

§ 3. Acetylation of the electro-dialysed starch

By the same method as described before, the acetylation was carried out by the use of pyridin and acetic acid anhydride at room temperature. The acetyl content of the product was measured with the following results.

TABLE 41.

Acetyl content of electro-dialysed and acetylated starch.

Starch	Acetyl group (%)
Potato (Kojima)	48.43
Dog-tooth violet	48.96
Wheat (Kojima)	48.43
Sorghum	47.39
Italian millet	46.86
Barley	52.64
Corn (Kingsford)	43 17

The elementary composition of the products was determined by the micro method of elementary analysis with the following resultes.

TABLE 42.

Elementary analysis of the acetyl electro-dialysed starches.

Starch	Sample (mg)	H_2O (mg)	CO_2 (mg)	H (%)	C (%)
Potato (Kojima)	4.555	2.945	7.980	6.987	47.77
	4.165	2.651	7.270	7.119	47.60
				7.05	47.68
Dog-tooth violet	5.090	3.130	8.810	6.879	47.21
	5.020	3.045	8.740	6.785	47.47
				6.83	47.34
Wheat (Kojima)	6.045	3.735	10.695	6.911	48.25
	4.350	2.715	7.750	6.982	48.59
				6.95	48.42
Sorghum	6.230	3.730	10.755	6.697	47.09
	4.620	2.675	7.950	6.477	46.93
				6.59	47.01
Italian millet	4.350	2.915	7.770	7.496	48.71
	4.925	3.340	8.770	7.586	48.56
				7.54	48.63
Barley	5.170	3.270	9.150	7.074	48.26
	3.345	2.110	5.950	7.058	48.52
				7.07	48.39
Corn (Kingsford)	6.225	3.500	10.690	6.290	46.82
	5.395	2.925	9.230	6.064	46.66
				6.18	46.74

The results were arranged in the following table.

TABLE 43.

Elementary composition of acetylated electro-dialysed starches.

Starch	C	H	O
Potato (Kojima)	47.68	7.05	45.27
Dog-tooth violet	47.34	6.83	45.83
Wheat (Kojima)	48.42	6.95	44.63
Sorghum	47.01	6.59	46.40
Italian millet	48.63	7.54	43.83
Barley	48.39	7.07	44.54
Corn (Kingsford)	46.74	6.18	47.08

The electro-dialysed starch was acetylated more easily than the original starch. The starches of potato, wheat and dog-tooth violet which were not acetylated at the room temperature in the untreated state were acetylated when they were electro-dialysed. The content of the acetyl group of the acetylated electro-dialysed starches was higher than that of the original acetyl starches. While the latter measured 40.02–45.19%, the former measured 43.17–52.64%. Comparing the results with the theoretical content of the acetyl group of acetyl glucose, it was found that the ratios of the acetyl group to the glucose were 3.2–4, or generally 3.80–4.00. Therefore, the acetylated electro-dialysed starches are considered to be the mixture of 4–5 molecules of tetraacetyl glucose and 1 molecule of triacetyl glucose, or rather, to be tetraacetyl glucose. The starches of the tubers were changed so as to be more easily acetylated than those of the cereal plants and the content of the acetyl group was higher in the case of the tuber starches than of the cereal.

Thus electro-dialysis was considered to result in some kind of changes in the particles of the starches. The changes were considered to be the changes such as to make the particles of the starches easily reacted upon chemically. The electro-dialysis was further believed to decompose the starches very slightly.

§ 4. Electrical conductivity of the solutions of the electro-dialysed starches

By the same method as that described before, 2% solution of the electro-dialysed starch was prepared. The electrical conductivity of this solution was measured at 18°C. using a cell whose cell constant was 0.6096.

TABLE 44.

Electrical conductivity of the solutions of the electro-dialysed starches.

Starch	$K \cdot 10^5$	Starch	$K \cdot 10^5$
Potato (Kojima)	4.692	Rice	0.926
Dog-tooth violet	1.163	Italian millet	0.908
Wheat (Kojima)	4.100	Barley	0.784
Sorghum	1.187	Corn (Kingsford)	0.752

The electrical conductivity was at maximum in the potato electro-dialysed starch and decreased in the order of the starches of wheat, sorghum, dog-tooth violet, rice, Italian millet, barley and corn. The order was almost identical with that of the original starches. These values of the electro-dialysed starches were compared with those of the original starches as follows.

TABLE 45.

Electrical conductivity of the original and the electro-dialysed starches and the ratios between these values.

Starch	Original starch	Electro-dialysed starch	Ratio
Potato (Kojima)	$3.429 \cdot 10^{-5}$	$4.692 \cdot 10^{-5}$	100 : 136.9
Dog-tooth violet	2.988	1.163	38.92
Wheat (Kojima)	3.492	4.100	117.4
Sorghum	2.730	1.187	43.48
Rice	2.615	0.926	35.42
Italian millet	2.102	0.908	43.20
Barley	0.893	0.784	87.78
Corn (Kingsford)	1.159	0.752	64.88

The electrical conductivity of the solutions of the electro-dialysed starches had increased in the cases of the potato and the wheat starches whose values were respectively 136.9% and 117.4% of the original values. However, the values had decreased in the cases of the other starches whose values were 35–87% of the original values.

As shown above, the phosphorus and the nitrogen content of the starches decreased as a result of electro-dialysis and reducing substances were separated from the starches. Therefore, the starches had decreased to the extent of substances liberated when they were dissolved in solutions by the treatment of electro-dialysis. The fact that the electrical conductivity of the solution of the electro-dialysed starch showed a lower value than that of the original starch could be easily deduced. But the author could not find the reason why there should be increase of the electrical conductivity in the cases of the potato and the wheat starches.

§ 5. Viscosity of the solutions of the electro-dialysed starches

For the purpose of determining the viscosity of the solutions of the electro-dialysed starches and also the differences of those values compared with the original starches, the following determinations were carried out. The solution of the starch was prepared as described before heating the material under pressure in an autoclave. The viscosity was determined by the OSTWALD's viscosimeter at 20°C. The flowing time of water was taken as 1 and the relative viscosities of the solutions were calculated. At the same time, the specific values of the viscosities were calculated taking the viscosity of the solution of the original starch of the same concentration as 100.

TABLE 46.

Viscosity of the solutions of electro-dialysed and original starches and their ratios when the latter values were taken as 100.

Starch	0.5 %	1.0 %	2.0 %	4.0 %
The electro-dialysed starches.				
Potato (Kojima)	1.091	1.163	1.273	1.923
Dog-tooth violet	1.345	1.818	2.218	5.654
Wheat (Kojima)	1.091	1.327	1.436	1.781
Sorghum	1.363	2.109	5.508	34.600
Rice	1.309	1.963	5.344	39.410
Italian millet	1.363	2.072	5.418	54.080
Barley	1.254	1.418	1.545	7.818
Corn (Kingsford)	1.291	1.781	2.581	21.820
The original starches.				
Potato (Kojima)	1.054	1.236	2.218	6.363
Dog-tooth violet	1.127	1.400	2.509	7.000
Wheat (Kojima)	1.091	1.327	2.636	13.600
Sorghum	1.327	2.090	7.654	53.390
Rice	1.273	1.963	6.908	—
Italian millet	1.309	2.018	6.527	—
Barley	1.109	1.309	1.781	9.745
Corn (Kingsford)	1.181	1.545	3.545	26.080

TABLE 46. (*Continued*)

Starch	0.5 %	1.0 %	2.0 %	4.0 %
The ratios of the two.				
Potato (Kojima)	103.51	94.08	57.40	30.22
Dog-tooth violet	119.34	129.86	88.41	80.76
Wheat (Kojima)	100.00	100.00	54.46	13.09
Sorghum	102.71	100.91	71.96	64.82
Rice	102.83	100.00	77.36	—
Italianm millet	104.12	102.67	83.01	—
Barley	113.07	108.33	86.76	80.23
Corn (Kingsford)	109.31	115.27	72.81	83.68

The ratio of the viscosities of the solutions of the electro-dialysed and the original starches varried with the changes of the concentrations of the solutions respectively. In the cases of the concentrations of 0.5% and 1.0% with the exception of the potato starch of 1.0% the ratios were always greater than 100.00 or in other words, the viscosities of the solutions were increased by the electro-dialysis over the corresponding values of the original starches. In the cases of the corn and the dog-tooth violet starches, the ratios of 1.0% solutions were higher than those of 0.5%, but in all other cases the reverse was true. When the concentrations of the solution were 2.0% and 4.0%, the viscosities of the electro-dialysed starches were always smaller than those of the original starches. The greater the concentration, the more the viscosities decreased. The viscosities of the 4.0% original starches of Italian millet and rice were so high that they were undetermined. The viscosity of these same solutions was so reduced by electro-dialysis as to become determinable.

§ 6. Gold value of the electro-dialysed starches

In the same way as previously described, the author determined the gold values of the electro-dialysed starches.

TABLE 47.

Gold values of the electro-dialysed starches.

Starch		Starch	
Potato (Kojima)	12	Rice	11
Dog-tooth violet	2–6	Italian millet	6–7
Wheat (Kojima)	7	Barley	4
Sorghum	13	Corn (Kingsford)	4

In this case, the author found that there were optimum limits of the quantity for the protection of the gold solution as was seen in the case of the original starches.

When the values were compared with those of the original starches, there were observed no marked differences. The same values were obtained for the starches of potato, barley and corn but for the wheat starch the value decreased from 8 of the original to 7 of the electro-dialysed. According to the findings it may be said that electro-dialysis does not change the gold value of the starch or in other words, electro-dialysis does not change the protective power of the starch at all.

Considering the facts that the electro-dialysis had decreased the phosphorus and the nitrogen content of the starch and had separated the reducing substances from the starch, yet the protective power of the starch did not change at all, it may be deduced that the protective power of the starch has no remarkable relation to the composition and quantity of the ash constituents.

§ 7. Adsorption of iodine by the electro-dialysed starch granules

Electro-dialysis separated phosphorus, nitrogen and reducing substances from the starch. Therefore, it seemed to be of great interest to know how the adsorption of iodine by such electro-dialysed starch granules was influenced. The adsorption was conducted by the same method as described before with the following results and the calculations of the constants 1/n, *k* and *k'* were carried out.

TABLE 48.

Adsorption of iodine by the electro-dialysed starch granules.

