On the Differences between some Colloidal Properties of Common and Glutinous Rice Starch.

By

Tetsutarō Tadokoro and Shōichi Satō.

(*From the Biochemical Laboratory, College of Agriculture, Hokkaido Imperial University Sapporo, Japan*).

CONTENTS.

INTRODUCTION.

The recent advance in colloidal chemistry has given us much information regarding the different properties of various starches. But in the present paper, we shall only deal with some of their most important results.

It is well known that the granules of starches vary in their appearance by their origin and they vary also somewhat in their properties; for instance, sago, tapioca and cassava starches yield more glutinous sol than the others. We can also see a similar difference between common and glutinous rice starches.

Commercial starch contains a small proportion of mineral matter; this amounts in potato-starch to about 0.22 %, sago 0.4 %, cassava 0.12 %, maize 0.11 % and wheat 0.23 % which to a certain extent can be removed by purification; for instance, we can achieve this object by the action of acid, by the precipitation with alcohol or by freezing. These phenomena were investigated thoroughly by FOUARD[1], HARRISON[2], MAQUENNE[3], MALFITANO and MOSCHKOFF[4], etc.

On heating with water, starch granules swell up and become a fully hydrated pseudo-solution, in the case of wheat-starch at 65° C, maize 70°, sago 72°, rice 74° and potato-starch 63° C. The viscosity of starch pseudo-solutions varies also according to the kinds of starch;

---

1) FOUARD:—Comp. rend., **144**, 501–503, 1366–1368, 1907.
2) HARRISON:—Jour. Soc. Dyers and Colorists, **32**, 40–44, 1916.
3) MAQUENNE:—Compt. rend., **146**, 317–318, 1908.
4) MALFITANO and MOSCHKOFF:—Compt. rend., **150**, 710–711, 1910.

for instance, MacNider[1] reported the viscosity of potato-starch to be 14.31, maize 2.49–2.86, cassava 3.88–3.97, wheat 1.24–1.26 and rice 1.00 for solutions containing 12 grs. in 30 c.c. of water. Concerning influential factors upon viscosity, Harrison(2), Gruzewska[2] and Maquenne(3), Stock[3], Pauli[4], Schorr[5] and Samec[6] stated that the age of starch solution is the most important factor and the presence of small quantities of acids or alkalies or other electrolytes, has also much influence on it; in the same manner, the thickening point is more or less depressed by the presence of electrolytes.

It was at one time believed that starch granules consisted of two distinct substances, an inner material or granulose (amylose) and an outer layer named amylopectin:[7] but it was denied by Harrison(2), Gruezewska[8] and Maquenne(3) who concluded that they do not differ in composition, but in physical structure.

The adsorption of alkalies and alkaline earths by starch solution was investigated by Aboth[9], Harrison(2), Fouard(4) and Tollens and material produced was reported to have the formula $C_{24}H_{39}O_{20}BaO$, $C_{24}H_{39}O_{20}K$ and $C_{24}H_{39}O_{20}Na$, but it has been lately confirmed that it has no definite ratio and the composition of the precipitate varies according to the concentration of alkalies and alkaline earths used in the reaction.

Starch solution on standing, separates into two phases, a phase of solid gel and a liquid phase, the phenomenon of which, is called

---

1) MacNider:—Jour. Ind. and Eng- chem., **4**, 417-422, 1912.
2) Gruzewska:—and Maquenne:—Compt. rend., **146**, 540–545, 1908.
3) Stock:—Jour. Soc. Dyer and Colorists, March, 1894, J.S.C.I., **22**, 1903.
4) Pauli:—Biochem. Zeitschr., **18**, 340, 1909.
5) Schorr:—Biochem. Zeitschr., **37**, 424, 1911.
6) Samec:—Koll. chem. Beihefte **4**, 132, 1912.
7) Maquenne:—Compt. rend., **137**, 797, 1266, 1903.
   „ „ „ **138**, 49, 1904.
   „ „ „ **142**, 1906.
   „ „ „ **140**, 1906.
   Roux:—Ann. Phys. et Chim., **8**, serie, 9, 179, 1906.
   Maquenne and Roux:—Jour. Inst. Brew., No. 6, 1905.
   Botazzi:—Atti. R. Accad. dei Lincei, **5**, 18, 11, 87, 1909.
   Wolff:—Ann. chim. appl., **10**, 389, 1905.
8) Gruzewska:—Compt. rend. **152**, 785, 1911.
   Jour. physiol. path. gen., **14**, 7, 32–, 1913.
9) Asboth:—Jour. soc. chem. Ind., 77, 1888.
10) Fouard:—Bull. soc. chim. **5**, 828–834, 1909.

syneresis. Concerning the starch iodide, PODOA[1] and HARRISON[2] confirmed Mylius-theory and concluded that it is an additional product and the change of colors is a physical modification of the particles of iodine starch. Another author[3] also stated that iodine starch is an adsorption compound and is influenced by temperature. The decoloration of iodine starch solution by the presence of chemicals and by the action of light was observed by CLEMENTI[4] and BORDIER[5].