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
Potato starch (Kojima)				
1 (About N/200)	0.37	22.11	$\bar{1}.56820$	1.34459
2 (,, N/100)	4.89	41.79	0.68931	1.62107
3 (,, N/75)	11.24	50.55	1.05077	1.70372
4 (,, N/50)	27.50	67.82	1.43933	1.83136
5 (,, N/25)	59.14	129.54	1.77188	2.11241
6 (,, N/10)	275.44	206.52	2.44002	2.11241
Dog-tooth violet starch				
1 (About N/200)	0.86	21.62	$\bar{1}.93450$	1.33486
2 (,, N/100)	6.84	39.84	0.83506	1.60032
3 (,, N/75)	13.69	48.10	1.13640	1.68215
4 (,, N/50)	32.75	61.57	1.51521	1.78937
5 (,, N/25)	82.61	106.07	1.91703	2.02560
6 (,, N/10)	271.28	210.68	2.43342	2.32352
Wheat starch (Kojima)				
1 (About N/200)	0.73	21.75	$\bar{1}.86332$	1.33746
2 (,, N/100)	5.87	40.81	0.76864	1.61077
3 (,, N/75)	11.49	50.30	1.06032	1.70157
4 (,, N/50)	28.35	66.97	1.45255	1.82588
5 (,, N/25)	64.77	123.91	1.81137	2.09310
6 (,, N/10)	278.86	203.10	2.44528	2.30771
Sorghum starch				
1 (About N/200)	1.96	20.52	0.29226	1.30643
2 (,, N/100)	9.78	36.90	0.99034	1.56703
3 (,, N/75)	14.91	46.88	1.17348	1.67099
4 (,, N/50)	22 48	72.84	1.35180	1.86237
5 (,, N/25)	37.88	150.80	1.57841	2.17840
6 (,, N/10)	257.60	224.36	2.41095	2.35094
Rice starch				
1 (About N/200)	0.49	21.99	$\bar{1}.69020$	1.34223
2 (,, N/100)	5.38	41.30	0.73078	1.61595
3 (,, N/75)	11.24	50.55	1.05077	1.70372
4 (,, N/50)	25.91	69.41	1.41347	1.84142
5 (,, N/25)	67.45	121.23	1.82898	2.08360
6 (,, N/10)	266.88	215.08	2.42632	2.33260
Italian millet starch				
1 (About N/200)	0.49	21.99	$\bar{1}.69020$	1.34223
2 (,, N/100)	5.87	40.81	0.76864	1.61077
3 (,, N/75)	11.00	50.79	1.04139	1.70578
4 (,, N/50)	28.35	66.97	1.45255	1.82588
5 (,, N/25)	66.97	121.71	1.82588	2.08532
6 (,, N/10)	251.51	230.45	2.40095	2.36257

TABLE 48. (*Continued*)

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
		Barley starch		
1 (About N/200)	0.24	22.24	$\bar{1}.38021$	1.34713
2 (,, N/100)	2.57	44.11	0.40993	1.64454
3 (,, N/75)	5.99	55.80	0.77743	1.74663
4 (,, N/50)	18.57	76.75	1.26881	1.88508
5 (,, N/25)	52.67	136.01	1.72156	2.13357
6 (,, N/10)	272.37	209.09	2.43595	2.32033
		Corn starch (Kingsford)		
1 (About N/200)	0.73	21.75	$\bar{1}.86332$	1.33746
2 (,, N/100)	6.35	40.33	0.80277	1.60563
3 (,, N/75)	12.22	49.57	1.08707	1.69522
4 (,, N/50)	31.53	63.79	1.49872	1.80475
5 (,, N/25)	86.27	102.41	1.93586	2.01034
6 (,, N/10)	275.26	206.70	2.43974	2.31534

TABLE 49.

Values of the constants of FREUNDLICH's adsorption isotherms.

Starch	Concentrations of iodine used					
	Low			High		
	$1/n$	k	k'	$1/n$	k	k'
Potato (Kojima)	0.26800	27.612	0.17583	0.45736	16.776	0.39515
Dog-tooth violet	0.30614	26.643	0.22100	0.58061	17.550	0.96852
Wheat (Kojima)	0.38164	21.301	0.29740	0.66629	6.420	0.64034
Sorghum	0.46936	14.235	0.36558	0.39262	27.012	0.40683
Rice	0.28300	26.406	0.18651	0.48017	15.085	0.42597
Italian millet	0.27264	27.825	0.18297	0.48395	14.967	0.42363
Barley	0.28499	33.497	0.23987	0.36290	28.615	0.35098
Corn (Kingsford)	0.28726	23.836	0.17338	0.54419	9.503	0.40880

From the results, the coefficients of correlation between $1/n$ and k and $1/n$ and k' were calculated.

TABLE 50.

Coefficients of correlation between 1/n and *k*, 1/n and *k'*.

	Concentrations of iodine used	
	Low	High
Between 1/*n* and *k*.	−0.8733	−0.6235
Between 1/*n* and *k'*.	0.9682	0.4847

When the concentrations of iodine used were low, there was a negative close relation between 1/n and *k*, or the greater the value of 1/n, the smaller was the value of *k*, and also there was a close positive relation between 1/n and *k'*, or the greater the value of 1/n, the greater was the value of *k'*. However, the coefficients of correlation were − 0.6235 and 0.4847, when the concentrations of iodine were high. The correlation in this case, was not so remarkable as in the other case.

§ 8. Mechanism of the hydrolysis of the electro-dialysed starches by the action of the diastase

Studies were made on the mechanism of the hydrolysis of electro-dialysed starch by the action of diastase by means of the method described before. One c.c. of potassium permanganate solution used in the study corresponded to 0.009707 g of copper. The following results were the means of 3–5 determinations.

TABLE 51.

Hydrolysis of electro-dialysed starches by the action of diastase.

Time (min.)	5	10	20	40	80	160	End
			Potato starch (Kojima)				
$KMnO_4$ (c.c.)	0.95	1.88	2.98	3.55	3.73	3.93	4.43
Cu (mg)	9.2	18.2	28.9	34.4	36.2	38.1	43.0
Maltose (mg)	5.6	13.1	22.0	26.6	28.0	29.7	33.8
%	16.57	42.01	65.08	78.70	82.84	87.87	100.00

TABLE 51. (*Continued*)

Time (min.)	5	10	20	40	80	160	End
Dog-tooth violet starch							
$KMnO_4$ (c.c.)	—	1.92	3.0	3.3	3.55	3.63	4.43
Cu (mg)	—	18.6	29.1	32.0	34.5	35.2	43.0
Maltose (mg)	—	13.4	22.2	24.6	26.6	27.3	33.8
%	—	39.64	65.68	72.78	78.70	80.77	100.00
Wheat starch (Kojima)							
$KMnO_4$ (c.c.)	1.62	2.37	2.97	3.67	4.05	4.30	4.55
Cu (mg)	15.7	23.0	28.8	35.6	39.3	41.7	44.2
Maltose (mg)	10.9	17.1	21.9	27.6	30.7	32.6	34.7
%	31.41	49.28	63.11	79.54	88.47	93.95	100.00
Sorghum starch							
$KMnO_4$ (c.c.)	1.15	1.98	2.83	3.13	3.38	3.52	4.13
Cu (mg)	11.2	19.2	27.5	30.4	32.8	34.2	40.1
Maltose (mg)	7.1	13.9	20.7	23.2	25.2	26.3	31.1
%	22.81	44.41	66.49	74.12	80.51	84.03	100.00
Rice starch							
$KMnO_4$ (c.c.)	1.15	2.25	3.22	3.52	3.65	3.80	4.50
Cu (mg)	11.2	21.8	31.2	34.2	35.4	36.9	43.7
Maltose (mg)	7.1	16.0	23.9	26.3	27.4	28.5	34.3
%	20.70	46.65	69.68	76.68	79.89	83.08	100.00
Italian millet starch							
$KMnO_4$ (c.c.)	—	0.73	2.12	3.07	3.25	3.5	4.43
Cu (mg)	—	7.1	20.6	29.8	31.5	34.0	43.0
Maltose (mg)	—	3.9	15.0	22.7	24.2	26.2	3.8
%	—	11.54	44.38	67.16	71.63	77.51	100.00
Barley starch							
$KMnO_4$ (c.c.)	—	1.67	2.5	3.05	3.45	3.5	4.0
Cu (mg)	—	16.2	24.3	29.6	33.5	34.0	38.8
Maltose (mg)	—	11.4	18.1	22.6	25.8	26 2	30.2
%	—	37.75	59.93	74.83	85.43	86.75	100.00
Corn starch (Kingsford)							
$KMnO_4$ (c.c.)	—	2.02	2.85	3.27	3.5	3.7	4.65
Cu (mg)	—	19.6	27.7	31.7	34.0	35.9	45.1
Maltose (mg)	—	14.2	20.9	24.3	26.2	27.9	35.5
%	—	40.00	58.87	68.45	73.80	78.59	100.00

The values of the two constants k and k' of the equation

$$\frac{1}{t^{k'}} \cdot \frac{x}{a(a-x)} = k$$

were calculated from the described results by the method of least squares.

TABLE 52.

Values of the two constants k and k'.

Starch	k	k'	Starch	k	k'
Potato (Kojima)	0.0007367	1.0042	Rice	0.001248	0.7950
Dog-tooth violet	0.002155	0.6304	Italian millet	0.0001888	1.1098
Wheat (Kojima)	0.0007749	1.0577	Barley	0.0009658	0.8849
Sorghum	0.001163	0.8118	Corn (Kingsford)	0.002094	0.5899

Introducing the values of the constants in the above equation, the percentages of maltose produced by hydrolysis were calculated and compared with those actually found as in the following table.

TABLE 53.

Percentages of maltose produced by hydrolysis.

Time (min.)	5	10	20	40	80	160
Potato starch (Kojima)						
Observed	16.57	42.01	65.08	78.70	82.84	87.87
Calculated	27.05	42.71	59.87	74.96	85.73	92.33
Difference	−10.48	−0.70	5.21	3.74	−2.89	−4.46
Dog-tooth violet starch						
Observed	—	39.64	65.68	72.78	78.70	80.77
Calculated	—	47.92	58.74	68.12	77.34	84.08
Difference	—	−8.28	6.94	4.66	1.36	−3.31

TABLE 53. (*Continued*)

Time (min.)	5	10	20	40	80	160
Wheat starch (Kojima)						
Observed	31.41	49.28	63.11	79.54	88.47	93.95
Calculated	29.83	46.95	64.81	79.31	88.86	94.32
Difference	1.58	2.33	-1.70	0.23	-0.39	-0.37
Sorghum starch						
Observed	22.81	44.41	66.49	74.12	80.51	84.03
Calculated	29.09	43.00	56.95	69.92	80.31	87.74
Difference	-6.28	1.41	9.54	4.20	0.20	-3.71
Rice starch						
Observed	20.70	46.65	69.68	76.68	79.89	83.08
Calculated	30.98	43.78	57.47	70.10	82.02	87.57
Difference	-10.28	2.87	12.21	6.58	-2.13	-4.49
Italian millet starch						
Observed	—	11.54	44.38	67.16	71.63	77.51
Calculated	—	19.55	34.41	53.10	70.96	84.06
Difference	—	-8.01	9.97	14.06	0.67	-6.55
Barley starch						
Observed	—	37.75	59.93	74.83	85.43	86.75
Calculated	—	42.52	57.77	71.65	82.35	89.60
Difference	—	-4.77	2.16	3.18	3.08	-2.85
Corn starch (Kingsford)						
Observed	—	40.00	57.87	68.45	73.80	78.59
Calculated	—	44.89	55.10	64.86	73.52	80.70
Difference	—	-4.89	2.77	3.59	0.28	-2 11

The calculated and the observed values nearly coincide, therefore, it follows that the adopted equation expresses the mechanism of the hydrolysis of the electro-dialysed starch by the action of diastase.

The values of k were 0.0007–0.0021 and were greater than the values 0.0006–0.0013 of the original starches as stated in a former paragraph. The starch was changed into a more easily hydrolysable form by the treatment of the electro-dialysis. The value of k of the Italian millet electro-dialysed starch was 0.000189 and was markedly small if compared with the other values. This fact has already been seen in the case of the original Italian millet starch as described before. However, the latter value was 0.000096 which was smaller than the value of the present investigation. Generally speaking, the starch had undergone some kind of changes upon the molecular structure by electro-dialysis and had changed into a form that was easily hydrolysed by the action of diastase.

To find the relation between k and k', the author had carried out the same calculation as previously described with the exception of the special case of the Italian millet starch.

Observation equations.

$$
\begin{aligned}
-3.1327 &= 1.0042\,a+b \quad \text{or} \quad & b+1.0042\,a+3.1327 &= 0\\
-3.1108 &= 1.0577\,a+b & b+1.0577\,a+3.1108 &= 0\\
-3.0151 &= 0.8849\,a+b & b+0.8849\,a+3.0151 &= 0\\
-2.6789 &= 0.5899\,a+b & b+0.5899\,a+2.6789 &= 0\\
-2.6665 &= 0.6304\,a+b & b+0.6304\,a+2.6665 &= 0\\
-2.9036 &= 0.7950\,a+b & b+0.7950\,a+2.9036 &= 0\\
-2.9343 &= 0.8118\,a+b & b+0.8118\,a+2.9343 &= 0
\end{aligned}
$$

Normal equations

$$
\begin{aligned}
7\,b+5.7739\,a+20.4414 &= 0\\
5.7739\,b+4.9465\,a+17.0559 &= 0
\end{aligned}
$$

Solving

$$
\begin{aligned}
a &= -1.0599\\
b &= -2.0459
\end{aligned}
$$

Therefore, $$\log k = -1.0599\,k'-2.0459.$$

Thus the author is able to say that the same deduction is substantiated from this calculation as in the former calculation or in other words that the relation between *log* k and k' can be expressed by an equation of a straight line.

When the values of the two constants k and k' of the original and the electro-dialysed starches are compared, it is observed that the values of k are always markedly increased by the electro-dialysis of the starch but the values of k' are decreased. It is concluded therefore, that the starch is changed into a more easily hydrolysed form by the action of electric current or in other words that the electro-dialysis somehow decomposes the starch molecule changing it to a more unstable form than the original starch in respect to the action of diastase.

Chapter III.

Oxidation of the Starches

The fact that when starch is treated with the oxidizing agents, soluble starch, dextrine and glucose are principally produced and that many other compounds—namely many acids and furfurals are also produced, has been reported by many investigators(112). The oxidizing agents used in these cases were very numerous viz., hydrogen peroxide, natrium bicarbonate, chlorine or chlorous acid, bleaching powder, manganese oxide, natrium peroxide, ferric chloride, calcium permanganate, hydrochloric acid and potassium bichromate, activin (natrium salt of *p*-toluensulfochloramide) and iron.

When M. SAMEC(86) treated the starch with natrium peroxide, hydrogen peroxide, ammonium persulfate, potassium permanganate, natrium perborate and air oxygen, he obtained the oxidized products of the starch. He compared many properties of these different products.

The present author intending to investigate the properties and the differences of the products of many sorts of starches carried out the following examinations.

§ 1. Method of oxidation and phosphorus content of oxidized starches

Use was made of three kinds of oxidizing agents; viz., potassium permanganate, natrium perborate and ammonium persulphate.

To 20 g of starch were added 52 c.c. of 2% potassium permanganate solution and 52 c.c. of water, then the preparate was stood for 2 hours at room temperature, while the oxidation of starch proceeded. The solution was made acid by the addition of sulphuric acid; to the solution was added very carefully and slowly a small amount of natrium thiosulphate finally the colour of solution disappeared, then the starch was separated, washed thoroughly with water, and dried at room temperature. This was called sample No. 1 of the oxidized starch.

To 10 g of starch were added 100 c.c. of water and then 4 g of natrium perborate; the mixture was stood for 4 days at room temperature, while the oxidation of starch proceeded. Then the starch was separated, washed carefully with water, and dried at room temperature. Thus sample No. 2 was obtained.

To 10 g of starch were added 100 c.c. of water and 5 g of ammonium persulphate; the whole was stood for 10 hours at room temperature, while the oxidation of starch proceeded. Then the starch was separated, washed carefully with water, and dried at room temperature. Sample No. 3 was thus obtained.

These samples were white powders and there was no difference in appearance between these samples and the original starches.

The water content of the oxidized starch was measured with the results as follows.

TABLE 54.

Water content of the oxidized starch.

Starch	Sample No. 1	Sample No. 2	Sample No. 3
Potato (Kojima)	11.39	17.30	11.31
Dog-tooth violet	9.47	11.51	12.48
Wheat (Kojima)	11.63	16.82	19.26
Sorghum	9.60	13.76	16.78
Rice	9.72	12.99	16.14
Italian millet	9.66	13.32	11.94
Barley	9.18	13.03	12.60
Corn (Kingsford)	9.78	11.82	12.03

These samples were ashed by NEUMANN's ashing method and the excess of acid was neutralized by natrium hydroxide solution. Then the phosphorus content of these solutions was measured by BELL-DOISY's method modified by BRIGGS, and the values were compared with those of phosphorus content of the original non-oxidized starch taken as 100.

TABLE 55.

Phosphorus content of the oxidized starch.

Starch	Sample No. 1		Sample No. 2		Sample No. 3	
	H_2O free %	% of P-content of original starch	H_2O free %	% of P-content of original starch	H_2O free %	% of P-content of original starch
Potato (Kojima)	0.054	100.8	0.046	87.08	0.051	96.45
Dog-tooth violet	0.023	93.87	0.025	98.70	0.022	88.39
Wheat (Kojima)	0.055	93.28	0.044	75.02	0.051	86.38
Sorghum	0.017	79.39	0.015	69.07	0.019	90.80
Rice	0.021	91.96	0.014	63.97	0.017	74.94
Italian millet	0.019	96.74	0.015	76.19	0.016	79.03
Barley	0.019	74.16	0.020	79.73	0.017	67.10
Corn (Kingsford)	0.016	79.45	0.018	87.86	0.016	76.03

According to this table, the phosphorus content of all these samples, except sample No. 1 of potato starch, was decreased by the action of the oxidizing agents. In general, sample No. 2, which was the starch oxidized by natrium perborate, had decreased most markedly in the phosphorus content; sample No. 3 which was oxidized by ammonium persulphate was next, and the effect of potassium permanganate upon the phosphorus content of the oxidized starch was the least pronounced.

Observing this result from the standpoint of the sorts of plants from which the starch was got, the phosphorus content of the starch of the tubers, such as potato and dog-tooth violet, showed the smaller decrease by oxidation than that of the starch of the cereal plants. Therefore, also in this case, the starch may properly classified in two kinds; the one is the starch of tubers, and the other is of cereal plants.

§ 2. Acetylation of the oxidized starches

The oxidized starch was acetylated at room temperature by pyridin and acetic acid anhydride. The method was the same as described before. In general, the reaction was very slow, and there were some starches which were not acetylated though they were stood for as long time as six months. The content of acetyl group of the starch which was fully acetylated was measured by the method described before.

TABLE 56.

Content of acetyl group of the acetyl oxidized starches.

Starch	Sample No. 1	Sample No. 2	Sample No. 3
Potate (Kojima)	—	40.41	—
Dog-tooth violet	49.49	55.81	—
Wheat (Kojima)	24.22	50.54	—
Sorghum	48.96	47.90	—
Rice	—	48.43	—
Italian millet	52.54	—	50.00
Barley	46.33	50.54	46.86
Corn (Kingsford)	50.54	47.39	—

In general, sample No. 2 was easily acetylated but sample No. 3 was acetylated with difficulty. The acetyl group content was mostly 46–52% excepting sample No. 1 of wheat starch. It seemed that the oxidized starch was acetylated more easily than the original starch, if they were treated by the same method, and also the number of kinds of starch which were acetylated was increased.

The acetyl group content was approximately 50%, and according to Table 10, it seemed that 1 glucose residue containing 4 acetyl groups, or the aggregate of tetraacetyl glucose.

§ 3. Viscosity of the solution of the oxidized starches

The oxidizing agent decreased the phosphorus content of starch, and made the starch easy to be acetylated, therefore, the author attempted to ascertain the viscosity of the solution of such oxidized starches. For this purpose, 0.5, 1.0, 2.0 and 4.0% starch solutions of every kind were prepared heating for 1 hour under a pressure of 1.3 kg per sq. cm., and the viscosity of those solutions was measured by OSTWALD's viscosimeter at 20°C. The numbers of the following table were calculated on the basis of the time of flow of water as 1.

TABLE 57.

Viscosity of the solution of oxidized starch.