The molecular formula of starch has been given by Brown and MORRIS[6] in the simplest form $[(C_{12}H_{20}O_{10})_{20}]_5$. LOBRY and WOLF[7] estimated the size of the starch molecule to be approximately $5\mu\mu$ and FRIEDENTHAL[8] obtained a molecular weight of 9450 against 32400 in the formula above.

It is well known that there are two different kinds, common and glutinous, in the starch of rice and such a case is also found in millet and Italian millet.

The typical difference between the two kinds of starch is shown by the iodine color reaction, in which, the common rice starch shows a blue color while the glutinous rice starch shows a red or purple color. To explain this phenomenon TANAKA[9] concluded that the red coloration of the latter is due to a characteristic chemical property of the starch itself and denied Dafert and Mayer's contamination theory of amylopectin, erythrodextrine or special albuminoids. But concerning the other differences between common and glutinous starches, no investigation can be found. Therefore, in order to determine those differences from the standpoint of colloidal chemistry, the following investigation was carried out.

---

1) PADOA and SAVARE:—The analyst. Nov., 1906.
Biochem. Zeitscher., **84**, 106–17, 1917.
2) HARRION:—Zeitscher., Chem. Ind. Kolloide., **95**, 46, 1919.
3) LANGE:—Biochem. Zeitscher., **95**, 46, 1919.
4) CLEMENTI:—Arch. farm. sper., **20**, 258–68, 1915.
5) BORDIER:—Compt. rend., **163**, 305–6, 1916.
6) BROWN and MORRIS:—Jour. chem. soc., **53**, 610, 1888.
7) LOBRY and WOLFF:—Trav. chim. des Pays, Bas., **23**, 155, 1904.
8) FRIEDENTHAL:—Physiol. Zentralbl., **12**, 849, 1899.
9) TANAKA:—Jour. Coll. Eng., Tōkyo Imp. Univ. **4**, 2, 1907.

I. PREPARATION OF STARCHES.

1. Materials.

The materials used in the manufacture of starch were as follows :—

a) White rice (common and glutinous) which was produced in the province of Etchū.

b) White rice (common and glutinous) which was produced in Hokkaidō.

c) Millet (common and glutinous) which was produced in Hokkaidō.

In the case of (a) though the common rice was unmixed with glutinous rice, the glutinous rice was mixed with two grains of common rice in 100 grains, which were separated carefully from the former. The separation of common rice from glutinous rice could be effected, as the former was translucent while the latter was opaque. On the contrary, in the case of (b) and (c), no mixture could be found.

2. Manufacture and Purification of Starches.

The method of manufacture of starch was carried out mainly according to Johne's method, as follows :— The material was washed well with distilled water till no opaqueness remained and placed upon sieves to drain, after which it was ground to flour with millstones. The flour was then passed through 2 m.m. sieves by means of brushes, the coarser particles which did not pass through being returned to the mill to be reground and again sifted, until the whole was thus passed through. The flour thus obtained was taken in a strong beaker of about 2 liter and treated with three times its volume of 0.3 % NaOH solution. The mixture was well stirred and allowed to stand for about 7 hours, at the end of which time, the upper liquor was siphoned off, the precipitate remaining at the base. The above process was repeated till no reaction of protein could be observed in the starch. (This was tested by Millon's reaction as well as by the biuret reaction.) The precipitate was washed with three times its volume of cold water and allowed to stand for about 7 hours to settle. The above treatment was repeated till no alkaline reaction could be observed in the starch. The precipitate at the bottom was strained through fine silk into the water in a large porcelain dish and the suspended solution thus obtained was transferred into a large strong beaker and allowed to stand for about 7 hours to settle when a deposit of three distinct layers was found, the middle layer of which consisted of pure starch. Therefore the middle layer was suspended again in the distilled water, filtered by a large nutzer by suction, washed well with distilled water, and finally, with 95 % alcohol and ether and dried below 50° C.

3. *Degree of Purification.*

1) The starches obtained above were entirely white. 2) The water suspensions of starch as well as starch paste were neutral to the litmas paper as well as to the phenolphthalein. 3) The contents of water, nitrogen and ash of starch were also determined with the following results.

TABLE I.