Starch	0.5%	1.0%	2.0%	4.0%
	Sample No. 1			
Potato (Kojima)	1.114	1.122	1.213	1.633
Dog-tooth violet	1.065	1.119	1.273	1.707
Wheat (Kojima)	1.096	1.122	1.247	1.598
Sorghum	1.037	1.059	1.081	1.241
Rice	1.037	1.041	1.052	1.192
Italian millet	1.041	1.041	1.104	1.289
Barley	1.044	1.037	1.080	1.207
Corn (Kingsford)	1.041	1.044	1.102	1.269
	Sample No. 2			
Potato (Kojima)	1.086	1.231	1.415	2.092
Dog-tooth violet	1.120	1.404	2.063	5.944
Wheat (Kojima)	1.046	1.111	1.484	3.092
Sorghum	1.099	1.263	1.772	3.815
Rice	1.122	1.355	1.957	4.574
Italian millet	1.160	1.481	2.517	9.276
Barley	1.052	1.191	1.484	3.092
Corn (Kingsford)	1.054	1.185	1.479	2.685
	Sample No. 3			
Potato (Kojima)	1.164	1.369	1.891	4.222
Dog-tooth violet	1.261	1.707	2.596	13.11
Wheat (Kojima)	1.185	1.354	1.750	3.111
Sorghum	1.189	1.420	1.894	3.092
Rice	1.092	1.176	1.442	2.259
Italian millet	1.089	1.231	1.550	2.741
Barley	1.115	—	1.690	3.667
Corn (Kingsford)	1.189	1.420	1.894	3.092

These numbers were calculated respectively on the basis of 100 for the viscosities of the original starch solutions of the same concentrations prepared under the same conditions.

TABLE 58.

Ratio of the viscosity of the solution of the oxidized starch to that of the original starch expressed in percent.

Starch	0.5%	1.0%	2.0%	4.0%
Sample No. 1				
Potato (Kojima)	74.27	40.80	14.30	3.59
Dog-tooth violet	76.90	53.86	19.58	—
Wheat (Kojima)	69.50	39.96	16.42	3.95
Sorghum	78.15	50.67	14.12	2.33
Rice	81.46	53.03	15.23	—
Italian millet	79.53	51.59	18.45	—
Barley	94.15	79.22	60.64	12.39
Corn (Kingsford)	88.15	67.51	31.09	4.87
Sample No. 2				
Potato (Kojima)	72.40	44.76	16.69	4.57
Dog-tooth violet	80.85	67.57	31.74	—
Wheat (Kojima)	66.31	39.57	17.55	4.62
Sorghum	82.82	60.43	25.15	7.15
Rice	88.15	69.03	29.81	—
Italian millet	88.62	73.39	38.56	—
Barley	94.86	90.99	83.39	31.74
Corn (Kingsford)	89.25	76.70	44.82	10.30
Sample No. 3				
Potato (Kojima)	77.61	49.78	22.30	9.27
Dog-tooth violet	91.01	82.15	39.94	—
Wheat (Kojima)	75.15	46.05	23.03	7.69
Sorghum	89.62	67.95	24.75	5.79
Rice	85.78	59.91	20.87	—
Italian millet	83.24	60.99	23.74	—
Barley	100.6	—	94.91	37.62
Corn (Kingsford)	92.98	79.68	44.88	11.14

The viscosity of the solution of the starch was decreased by the action of the oxidizing agent. This phenomena is connected closely with the decrease in the phosphorus content. According to M. SAMEC the oxidizing agent separated the phosphorus from the starch and the existence of phosphorus caused the viscosity of the starch solution. Therefore, the starch which was treated by the oxidizing agent seemed to be very changed in the part where phosphorus is contained, i.e. in SAMEC's amylopectin.

Among the starches examined the viscosity of the solution of barley starch was always decreased least by oxidation, but that of wheat starch was the greatest. By the solution of oxidized starch of the same kind, the decreasing of the viscosity became by and by greater than in the case of original starch solution as the concentration of the solution became higher. This showed that the starch had decreased in the degree of aggregation as a result of the action of the oxidizing agent. Therefore, it seems that the constitution of the molecule is changed to a very simple form, and that the starch molecule was decomposed very much at the same time by the oxidizing agent.

§ 4. Adsorption of iodine by the oxidized starch granules

It has been observed in the above paragraphs that the starch is changed in respect to degree of aggregation of its molecule by oxidation, that the phosphorus content decreases and that its chemical construction is changed. Then, the author, intending to know how much change there is in the ability of adsorption of iodine by oxidized starch, treated the oxidized starch as described before. To 0.5 g of oxidized starch were added respectively 20 c.c. portions of about N/10, N/25, N/50, N/75, N/100 and N/200 iodine potassium iodide solution; the mixture was shaken for 30 minutes and stood for 30 minutes; then the oxidized starch was separated by a centrifugal machine, and the iodine content in 10 c.c. of the supernatant solution was measured by titration method. These numbers were calculated as the equivalents of 1 g of oxidized starch.

TABLE 59.

Amount of iodine adsorbed by oxidized starch.

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
Sample No. 1				
Potato starch (Kojima)				
1 (About N/200)	0.73	25.13	$\bar{1}$.86322	1.40019
2 (,, N/100)	6.34	44.16	0.80209	1.64503
3 (,, N/75)	13.66	54.17	1.13545	1.73376
4 (,, N/50)	28.79	72.71	1.45924	1.86159
5 (,, N/25)	62.95	142.89	1.79900	2.15500
6 (,, N/10)	—	—	—	—
Dog-tooth violet starch				
1 (About N/200)	0.49	23.91	$\bar{1}$.69020	1.37858
2 (,, N/100)	5.37	42.94	0.72997	1.63286
3 (,, N/75)	12.69	51.73	1.10346	1.71374
4 (,, N/50)	30.74	64.90	1.48770	1.81224
5 (,, N/25)	92.60	101.63	1.96661	2.00702
6 (,, N/10)	274.74	206.42	2.43892	2.31475
Wheat starch (Kojima)				
1 (About N/200)	0.73	23.67	$\bar{1}$.86332	1.37420
2 (,, N/100)	5.73	42.58	0.75815	1.62921
3 (,, N/75)	12.69	51.73	1.10346	1.71374
4 (,, N/50)	26.84	68.81	1.42878	1.83765
5 (,, N/25)	62.00	132.25	1.79239	2.12139
6 (,, N/10)	279.26	201.91	2.44601	2.30516
Sorghum starch				
1 (About N/200)	3.90	21.96	0.59106	1.34163
2 (,, N/100)	12.20	38.31	1.08636	1.58331
3 (,, N/75)	18.54	49.29	1.26811	1.69276
4 (,, N/50)	27.21	74.30	1.43473	1.88326
5 (,, N/25)	68.32	137.52	1.83455	2.13836
6 (,, N/10)	325.50	201.06	2.51255	2.30333
Rice starch				
1 (About N/200)	1.22	24.64	0.08636	1.39164
2 (,, N/100)	7.81	42.70	0.89265	1.63043
3 (,, N/75)	14.15	53.68	1.15076	1.72981
4 (,, N/50)	27.33	74.18	1.43664	1.87029
5 (,, N/25)	70.76	135.08	1.84979	2.13059
6 (,, N/10)	320.64	196.91	2.51804	2.29427
Italian millet starch				
1 (About N/200)	0.49	25.38	$\bar{1}$.69020	1.40449
2 (,, N/100)	4.27	46.24	0.63043	1.66502
3 (,, N/75)	6.25	61.58	0.79588	1.78944
4 (,, N/50)	24.62	76.86	1.39129	1.88570
5 (,, N/25)	59.90	145.94	1.77743	2.16418
6 (,, N/10)	307.93	218.62	2.48845	2.33975

TABLE 59. (*Continued*)

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
Barley starch				
1 (About N/200)	0.49	23.91	$\bar{1}.69020$	1.37858
2 (,, N/100)	3.68	44.63	0.56585	1.64963
3 (,, N/75)	8.30	56.12	0.91908	1.74912
4 (,, N/50)	20.01	75.64	1.30125	1.87875
5 (,, N/25)	53.19	141.03	1.72583	2.14931
6 (,, N/10)	282.80	198.37	2.45148	2.29747
Corn starch (Kingsford)				
1 (About N/200)	0.49	23.91	$\bar{1}.69020$	1.37858
2 (,, N/100)	4.27	44.04	0.63043	1.64385
3 (,, N/75)	10.37	54.05	1.01578	1.73280
4 (,, N/50)	27.21	68.44	1.43473	1.83531
5 (,, N/25)	88.33	105.90	1.94611	2.02490
6 (,, N/10)	285.48	195.69	2.45557	2.29157
Sample No. 2				
Potato starch (Kojima)				
1 (About N/200)	1.10	24.77	0.04139	1.39393
2 (,, N/100)	8.91	41.60	0.94988	1.61909
3 (,, N/75)	17.08	50.75	1.23249	1.70544
4 (,, N/50)	38.80	62.71	1.58883	1.79734
5 (,, N/25)	90.04	115.80	1.95444	2.06371
6 (,, N/10)	323.06	203.50	2.50928	2.30856
Dog-tooth violet starch				
1 (About N/200)	0.49	25.38	$\bar{1}.69020$	1.40449
2 (,, N/100)	5.12	45.38	0.70927	1.65686
3 (,, N/75)	13.18	54.66	1.11992	1.73767
4 (,, N/50)	34.65	66.86	1.53970	1.82517
5 (,, N/25)	108.34	97.50	2.03479	1.98900
6 (,, N/10)	318.18	208.38	2.50267	2.31886
Wheat starch (Kojima)				
1 (About N/200)	0.98	24.89	$\bar{1}.99123$	1.39602
2 (,, N/100)	9.03	41.48	0.95569	1.61784
3 (,, N/75)	17.93	49.90	1.25358	1.69810
4 (,, N/50)	37.58	63.93	1.57496	1.80570
5 (,, N/25)	81.25	124.59	1.90982	2.09548
6 (,, N/10)	316.56	210.00	2.50045	2.32222
Sorghum starch				
1 (About N/200)	2.93	22.94	0.46687	1.36059
2 (,, N/100)	10.25	40.26	1.01072	1.60487
3 (,, N/75)	16.59	51.24	1.21985	1.70961
4 (,, N/50)	24.89	76.62	1.39602	1.88434
5 (,, N/25)	55.14	150.69	1.74147	2.17808
6 (,, N/10)	312.81	213.74	2.49528	2.32988

TABLE 59. (*Continued*)

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
		Rice starch		
1 (About N/200)	1.13	25.13	0.05308	1.40019
2 („ N/100)	5.37	45.14	0.72997	1.65456
3 („ N/75)	11.71	56.12	1.06856	1.74912
4 („ N/50)	29.77	71.74	1.47378	1.85576
5 („ N/25)	85.40	120.44	1.93146	2.08077
6 („ N/10)	312.81	213.74	2.49523	2.32988
		Italian millet starch		
1 (About N/200)	0.49	25.38	$\bar{1}.69020$	1.40449
2 („ N/100)	4.03	46.48	0.60531	1.60727
3 („ N/75)	10.98	56.85	1.04060	1.75473
4 („ N/50)	28.30	69.20	1.45179	1.84011
5 („ N/25)	79.06	126.78	1.89796	2.10305
6 („ N/10)	311.83	214.72	2.49392	2.33187
		Barley starch		
1 (About N/200)	0.49	25.38	$\bar{1}.69020$	1.40440
2 („ N/100)	2.93	47.58	0.46687	1.67742
3 („ N/75)	8.30	59.54	0.91908	1.77481
4 („ N/50)	22 20	79.30	1.34635	1.89927
5 („ N/25)	68.81	137.03	1.83765	2.13682
6 („ N/10)	315.49	211.06	2.49897	2.32440
		Corn starch (Kingsford)		
1 (About N/200)	0.49	25.38	$\bar{1}.69020$	1.40440
2 („ N/100)	—	—	—	—
3 („ N/75)	9.76	58.07	0.98945	1.76395
4 („ N/50)	29.52	71.98	1.47012	1.85721
5 („ N/25)	95.16	110.68	1.97845	2.04407
6 („ N/10)	314.27	208.28	2.49730	2.31865
		Sample No. 3		
		Potato starch (Kojima)		
1 (About N/200)	0.77	23.67	$\bar{1}.88649$	1.37420
2 („ N/100)	4.39	43.92	0.64246	1.64246
3 („ N/75)	8.05	56.36	0.90580	1.75097
4 („ N/50)	18.54	77.10	1.26811	1.88705
5 („ N/25)	49.78	144.45	1.69705	2.15972
6 („ N/10)	265.47	215.70	2.42401	2.33385
		Dog-tooth violet starch		
1 (About N/200)	—	—	—	—
2 („ N/100)	5.12	43.19	0.70927	1.63538
3 („ N/75)	12.20	52.22	1.08636	1.71784
4 („ N/50)	31.23	64.42	1.49457	1 80902
5 („ N/25)	94.67	99.55	1.97621	1.99804
6 („ N/10)	—	—	—	—

TABLE 59. (*Continued*)

	Iodine left C (mg)	Iodine adsorbed x (mg)	log C	log x
	Wheat starch (Kojima)			
1 (About N/200)	0.98	23.42	$\bar{1}.99123$	1.36959
2 (,, N/100)	7.56	40.75	0.87852	1.61013
3 (,, N/75)	15.86	48.56	1.20030	1.68628
4 (,, N/50)	36.14	60.51	1.54580	1.78183
5 (,, N/25)	97.11	97.11	1.98726	1.98726
6 (,, N/10)	—	—	—	—
	Sorghum starch			
1 (About N/200)	0.85	23.55	$\bar{1}.92942$	1.37199
2 (,, N/100)	7.93	40.38	0.89927	1.60617
3 (,, N/75)	15.74	48.68	1.19700	1.68735
4 (,, N/50)	34.65	61.00	1.53970	1.78533
5 (,, N/25)	96.62	97.60	1.98507	1.98945
6 (,, N/10)	282.55	198.62	2.45109	2.29802
	Rice starch			
1 (About N/200)	2.56	21.84	0.40824	1.33925
2 (,, N/100)	7.69	40.63	0.88593	1.60885
3 (,, N/75)	12.20	52.22	1.08636	1.71784
4 (,, N/50)	22.33	73.32	1.34889	1.86522
5 (,, N/25)	44.90	149.33	1.65225	2.17415
6 (,, N/10)	266.20	214.96	2.42521	2.33236
	Italian millet starch			
1 (About N/200)	0.49	23.91	$\bar{1}.69020$	1.37858
2 (,, N/100)	3.54	44.77	0.54900	1.65099
3 (,, N/75)	8.78	55.63	0.94349	1.74531
4 (,, N/50)	23.06	72.59	1.36286	1.86088
5 (,, N/25)	64.90	129.32	1.81224	2.11166
6 (,, N/10)	268.40	212.77	2.42878	2.32791
	Barley starch			
1 (About N/200)	0.49	23.91	$\bar{1}.69020$	1.37858
2 (,, N/100)	2.68	45.63	0.42813	1.65925
3 (,, N/75)	6.83	57.58	0.83442	1.76027
4 (,, N/50)	20.50	75.15	1.31175	1.87593
5 (,, N/25)	71.98	122.24	1.85721	2.08721
6 (,, N/10)	274.01	207.16	2.43776	2.31630
	Corn starch (Kingsford)			
1 (About N/200)	0.49	23.91	$\bar{1}.69020$	1.37858
2 (,, N/100)	3.05	45.26	0.48430	1.65571
3 (,, N/75)	7.81	56.61	0.89265	1.75289
4 (,, N/50)	22.25	73.40	1.34733	1.86570
5 (,, N/25)	81.01	113.22	1.90854	2.05392
6 (,, N/10)	—	—	—	—

From these results, the constants 1/n, *k* and *k'* were calculated by the method described before.

TABLE 59.

Constants of the FREUNDLICH's adsorption isotherms.

Starch	Concentration of iodine solution used was					
	Low			High		
	1/*n*	*k*	*k'*	1/*n*	*k*	*k'*
			Sample No. 1			
Potato (Kojima)	0.27312	27.344	0.18039	0.86381	3.991	1.55764
Dog-tooth violet	0.24008	28.420	0.14923	0.52800	10.173	0.39035
Wheat (Kojima)	0.28989	25.713	0.19047	0.43838	18.195	0.37591
Sorghum	0.60746	9.121	0.60591	0.37424	97.062	1.28756
Rice	0.59571	13.317	0.81572	0.37801	23.385	0.31840
Italian millet	0.29106	31.892	0.23815	0.39310	24.468	0.36974
Barley	0.30817	29.734	0.24988	0.34681	29.864	0.32878
Corn (Kingsford)	0.26227	29.245	0.17901	0.51247	11.314	0.38995
			Sample No. 2			
Potato (Kojima)	0.26094	24.001	0.14556	0.50678	10.817	0.35846
Dog-tooth violet	0.22835	30.298	0.14671	0.50919	10.301	0.34709
Wheat (Kojima)	0.25304	24.580	0.14116	0.69681	4.834	0.59526
Sorghum	0.56388	11.556	0.56813	0.37220	27.035	0.35362
Rice	0.32227	24.945	0.23110	0.46327	15.053	0.36935
Italian millet	0.25773	30.691	0.18206	0.46709	15.200	0.38292
Barley	0.29600	27.274	0.21073	0.36407	26.946	0.33321
Corn (Kingsford)	0.25901	30.871	0.18475	0.44949	15.221	0.33955
			Sample No. 3			
Potato (Kojima)	0.37125	25.874	0.33621	0.37100	28.867	0.37446
Dog-tooth violet	0.22116	30.074	0.13857	0.39247	16.689	0.25110
Wheat (Kojima)	0.32516	20.799	0.19657	0.46529	11.550	0.28738
Sorghum	0.25448	24.316	0.14103	0.56330	7.984	0.39093
Rice	0.55874	12.937	0.61384	0.35956	29.983	0.35938
Italian millet	0.28800	29.900	0.21860	0.43290	19.570	0.38924
Barley	0.30724	31.230	0.26079	0.39113	23.023	0.34320
Corn (Kingsford)	0.29450	30.581	0.23386	0.33545	25.925	0.26307

In the case of the adsorption of iodine by oxidized starch, the values of the constants 1/n, *k* and *k′*, when the concentration of iodine solution was low, were very different from those resulting when the concentration of iodine solution was high, as was seen in the case of the adsorption of iodine by original starch. In the case of the low concentration of iodine, in general, the constants 1/n, *k* and *k′* of oxidized starch sample No. 3, that is, the starch oxidized by ammonium persulphate, were the greatest, and the constants of oxidized starch sample No. 1, that is the starch oxidized by potassium permanganate, were the second, and those of oxidized starch sample No. 2, i.e. the starch oxidized by natrium perborate were the lowest. But, if the concentration of iodine solution was high, the opposite results were observed.

Comparing these results with those of adsorption of iodine by the original starch, it seems that the constants 1/n and *k′* of oxidized starch sample No. 3 were greater than those of original starch, but the constant *k* was smaller, when the concentration of iodine was low; however, in the case of high concentration of iodine, the opposite results were gained. In the case of oxidized starch of the other two kinds, i..e oxidized starches sample No. 1 and 2, not very different values of constants were shown from those of the original starch.

The coefficients of correlation between 1/n and *k*, and between 1/n and *k′* were calculated by the same method as described before.

TABLE 60.

Coefficients of correlation between 1/n and *k*, 1/n and *k′*.

	Concentration of iodine used was	
	Low	High
Oxidized starch sample No. 1		
Between 1/*n* and *k*	−0.9334	−0.4871
Between 1/*n* and *k′*	0.9439	0.6344
Oxidized starch sample No. 2		
Between 1/*n* and *k*	−0.9112	−0.9081
Between 1/*n* and *k′*	0.9920	0.8751
Oxidized starch sample No. 3		
Between 1/*n* and *k*	−0.8189	−0.8871
Between 1/*n* and *k′*	0.9787	0.6089

From these results, it is recognised that there is great correlation between 1/n and *k*, and also between 1/n and *k'* in the case of the oxidized starch, and that the coefficient between 1/n and *k* is always negative, when the concentration of the iodine solution is low. In the case of a high concentration of iodine solution, however, only in the case of oxidized starch sample No. 2, is there great correlation, but with the other two oxidized starches, it is not so distinct. But, in all cases, the coefficient beween 1/n and *k* is always negative, and it is understood in general that when the constant 1/n becomes greater, then the constant *k* becomes smaller.

Chapter IV

Phosphoration of the Starches

According to SAMEC's studies, the starches are composed of amylose and amylopectin. The latter is the component that gives the solution of the starch its viscosity and it contains a large amount of phosphorus than amylose which has almost no phosphorus. The viscosity of the solution of the starch is due to the phosphorus containing component of the starch. Therefore, if phosphorus were combined with starch, the viscosity of the solution of the phosphorated starch should be higher than that of the original and the other physico-chemical properties should differ from those of the original starch.