Starch	Water %	Ash %	Nitrogen %
*1. Etchū common rice starch	11.09	0.132	—
*2. Etchū glutinous rice starch	12.20	0.130	—
*3. Hokkaidō common rice starch	11.72	—	—
*4. Hokkaidō glutinous rice starch	10.46	—	—
*5. Hokkaidō common millet starch	10.90	—	—
*6. Hokkaidō glutinous millet starch	9.59	—	—

By the above table, we were able to prove that these starches are almost pure.

*Hereafter, these starches are to be expressed as follows:—
*1. Common starch No. 1.
*2. Glutinous starch No. 1.
*3. Common starch No. 2.
*4. Glutinous starch No. 2.
*5. Common millet starch.
*6. Glutinous millet starch.

II. SOME COLLOIDAL PROPERTIES OF STARCH GRANULES.

1. Swelling of Starch Granules.

The term "swelling" of starch is commonly used to express the gelatination into paste, because the starch granules swell up in high temperature and break out into paste. Many authors have already investigated the temperature of swelling and have also reported very thoroughly the influences of the different electrolytes on swelling. In the present paper, we have used this term "swelling" not to express the gelatination, but to express the increase of volume of starch granules in cold solution.

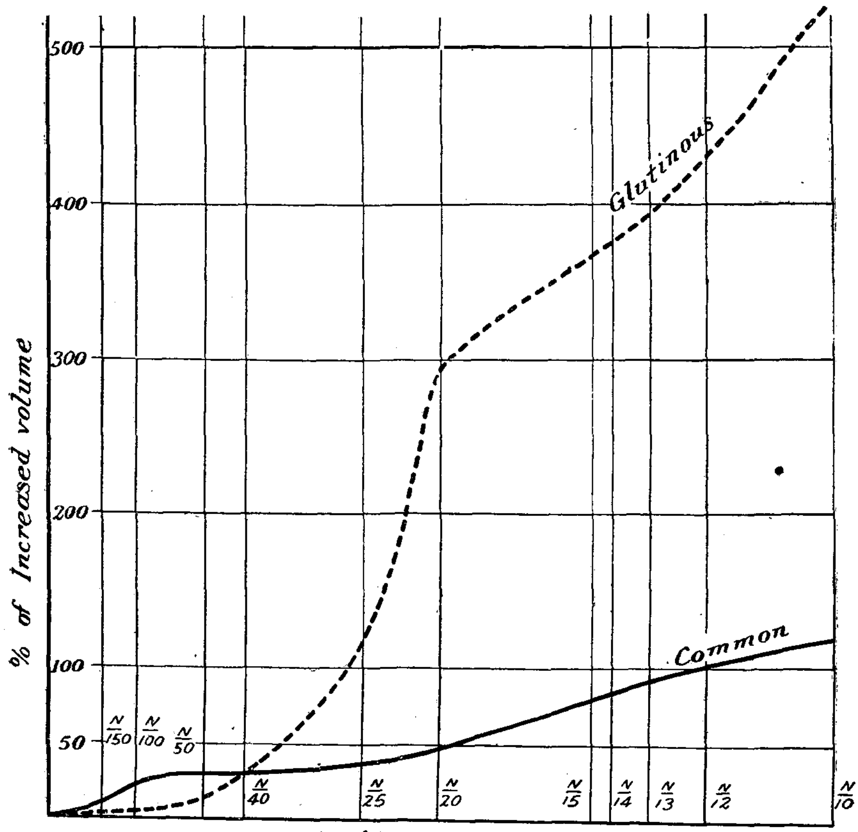
In the following experiments, we took 2 grs. of air dried starch whicn was prepared by the above method and mixed it with 25 c.c. of iodine potassium iodide solution or calcium chloride solution or HCl solution in measuring tubes. After stirring for 5 minutes, each tube was allowed to stand at 17° C for 22 hours to settle, we then measured their increased volumes of the starch granules, comparing with control sample which was treated with distilled water. In the case of treatment with HCL and $CaCL_2$ solution of different concentrations such as N/10, N/25, N/50, N/100, N/150, no noticeable difference could be discovered. But the samples which were treated with iodine potassium iodide solution showed the following values of increased volume which were expressed in relative value of original volume in water (H_2O = 100).

TABLE 2.

Concentration of I-KI sol.	Common starch granules		Glutinous starch granules	
	Observed vol.	% of increased vol.	Observed vol.	% of increased vol.
N/10	3.67 cc.	217	13.66 cc.	592
N/12	3.45 cc.	204	12.11 cc.	535
N/13	— cc.	—	11.75 cc.	519
N/14	3.08 cc.	182	10.65 cc.	470
N/15	2.68 cc.	164	9.92 cc.	438
N/20	2.43 cc.	144	9.17 cc.	405
N/25	2.15 cc.	127	4.80 cc.	181
N/40	2.13 cc.	126	3.03 cc.	133
N/50	2.12 cc.	125	2.54 cc.	112
N/100	2.11 cc.	125	2.27 cc.	104
N/150	1.81 cc.	110	2.26 cc.	100
H_2O(control)	1.69 cc.	100	2.26 cc.	100

Here we traced the following curves, taking % of increasing volume on the ordinate and the concentration of iodine solution on the abscissa.