The author intending the phosphoration of the starch carried out the following treatment. According to the method described by NEUBERG and KRETSCHMER(63), to 6 g of each starch were added 150 c.c. of water; each mixture was heated and made into a solution. To the cooled solution were added 16 g of calcium carbonate, the whole was cooled and shaken well whereupon a mixture of 5 g of phosphorus oxychloride and 10 c.c. of chloroform was added drop by drop. The product of the reaction was separated, washed throughly with water and dried in a desiccator of sulphuric acid of diminished pressure.

§ 1. Ash, phosphorus and calcium content of the phosphorated starches

The ash content of the phosphorated starch was determined by the ordinary method combusting the matter. The calcium content was determined by the precipitation of calcium oxalate from the solution of the ash in hydrochloric acid. The phosphorus content of the material was determined by IVERSEN's micro method (41).

TABLE 61.

Ash, phosphorus and calcium content of the phosphorated starch.

Starch	Ash (%)	Phosphorus (%)	Calcium (%)
Potato (Kojima)	0.92	0.350	0.218
Dog-tooth violet	0.82	0.216	0.056
Wheat (Kojima)	1.44	0.362	0.168
Sorghum	1.04	0.273	0.128
Rice	1.10	0.240	0.138
Italian millet	0.86	0.273	0.080
Barley	0.84	0.201	0.048
Corn (Kingsford)	0.74	0.225	0.072

The ash and phosphorus content described above were compared with those of the original starch taking the latter as 1.00.

TABLE 62.

Ratios of the ash and phosphorus content of the phosphorated starch to those of the original starch.

Starch	Ash	Phosphorus	Starch	Ash	Phosphorus
Potate (Kojima)	3.49	6.60	Rice	7.64	10.91
Dog-tooth violet	7.32	8.64	Italian millet	4.72	13.66
Wheat (Kojima)	3.21	6.13	Barley	11.20	8.04
Sorghum	8.81	13.00	Corn (Kingsford)	9.74	10.72

The starches increased in ash and phosphorus content greatly as a result of phosphoration. They came to contain calcium by the same treatment. The ash content reached to 3–11 times the original figure and the ratio to content in original starch was the greatest in the barley starch, then followed the starches of corn, sorghum, rice, dog-tooth violet, Italian millet, potato and wheat. The ash content lay between 1.44–0.74%, the ash content of wheat starch being the greatest, then followed those of rice, soghum, potato, Italian millet, barley, dog-tooth violet and corn. The order of the ash content in the treated starches was almost the reverse of the order of the ratio to ash content in the original starches. The content of the phosphorus of the phosphorated starches lay between 0.362–0.201%, which amounted to 6–14 times that of the original starches. The ratio of increase was the greatest in the Italian millet starch, then followed the starches of sorghum, rice, corn, dog-tooth violet, barley, potato and wheat. The absolute content of the phosphorus of the phosphorated starches was the greatest in that of wheat, followed by those of potato, sorghum, Italian millet, rice, corn, dog-tooth violet and barley.

Under the assumption that the combination between the phosphorus and the calcium occurred in the form $CaHPO_4$, the author calculated the equivalent numbers and the equivalent ratio of the phosphorus and the calcium as the following table shows.

TABLE 63.

Equivalent numbers and equivalent ratios of the phosphorus and calcium of the phosphorated starches.

Starch	Equivalent numbers in 100 g of the compounds		Equivalent ratio
	P	Ca	
Potato (Kojima)	0.01127	0.003194	3.527
Dog-tooth violet	0.006952	0.001397	4.975
Wheat (Kojima)	0.01165	0.004192	2.779
Sorghum	0.008786	0.003194	2.751
Rice	0.007723	0.003443	2.243
Italian millet	0.008786	0.001996	3.527
Barley	0.006469	0.001198	5.401
Corn (Kingsford)	0.007241	0.001797	4.031

The equivalent ratios of the phosphorus and calcium were always greater than 2. The value of the rice starch was the smallest, then followed those of the starches of sorghum, wheat, potato, corn, Italian millet, dog-tooth violet and barley. The quantities of the phosphorus combined with the starches were greater than those of the calcium combined. The excess of the phosphorus was considered to combine with the starches directly.

§ 2. Viscosity of the solution of the phosphorated starches

The viscosity of the solution of the starches is considered to be caused by the presence of amylopectin which contains phosphorus. Therefore it is to be expected that the viscosity of the solution of the phosphorated starches would show higher values than those of the original starches.

Given quantities of the phosphorated starch or the original starch and given quantities of water were mixed; the mixture was heated in a boiling water bath for 4 minutes; the solution was made up to 0.5% of the starch and the viscosity of the solution was estimated after 20 minutes, 1, 2, 3, 4, 5, 6, 7 and 8 days using the OSTWALD's viscosimeter at 20°C. The electrical conductivity of the solutions was also measured at 18°C. The cell constant of the one used was 0.7256 (18°C.).

TABLE 64.

Viscosity and electrical conductivity of solutions of phosphorated and original starch.

	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
	Potato starch (Kojima)			
20 minutes	6.352	9.128	$0.864.10^{-5}$	$1.559.10^{-5}$
1 day	4.833	6.720	0.888	1.588
2 days	4.667	5.759	0.888	1.588
3 ,,	4.537	6.296	0.786	1.531
4 ,,	—	—	—	—
5 ,,	—	—	—	—
6 ,,	4.408	4.259	0.747	1.627
7 ,,	3.649	3.592	0.778	1.776
8 ,,	3.519	3.352	0.786	1.931

TABLE 64. (*Continued*)

	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
Dog-tooth violet starch				
20 minutes	1.315	7.945	1.109	1.282
1 day	1.277	7.776	1.126	1.327
2 days	1.296	8.147	1.126	1.300
3 ,,	1.277	7.982	1.076	1.354
4 ,,	1.333	7.667	1.109	1.213
5 ,,	—	—	—	—
6 ,,	1.259	6.907	1.177	1.464
7 ,,	1.259	5.964	1.221	1.550
Wheat starch (Kojima)				
20 minutes	4.185	4.193	1.428	2.806
1 day	3.334	4.629	1.464	3.157
2 days	3.611	7.832	1.484	3.157
3 ,,	—	—	—	—
4 ,,	3.519	2.333	1.419	3.536
5 ,,	—	—	—	—
6 ,,	3.334	1.926	1.419	3.866
7 ,,	3.296	1.870	1.419	4.064
8 ,,	2.982	1.741	1.464	4.360
Sorghum starch				
20 minutes	1.555	2.741	1.522	1.607
1 day	1.518	2.592	1.706	1.746
2 days	1.555	2.592	1.746	1.755
3 ,,	1.518	2.648	1.827	1.736
4 ,,	1.481	2.573	1.785	1.706
5 ,,	—	—	—	—
6 ,,	1.500	2.333	1.888	1.686
7 ,,	1.573	2.296	2.158	1.837
Rice starch				
20 minutes	1.296	4.648	1.419	2.180
1 day	1.277	5.408	1.391	2.203
2 days	1.259	7.482	1.446	2.282
3 ,,	1.296	8.241	1.381	2.237
4 ,,	1.277	6.944	1.346	2.225
5 ,,	—	—	—	—
6 ,,	1.259	5.666	1.381	2.399
7 ,,	—	—	—	—
8 ,,	1.259	4.426	1.391	2.505

TABLE 64. (*Continued*)

	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
Italian millet starch				
20 minutes	1.407	5.137	1.026	1.446
1 day	1.407	4.926	1.050	1.464
2 days	1.407	4.852	1.026	1.464
3 ,,	1.389	4.722	1.067	1.474
4 ,,	1.371	4.667	1.083	1.511
5 ,,	—	—	—	—
6 ,,	—	—	—	—
7 ,,	1.371	4.093	1.118	1.685
8 ,,	1.333	3.963	1.177	1.746
Barley starch				
20 minutes	1.203	2.519	0.434	0.786
1 day	1.222	2.592	0.428	0.709
2 days	1.203	2.556	0.441	0.888
3 ,,	1.222	2.500	0.400	0.848
4 ,,	—	—	—	—
5 ,,	—	—	—	—
6 ,,	1.203	2.704	0.400	0.763
7 ,,	1.185	2.129	0.305	0.786
8 ,,	1.222	2.463	0.318	0.778
Corn Starch (Kingsford)				
20 minutes	1.185	2.944	1.265	1.984
1 day	1.203	2.519	1.195	1.941
2 days	1.185	2.774	1.187	1.858
3 ,,	1.185	2.774	1.203	1.827
4 ,,	1.185	2.556	1.187	1.941
5 ,,	—	—	—	—
6 ,,	1.166	2.407	1.134	2.102
7 ,,	1.148	2.148	1.169	2.214

It may be seen from the table that the viscosity of the solution of the phosphorated starch was higher than that of the original starch. The former value was twice, or more, that of the latter value. The electrical conductivity of the solution of the phosphorated starch was greater than that of the original starch. The former value was about twice that of the latter value.

The changes in viscosity and electrical conductivity of the solution of the phosphorated starch by aging were also observed. The viscosity was increased by the aging in the solutions of the phosphorated starches of the dog-tooth violet, rice and wheat; they reached to the maximum values and then decreased; the viscosity of the other cases was decreased by aging. The electrical conductivity of the solutions of the phosphorated starches increased generally, though there were observed slight daily changes.

By the phosphoration of the starch, the viscosity and electrical conductivity of the solution of the starch were increased; the viscosity of the solution of the phosphorated starch was decreased and the electrical conductivity was increased by the aging of the solution. It was considered that the particles of the phosphoraed starch had decreased in size or in their complexity of combination in solution.

To examine the changes in the viscosity and in the electrical conductivity of the solution of the phosphorated starch resultant upon differences in the time of heating of the solution, the following examinations were carried out. A 0.5% suspension of the starches was prepared, and portions were heated in a boiling water bath for 4 minutes, 1, 2, 3, 4 and 5 hours respectively with a reflux condenser. The viscosity and the electrical conductivity of the obtained solutions were estimated by the same apparatus under the same conditions as in former described determinations. The temperature of the heating was 96°C.

TABLE 65.

Viscosity and electrical conductivity of solutions of phosphorated and original starches prepared by different heating.