Fig. 1.



From these results and curves, we found a great difference between the swelling phenomena of common and glutinous starch granules. When we examined them under a microscope, we found that all glutinous starch granules in the concentration of iodine solution higher than N/25 swelled up to two or three times their original volume.

2. *Adsorption of Iodine by Starch Granules.*

DEMOUSSY[1] treated rice starch, which had been demineralized by dilute hydrochloric acid and washed with water till it gave no reaction

1) DEMOUSSY:—R. A. Coll. Chem., London Chem. Soc. (1919).

of chlorine, with a number of acid salts, bases, and neutral salts. He found some of the substances removed from solution in every case and concluded that "starch possesses an acid energy comparable to that of carbonic acid and it should act on salts with a facility corresponding to the weakness of their acids." The reactions with bases were also attributed to the acid properties of starch, while, Hoyes LLOYD[1] thought that it seems more reasonable to consider the loss of neutral salt such as potassium chloride from solution in his experiment to be caused by adsorption of that salt and made a detailed investigation on the adsorption of three substances, hydrochloric acid, sodium hydroxide and sodium chloride by rice, cassava, arrowroot, potato, and maize starch granules. And he concluded that 1) The adsorption of hydrochloric acid, sodium hydroxide, and sodium chloride varies with different starches but not as much as would be expected, considering the great differences in the size of starch granules. 2) The adsorption is not a function of the granule surface per unit weight. 3) The amount of the adsorption is much greater for sodium hydroxide than for either hydro-chloric acid or sodium chloride. 4) In the case of starch hydrochloric acid, the ordinary adsorption rule is followed for solutions up to about 0.4 N, except in the case of maize starch.

But he did not touch on the study of the adsorption of iodine by starches and there seems to be no investigation yet made on that problem. Therefore, we carried out the following experiment, testing the adsorption of iodine by common and glutinous rice starches.

METHOD OF OPERATION.

1 gr. of water free starch was taken in each bottle and to it were added 40 c.c. of iodine solution of various concentrations, such as N/200, N/150, N/100, N/75, N/50, N/25, N/15, N/14, N/13, N/12, N/10. Each bottle was shaken on the shaking apparatus for 30 minutes when the equilibrium of adsorption of iodine solution by starch was obtained. The solution in each bottle was removed into a centrifugal glass tube as completely as possible and centrifuged for 15 minutes when the clear supernatant liquid was separated from the starch iodide. 5 c.c. of each supernatant liquid was titrated 5 times with N/10 or N/100 sodium thiosulphate solution and the average titration number was obtained. The above experiment was repeated

1) HOYES LIOYD:—Wochschr. f. Brau. 432, 1911.

or verification and the quantity of iodine absorbed by starch from iodine solution of various concentrations was determined as follows.

In subsequent tables, the results obtained from the above experiments are given, where

C≐concentration of iodine solution at equilibrium.

X/M=amount of iodine adsorbed by 1 gr. starch.

TABLE 3.

Con. of I_2 solution used in the reaction	Glutinous Rice Starch				Common Rice Starch			
	X/M (mg.)	C (mg.)	Log. X/M	Log. C	X/M (mg.)	C (mg.)	Log. X/M	Log. C.
N/200	19.2812	6.0888	1.285132	0.784526	24.3552	1.0148	1.38659	0.006384
N/100	36.5328	14.2073	1.562680	1.152560	45.6660	5.0740	1.65959	0.705350
N/75	45.6660	21.3108	1.659594	1.328580	54.7992	12.1776	1.738780	1.085578
N/50	71.0360	30.4440	1.851476	1.483500	74.0804	27.3996	1.867000	1.437750
N/25	169.4716	33.4884	2.229092	1.524894	141.0572	61.9028	2.149406	1.791771
N/20	202.9600	50.7400	2.307412	1.705350	162.3680	91.3320	2.210509	1.960620
N/15	228.3300	106.5540	2.358567	2.027550	202.9600	131.9240	2.307412	2.120306
N/14	228.3300	126.8500	2.358567	2.103290	202 9600	152.2200	2.307412	2.182468
N/13	243.5520	142.0720	2.386590	2.152500	233 4040	152.2200	2.368100	2.182468
N/12	243.5520	172.5160	2.386590	2.236840	243.5520	172.5160	2.386590	2.236840
N/10	262.8332	244.5668	2.419678	2.388406	262.8332	244.5668	2.419678	2.388406

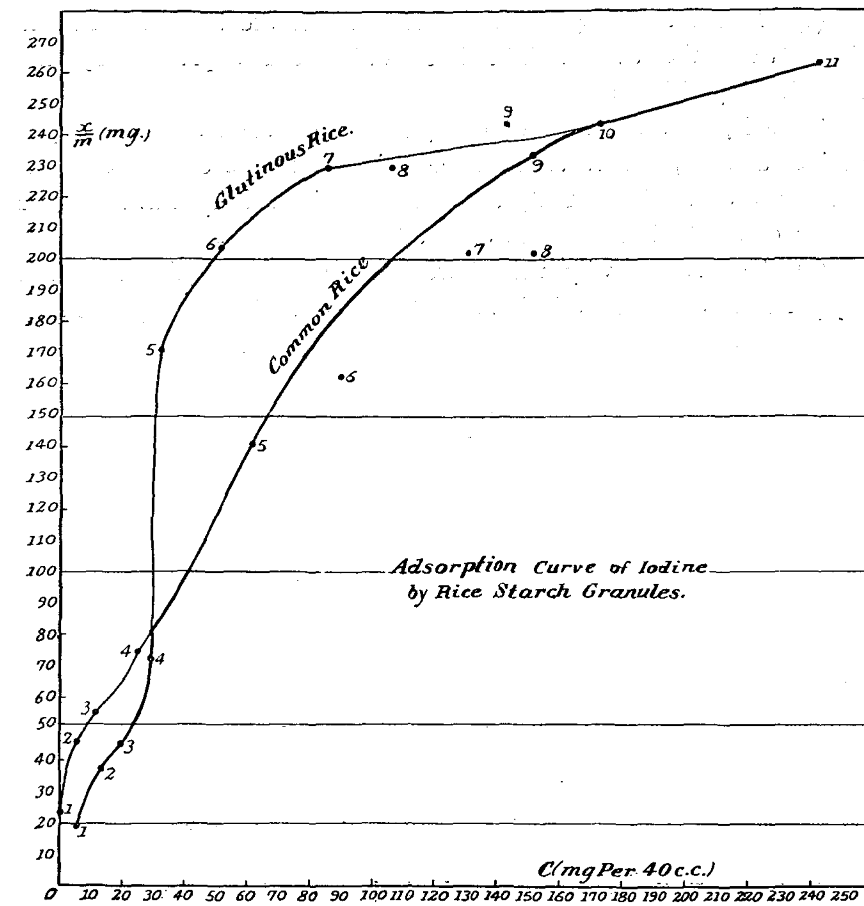
If we took C on the abscissa and X/M in the orinate, the following curves are obtained. (See *Fig. 2 & 3*)

CONCLUSIONS.

(1) If we observe from the results obtained in the above experiment, whether the reaction of adsorption by starches agrees with Freundlich's adsorption law or not, we obtain the following conclusions. Freundlich's adsorption formula $X/M=K.C.^{1/n}$ is generally admitted to express an ordinary adsorption effect, where X/M=amount adsorbed by 1 gr. of starch; C=concentration of solution at equilibrium; and k and 1/n=constants. From this equation, $\log X/M=\log k + 1/n \log C$, which is the equation of a straight line. Since this is the case, if corresponding values for log X/M and log C are plotted, we should obtain a straight line so long as the adsorption is following the ordinary law and so long as no other reaction occurs.

Therefore, we plotted corresponding values for log X/M and log

Fig. 2.



C obtained in the above experiment, taking log X/M on the ordinate and log C on the abscissa and obtained the following lines. (Fig. 3). From the above table and the lines on (Fig. 3), the following conclusions were obtained.

(a) Logarithms of adsorption by glutinous rice starch do not simply express one straight line as expressed by one Freundlich's adsorption formula but evidently express two straight lines which have a markedly different direction from each other.