Time of heating	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
	Potato starch (Kojima)			
4 minutes	5.315	5.538	$0.833.10^{-5}$	$1.540.10^{-5}$
1 hour	13.68	10.74	1.001	1.931
2 hours	8.112	6.500	1.354	2.421
3 ,,	5.684	6.500	1.607	2.604
4 ,,	4.333	5.315	1.878	2.806
5 ,,	3.741	4.388	2.037	3.227

TABLE 65. (*Continued*)

Time of heating	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
	Dog-tooth violet starch			
4 minutes	1.111	3.592	1.373	1.152
1 hour	1.259	6.592	1.042	1.570
2 hours	1.333	6.277	1.177	1.858
3 ,,	1.333	5.056	1.282	2.315
4 ,,	1.352	4.074	1.419	2.422
5 ,,	1.333	3.519	1.806	2.819
	Wheat starch (Kojima)			
4 minutes	4.612	—	0.952	2.352
1 hour	13.55	18.15	0.992	2.363
2 hours	9.499	8.166	1.076	2.445
3 ,,	7.131	7.278	1.195	2.755
4 ,,	5.099	6.778	1.256	3.157
5 ,,	3.611	4.796	1.436	3.401
	Sorghum starch			
4 minutes	1.611	2.926	0.968	1.533
1 hour	1.592	2.241	1.177	1.817
2 hours	1.611	2.167	1.282	1.941
3 ,,	1.574	2.000	1.346	2.259
4 ,,	1.592	1.814	1.354	2.479
5 ,,	1.537	1.741	1.531	2.616
	Rice starch			
4 minutes	1.074	5.037	0.973	1.265
1 hour	1.407	7.314	0.888	1.686
2 hours	1.444	5.815	0.925	1.920
3 ,,	1.407	4.963	1.042	2.004
4 ,,	1.407	4.408	1.195	2.214
5 ,,	1.407	3.444	1.318	2.399
	Italian millet starch			
4 minutes	1.074	2.648	0.809	1.213
1 hour	1.407	5.705	0.825	1.858
2 hours	1.481	4.222	0.888	2.259
3 ,,	1.463	3.067	0.952	2.352
4 ,,	1.463	3.334	1.076	2.494
5 ,,	1.463	3.273	1.213	2.591

TABLE 65. (*Continued*)

Time of heating	Viscosity		Electrical conductivity	
	Original	Phosphorated	Original	Phosphorated
	Barley starch			
4 minutes	1.055	1.907	0.428	0.694
1 hour	1.185	3.222	0.469	1.265
2 hours	1.222	2.926	0.562	1.607
3 ,,	1.203	2.777	0.687	1.934
4 ,,	1.241	2.625	0.825	1.962
5 ,,	1.222	2.463	1.009	2.180
	Corn starch (Kingsford)			
4 minutes	1.222	2.167	0.519	0.888
1 hour	1.296	3.649	0.562	1.391
2 hours	1.241	3.500	0.709	1.706
3 ,,	1.277	3.334	0.944	2.203
4 ,,	1.315	3.334	0.920	2.102
5 ,,	1.277	2.777	1.126	2.591

Notwithstanding the length of the heating, the viscosity and the electrical conductivity of the solutions of phosphorated starch were higher than the same values of solutions of the original starches. By 1–2 hours' heating, the solutions of both sorts of starches gained the maximum values, subsequently by heating longer than 1–2 hours the viscosity of the solutions decreased little by little. This fact was especially marked in the case of the phosphorated starch. In the case of the original starch, it was not quite so marked and there were observed some starches which did not change in viscosity at all as a result of prolonged heating of the solutions. The electrical conductivity of the solutions of the phosphorated and the original starches increased in a regular manner concommitant with increase in the duration of the heating. The following considerations may be deduced from the above described facts, viz., that the particles of the starch had simplified their complex constitution by the heating of the solution and that this decomposition had given rise to the increase of the electrical conductivity and the decrease of the viscosity of the solutions.

§ 3. Electrometric titration of the phosphorated starches

It was a well known fact that starch is an electro-negatively charged substance and that in the field of an electrical current starch migrates to the anode. The electrical charge should be increased by the phosphoration of the starch which means the addition of an electro-negative charge to the starch. The electro-negative charge is considered to be neutralised by the addition of caustic alkali. Intending to determine the quantities of the natrium hydroxide necessary to secure electrical neutrality, the present author carried out electrometric titration of the phosphorated starches.

The suspensoid solution of the phosphorated starch was prepared by the mixing of 0.1 g of the material and redistilled water in a beaker. To the suspensoid solution was titrated N/100 natrium hydroxide solution by means of SHIBATA's electrometric titration apparatus.

TABLE 66.

Electrometric titration of the phosphorated starch.
The material used amounted to 0.1 g each.

Potato starch (Kojima)									
c.c. of the N/100 NaOH	—	0	0.5	0.6	0.7	0.8	0.9	1.0	1.1
Observed value	—	175	140	135	130	115	100	95	90
c.c. of the N/100 NaOH	1.2	1.3	1.4	1.5	1.7	1.8	1.9	2.0	2.5
Observed value	85	80	75	70	50	45	40	37	35
Dog-tooth violet starch									
c.c. of the N/100 NaOH		0	0.5	1.0	1.5	2.0	2.5	3.0	—
Observed value		190	170	140	60	50	40	35	—
c.c. of the N/100 NaOH		0	1.0	1.1	1.2	1.3	1.4	1.5	—
Observed value		190	140	120	100	85	72	60	—
Wheat starch (Kojima)									
c.c. of the N/100 NaOH		0	0.5	1.0	1.5	2.0	2.5	3.0	—
Observed value		220	205	130	95	65	55	50	—
c.c. of the N/100 NaOH		0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Observed value		205	200	185	150	130	120	115	110

TABLE 66. (*Continued*)

	Sorghum starch							
c.c. of the N/100 NaOH	0	0.5	1.0	1.5	2.0	2.5	3.0	—
Observed value	180	160	100	60	50	40	37	—
c.c. of the N/100 NaOH	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Observed value	160	155	145	135	125	110	95	85
	Rice Starch							
c.c. of the N/100 NaOH	0	0.5	1.0	1.5	2.0	2.5	3.0	—
Observed value	150	135	110	30	20	15	12	—
c.c. of the N/100 NaOH	0	1.0	1.1	1.2	1.3	1.4	1.5	2.0
Observed value	160	120	95	70	55	50	45	30
	Italian millet starch							
c.c. of the N/100 NaOH	0	0.5	1.0	1.5	2.0	2.5	3.0	—
Observed value	180	170	155	85	80	70	60	—
c.c. of the N/100 NaOH	0	1.0	1.1	1.2	1.3	1.4	1.5	—
Observed value	210	150	130	120	105	100	95	—
	Barley starch							
c.c. of the N/100 NaOH	0	0.5	1.0	1.5	2.0	2.5	—	—
Observed value	215	190	105	70	55	50	—	—
c.c. of the N/100 NaOH	0	0.5	0.6	0.7	0.8	0.9	1.0	1.1
Observed value	215	190	170	140	130	120	110	100
	Corn starch (Kingsford)							
c.c. of the N/100 NaOH	0	0.5	1.0	1.5	2.0	2.5	—	—
Observed value	205	180	120	70	50	45	—	—
c.c. of the N/100 NaOH	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2
Observed value	130	115	105	90	80	70	65	55

The figures were plotted in the coordinate system taking the quantities of the natrium hydroxide as abscissa and the observed values as ordinate. The inflexion point of the curve was determined from the figure and the value corresponding to the inflexion point was obtained. The quantities of natrium hydroxide corresponding to the inflexion point were considered to indicate the quantities necessary to neutralise the substance. The value was also calculated to the equivalent number of mg for 1 g of the starch.

TABLE 67.

Quantities of natrium hydroxide to neutralise the phosphorated starch.

Starch	c.c. of N/100 NaOH o. 1 g of material	mg of NaOH for 1 g of material
Potato (Kojima)	1.3	5.2
Dog-tooth violet	1.25	5.0
Wheat (Kojima)	0.9	3.6
Sorghum	1.0	4.0
Rice	1.15	4.6
Italian millet	1.1	4.4
Barley	0.75	3.0
Corn (Kingsford)	0.85	3.4

From these values the molecular equivalent of natrium hydroxide to 100 g of the phosphorated starch was calculated and the equivalent was compared with the difference between the equivalent of the phosphorus and the calcium of the phosphorated starch. If the phosphorus was considered to be contained in the phosphorated starch in the form of phosphoric acid, the quantities of phosphorus which were not saturated with the calcium could be obtained by the subtraction of the equivalents of the phosphorus and the calcium.

TABLE 68.

Difference of the equivalents of phosphorus and calcium and the equivalent of natrium hydroxide needed to neutralise phosphorated starch corresponding to 100 g of the materials.

Starch	Difference	Equivalent of NaOH
Potato (Kojima)	0.00808	0.0130
Dog-tooth violet	0.00556	0.0125
Wheat (Kojima)	0.00746	0.0090
Sorghum	0.00559	0.0100
Rice	0.00428	0.0115
Italian millet	0.00679	0.0110
Barley	0.00527	0.0075
Corn (Kingsford)	0.00544	0.0085

The equivalent of natrium hydroxide was markedly greater than that of the difference between the equivalent of the phosphorus and the calcium. The neutralisation of the phosphorated starch by natrium hydroxide required greater quantities of natrium hydroxide than the quantities of the phosphorus which were contained in free form in the molecule. The excess in the quantities of the natrium hydroxide was considered to be employed for the neutralisation of the negative charge of the starch molecule which was observed by the electrophoresis and other means. This consideration gives an one side recognisation of the negative character of the starch molecule.

Conclusions

The author had carried out his experiments using 14 starches obtained from 11 species of plants. These were the potato, dog-tooth violet, wheat, barley, common rice, common Italian millet, common sorghum, corn, cassava, buckwheat and arrowroot.

From the results of his experiments, the author has come to the following conclusions.

(1). By the comparison of the starches of the cereal plants and the starches of the tubers, it was observed that the ash content of the latter were higher than the ash content of the former. The ash content was seen to differ markedly according to the difference of the method of the manufacturing of the starches.

(2). The content of the phosphorus of the starches was 0.058–0.035%. The phosphorus content of the starches differed very markedly according to the method of the preparation of the starches. The treatment with natrium hydroxide solution seemed to diminish the phosphorus content of the starches.

(3). It was observed that the ash constituents of the starch had to play an important role in the construction of the starch and that the ratio of the ash constituents other than phosphorus, to the phosphorus was almost constant in each starch.

(4). The nitrogen content of the starches ranged between 0.004% and 0.05%, mainly 0.02% or so.