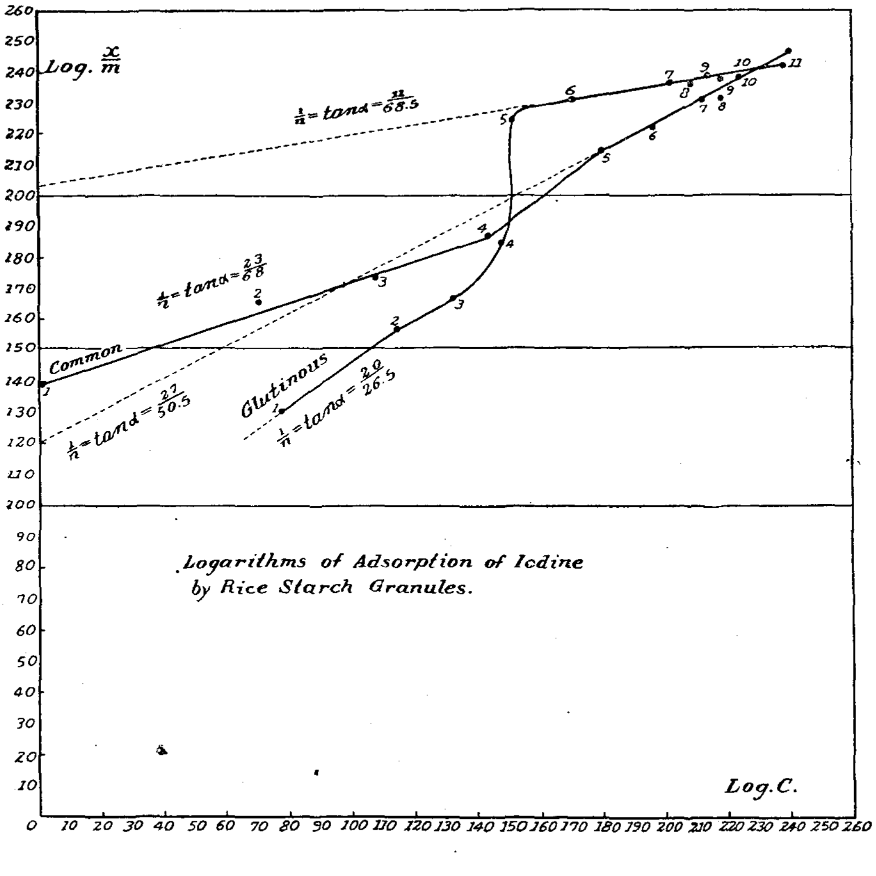
While, in the case of common rice starch, though logarithms of adsorption seem to express almost only one straight line but in this case also, as in the case of glutinous rice starch, we notice two straight lines which have however only a slightly different direction from each other.

(b) In the case of glutinous starch, there is the following relation ship between the two straight lines which are expressed by the adsortpion logarithms :—

That is, in the course of changing the direction of one straight line into another, one curve is plotted. While in the case of common starch, no curve is plotted, since two straight lines have only a slightly different direction from each other.

(c) The reason why the above reaction of adsorption does not simply follow one Freundlich's adsorption formula but is expressed by

Fig. 3.



two straight lines as expressed by a combination of two Freundlich's adsorption formula is mainly due to the influence of swelling of starch granules. This is in perfect agreement with the fact, as will be seen in the experimental part of swelling of starch granules (see page 7-8). And especially, in the case of glutinous rice starch, we notice the greatest swelling in the portion where a logarithmic curve exists. (at concentrations from N/100 to N/25).

2) In the dilute concentration of iodine which is lower than about N/50, glutinous rice starch is weaker than common rice starch in its power of adsorbing iodine.

But in the strong concentration of iodine when higher than N/50, glutinous rice starch becomes stronger than common rice starch in its power of adsorbing iodine.

This is also due to the fact that in the case of glutinous rice starch, the degree of swelling increases more rapidly and its adsorption surface becomes much greater than that of common rice starch. But after which, as the concentration of iodine becomes stronger, the power of glutinous rice starch to adsorb iodine is closely nearing that of common starch until both coincide with each other. (at the concentrations of N/10 iodine solution.) This is principally due to the fact that in such a high concentration, the glutinous rice starch granules swell up to their utmost limit, after which, the power of glutinous rice starch to adsorb iodine increases less rapidly than that of common starch.

3) If we show the constants (K and 1/n), considering that the above reaction is expressed by the combination of two Freundlich's adsorption formula, the following is observed:—

a) Constants obtained from the straight lines expressed by logarithms of adsorption.

TABLE 4.

Constants	Glutinous rice starch		Common rice starch	
	α	β	α	β
log. k	2.03	0.69	1.20	1.39
1/n	$\frac{11.0}{68.5}=0.1605$	$\frac{20}{26.5}=0.7547$	$\frac{27}{50.5}=0.5347$	$\frac{23}{68}=0.34$

(b) Constants obtained by calculation.

I) In the case of glutinous rice starch

α) Taking two values for log X/M and log C,

2.419678 = log k + 1/n 2.388406
2.307412 = log k + 1/n 1.705350

Subtracting 0.112266 = 1/n 0.683056
∴ 1/n 0.212266/0.683056 = 0.1643
Substituting 1/n in one of the above equation
2.419678 = log k + 0.1643 × 2.388406
k = 106.478

β) Taking two values for log X/M and log C,

1.562680 = log k + 1/n 1.152500
1.285132 = log k + 1/n 0.784526

Subtracting 0.277548 = 1/n 0.367974
1/n = 0.277548/0.367974 = 0.7543
Substituting 1/n in one of the above equation
1.285132 = log k + 0.7543 × 0.784526
k = 4.93577

II) In the case of common rice starch

α) Taking two values for log X/M and log C,

2.386590 = log k + 1/n 2.236840
2.149406 = log k + 1/n 1.791711

Subtracting 0.237184 = 1/n 0.445129
∴ 1/n 0.237184/0.445129 = 0.5528
Substituting 1/n in one of the above equation
2.386590 = log k + 0.5328 × 2.236840
∴ k = 15.66

β) Taking two values for log X/M and log C,

1.869700 = log k + 1/n 1.437750
1.386590 = log k + 1/n 0 006384

Subtracting 0.483110 = 1/n 1.431366
1/n = 0.483110/1.431366 = 0.34
Substituting 1/n in one of the above equation
1.869700 = log k + 0.38 × 1.437750
k = 24.04

APPENDIX.

The adsorption of iodine by glutinous and common millet starches.

In order to examine in the adsorption phenomenon of iodine as to whether there are similar differences between the glutinous and common starches of other grains, with the differences between glutinous and common rice starches, we carried out the following experiment with glutinous and common millet starches. The method of operation is just the same as in the case of rice starches. In subsequent tables, the results obtained from the above experiment are given, where, C = concentration of iodine solution at equilibrium. X/M = amount of iodine adsorbed by 1 gr. of starch.

TABLE 5.

Conc. of I_2 solution used in the reaction	Common Millet Starch				Glutinous Millet Starch			
	X/M (mg.)	C (mg.)	Log. X/M	Log. C	X/M (mg.)	C (mg.)	Log. X/M	C Log.
N/200	20.2960	5.0740	1.307412	0.307412	24.8626	0.5074	1.395554	1.705350
N/100	39.5772	11.1628	1.597447	1.047777	47.6956	3.0444	1.678484	0.483500
N/75	44.6512	22.3256	1.649830	1.348810	56.8288	10.1480	1.754572	1.006384
N/50	71.0360	30.4440	1.851476	1.483500	71.0360	30.4440	1.851476	1.483500
N/25	162.3680	40.5920	2.210509	1.608442	116.7020	86.2580	2.067070	1.935800
N/20	182.6640	60.8880	2.261644	1.784534	121.7760	121.7760	2.085578	2.085578
N/15	233.4040	101.4800	2.368100	2.006884	187.7380	147.1460	2.273556	2.167760
N/14	233.4040	121.7760	2.368100	2.085578	192.8120	162.3680	2.285132	2.210509
N/13	243.5520	142.0720	2.386559	2.152500	208.0340	177.5900	2.318123	2.249416
N/12	253.7000	162.3680	2.404320	2.210509	208.0340	208.0340	2.318123	2.318123
N/10	263.8480	243.5520	2.421355	2.386590	263.8480	243.5520	2.421355	2.386590

If we take C on the abscissa and X/M on the ordinate the following curves are obtained (Fig. 4 & 5).

Fig. 4.