(5). The ratio of the phosphorus and the nitrogen of the starches of the tubers was markedly small in comparison to the same values of the cereal plant starches.

(6). By acetylation with acetic acid anhydride at its boiling point there were obtained the acetyl starch which was built up with 2 glucose residues and 7 acetyl groups or with a mixture of equal quantities of the triacetyl glucose and tetraacetyl glucose or with an aggregate of the heptaacetyl maltose.

By acetylation with acetic acid anhydride with pyridin at room temperature, there was obtained an aggregate of the triacetyl glucose.

The acetylation of the starch progressed in inverse proportion to the content of phosphorus. It was considered by the author that the starches of the cereal plants contained amylopectin which was more unstable to the action of heating than the starches of the tubers.

(7). By benzoylation of the starches, the compound which contains 3 benzoyl groups to 2 glucose residues or the compound whose ratio was 1.5 was the most easily obtained.

The results of acetylation and benzoylation of the starches showed the same tendency, viz., that the starches which are easily acetylated without heating are also easily benzoylatable.

(8). By the nitration of the starches, the author obtained compounds which were the aggregate of dinitroglucose, the aggregate of the mixture of equal quantities of dinitroglucose and mononitroglucose and the aggregate of the mixture of 2 dinitroglucose and 1 mononitroglucose.

(9). Comparing the results of acetylation, benzoylation and nitration of the starches, the author was able to say that the treatment of the starches with acid either hot or cold had effected some changes upon the constitution of the starch molecules.

(10). The mechanism of the hydrolysis of the starches by the action of diastase was shown to be expressed well by the author's equation.

$$\frac{1}{t^{k'}} \cdot \frac{x}{a(a-x)} = k \,.$$

The relation between log k and k' of the equation could be expressed by an equation of a straight line.

(11). No direct relation was observed between the electrical conductivity of the solution of the starches and the phosphorus content as has been already reported by SAMEC and HAERDTL. Neither were any direct relations observed between the conductivity and the ash content of the starches nor between their conductivity and nitrogen content.

On the whole, however, the electrical conductivity of the solution of the starches seemed to be increased when there was an increase in the content of ash, phosphorus or nitrogen of the starch.

(12). The highest viscosity was observed in the case of the sorghum starch rather than in the potato. To the sorghum succeeded the starches of rice and Italian millet. By the aging of the solutions of the starches, the viscosity reached its maximum in 1–4 days, then a decrease was observed. The barley starch alone showed increasing viscosity by the aging, within the limits of the present investigation.

(13). In general, the influences of salts upon the viscosity of the solutions of the starches investigated may be summarised as follows. When the concentration of the salt was low, the viscosity of the solutions of some starches was increased, but when the concentration of the salt was increased, the viscosity of the solutions was decreased in all cases.

Comparing the effect of the cations added, that of the natrium ion was the smallest. There was an increase in the influence excited in the order kalium ion, barium ion and calcium ion. These facts coincide well with HOFMEISTER's series.

(14). The author was able to show that the protective action of the starches upon gold solution had an optimum limit in quantity. The gold value of the starches was 2–13.

(15). The heat liberated by combustion of the starches was about 3900 calories. No difference was found which could be ascribed to differences in place of formation of the starches, i.e. there was no difference in the heat of combustion between the starches formed in the part of a plant above the ground and those from an underground part of a plant. The heat of combustion was the greatest in the dog-tooth violet starch following which came those of corn, Italian millet, wheat, rice, potato, sorghum and barley.

(16). The values of the constants 1/n, k and k' of the FREUNDLICH's adsorption isotherms varied when the concentrations of the solutions of iodine were different. The value of 1/n was lower in the case of a low concentration of iodine than in the case of a high concentration, the value of k was higher and the value of k' was lower. When the concentration of iodine was low, the values of 1/n, k and k' were smaller in the case of the starches of the tuber plants than in the case of those of the cereal plants and when the concentration of iodine was high the relation was reversed.

There were close correlations between 1/n and *k*, 1/n and *k'* when the concentrations of iodine used were low. Between 1/n and *k*, a negative correlation was observed. Between 1/n and *k'* a positive correlation was observed. However, when the concentrations of iodine used were high, a negative correlation between 1/n and *k* was observed; the coefficient of correlation between 1/n and *k'* was 0.4260 which is an insufficient correlation.

It was found that definite quantities of iodine amounting to about 1/10 of the constant *k'* were combined with the starch in a form not removable by washing with potassium iodide solution. The mode of combination between the starch and the iodine was supposed to be either the formation of an adsorbed compound, a solid solution or a chemical combination between them.

(17). Electro-dialysis of the starch particle was carried out by means of PAULI's electro-dialysator. Electro-dialysed starch was thus obtained.

As an effect of the electric current, reducing substances were separated from the starches and also substances which showed reducing power after hydrolysis by acid. The amount of the substances in the middle cell was the greatest, which suggested that the starches had separated mostly a particle so great that it could not pass through the dialysis membrane.

The phosphorus of the starches was caused to migrate to the anode by the electric current. The phosphorus seemed to be charged as an anion, which was a complex organic compound. But this organic compound of phosphorus was considered to have not the least reducing power.

(18). The phosphorus and nitrogen content of the starches were both decreased by electro-dialysis.

The starch particle was changed in its construction in some way as an effect of electro-dialysis. This agreed well with ROSENTHAL's, NEUBERG's and LOEB's reports.

(19). The electro-dialysed starches were acetylated more easily than the original. The acetyl electro-dialysed starches were considered to be the aggregates of tetraacetyl glucose.

The starches of the tubers were changed becoming more easily acetylated than those of the cereal plants. The content of the acetyl group was higher in the case of the starches of the tubers than in those of the cereal plants.

(20). The electrical conductivity of the solutions of the electro-dialysed starches increased in the cases of the potato and wheat starches. However, the values decreased in the other starches.

(21). The viscosity of the solutions were increased by electro-dialysis over the corresponding values of the original starch solutions when the concentrations of the starches were low. When the concentrations of the starch solutions were higher, the viscosity of the electro-dialysed starches were always smaller than those of the original.

(22). By the determination of the gold value of the electro-dialysed starch, it was learned that electro-dialysis did not change the gold value of the starch, or in other words, electro-dialysis did not change the protective power of the starch at all.

(23). The adsorption of iodine by the electro-dialysed starch granule was investigated. The values of constants of FREUNDLICH's adsorption isotherms were calculated. The correlation between these constants was considered. When the concentrations of iodine used were low, there was a close negative relation between $1/n$ and k and a close positive relation between $1/n$ and k'.

(24). The hydrolysis of the electrodialysed starch was carried out and the two constants k and k' of the above given equation were calculated. In the case of hydrolysis of the electro-dialysed starches by the action of diastase, the mechanism was expressed fairly well by that equation and the relation between $\log k$ and k' could be expressed by an equation of a straight line.

(25). When the values of the two constants of the original and the electro-dialysed starches were compared, it was observed that the values of k were always markedly increased by the electro-dialysis and the values of k' were decreased. It was concluded therefore, that the starches were changed into a more easily hydrolysed form by the action of the electric current.

(26). Considering from the facts that the electro-dialysis (a) had decreased the phosphorus and the nitrogen content of the starches, (b) had separated the reducing and non-reducing substances from the starch which was hydrolysed into the reducing form by the action of acid, (c) had produced an easily acetylable substance and (d) had changed the starches into a more easily hydrolysed form by the action of diastase, the author was able to deduce that the electro-dialysis had exerted some sort of changes upon the particles of the starches, which made the particles of the starches more susceptible to chemical reaction. The electro-dialysis was believed to decompose the starches very slightly.

(27). Oxidation of the starches was carried out by the use of three kinds of oxidizing agents, viz., potassium permanganate, natrium perborate and ammonium persulphate.

(28). The phosphorus content of the starches was decreased by the action of the oxidizing agents. The treatment with natrium perborate decreased the phosphorus content most greatly, the treatment with ammonium persulphate was the next and the effect of potassium permanganate upon the phosphorus content of the oxidized starch was the least.

(29). The oxidized starches were acetylated more easily than the original non-oxidized starches. The acetyl oxidized starch seemed to be an aggregate of tetraacetyl glucose.

(30). The viscosity of the solution of the starches was decreased by the action of the oxidizing agents. The starches decreased in the aggregation of their molecules as a result of the action of the oxidizing agents, the constitution of the starch molecule changed into a very simple form and the starch molecule was decomposed very much at the same time by the oxidizing agents.

(31). The adsorption of iodine by the oxidized starch granules was examined and the constants of FREUNDLICH's adsorption isothems were calculated.

Marked differences between the constants 1/n, *k* and *k'* were observed in the case of the original and the oxidized starches treated by ammonium persulphate. However, in the case of oxidized starch of the other two kinds no marked differences were observed.

Between 1/n and *k* were observed negative correlations and between 1/n and *k'* were observed positive correlations.

(32). The starch was phosphorated by the action of phosphorus oxychloride and some properties of the compounds were examined.

(33). The starches increased greatly in ash and phosphorus content as a result of phosphoration. They gained calcium by the same treatment. The quantities of phosphorus combined with the starches were greater than those of the calcium. The excess of the phosphorus was considered to combine directly with the starches.

(34). The viscosity of the solution of the phosphorated starches was higher than that of the original starches. The electrical conductivity of the solution of the phosphorated starches was greater than that of the original.

The viscosity increased by aging in the solutions of the phosphorated starches to maximum values and then decreased, in general. The electrical conductivity of the solutions of the phosphorated starches increased generally, though there were observed slight daily changes.

(35). Notwithstanding the length of the heating, the viscosity and the electrical conductivity of the solutions of the phosphorated starches were higher than the corresponding values of the solutions of the original starches. At a definite duration of heating, the solutions of both the starches had shown maximum values, subsequently by longer heating the viscosity of the solutions was decreased gradually and the electrical conductivity of the solutions of both starches increased in a regular manner concomittant with an increase in the length of the heating.

(36). By the electrometric titration of the phosphorated starches, the author was able to conclude that the equivalent of natrium hydroxide need to secure electrical neutrality was markedly greater than that of the difference between the equivalents of phosphorus and calcium. The neutralisation of the phosphorated starches with natrium hydroxide required greater quantities of the natrium hydroxide than the quantities of the phosphorus which were contained in free form in the molecule. The excess of the natrium hydroxide was considered to be employed for the neutralisation of the negative charge of the starch molecule which was observed by electrophoresis and other methods.

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