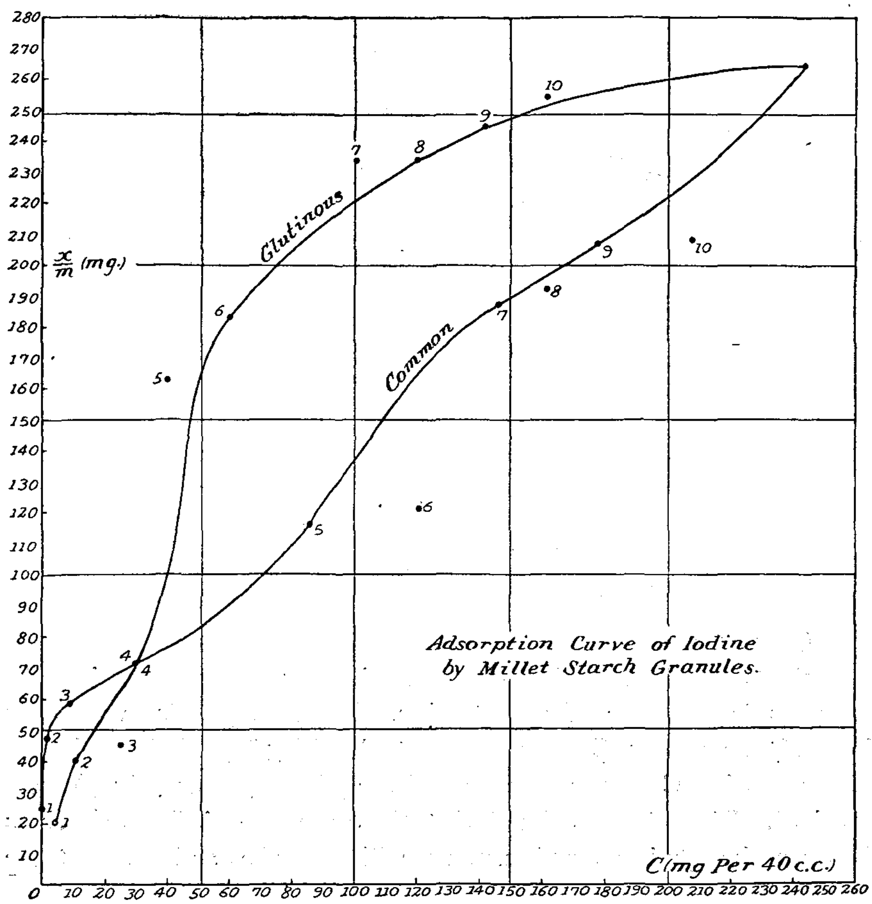
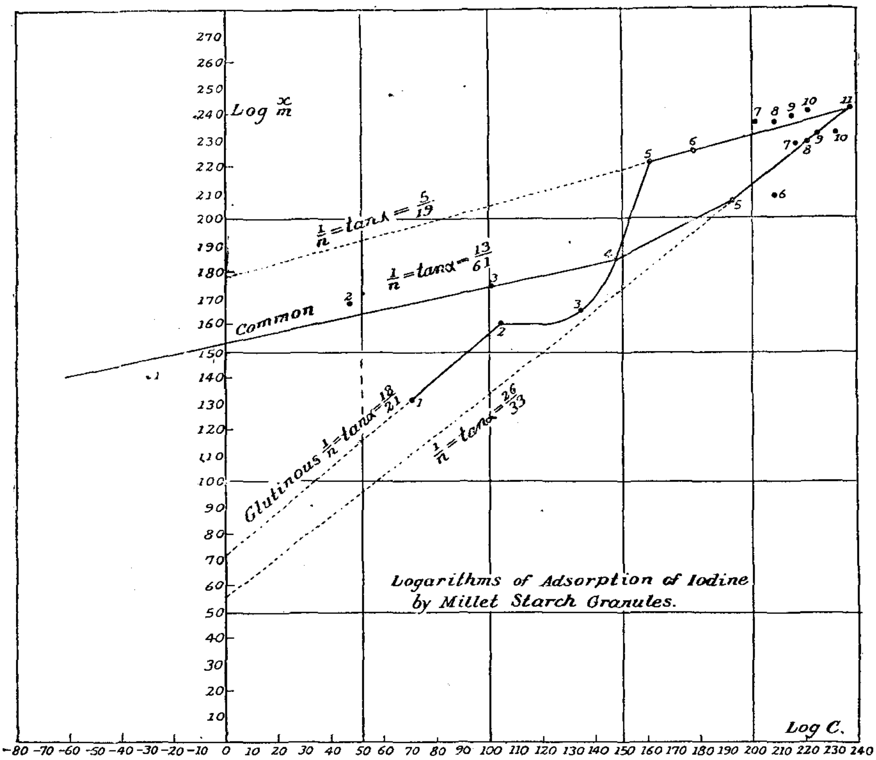


Fig. 5.



CONCLUSIONS.

1) Conclusions obtained from the above experiment are just the same as in the case of rice starches. The corresponding values for long X/M and log C were also plotted, taking log X/M on the ordinate and log C on the abscissa and the following lines (Fig. 5) were obtained. Thus, it was found that there are also similar differences between the glutinous and common millet starches as between those of rice.

2) If we show the constants (k and 1/n), considering that the above reaction is expressed by the combination of two Freundlich's absorption formula, the following is observed :—

a) Constants obtained from the straight lines expressed by logarithms of adsorption.

TABLE 6.

Constants	Glutinous Millet Starch		Common Millet Starch	
	α	β	α	β
log. k	1.78	0.71	1.53	0.55
1/n	$\frac{5}{19}=0.26$	$\frac{18}{21}=0.857$	$\frac{13}{61}=0.213$	$\frac{26}{33}=.788$

b) Constants obtained by calculation.

I) In the case of glutinous millet starch

α) Taking two values for log. X/M and log C,

2.421355 = log k + 1/n 2.386590
2.210509 = log k + 1/n 1.608442

Subtracting 0.210846 = 1/n 0.778148
∴ 1/n = 0.210846/0.778148 = 0.27
Substituting 1/n in one of the above equation
2.421355 = log k + 0.27 × 2.386590
k = 59.84

β) Taking two values for log X/M and log C,

1.597447 = log k + 1/n 1.047777
1.307412 = log k + 1/n 0.705350

Subtracting 0.290035 = 1/n 0.342427
∴ 1/n = 0.290035/0.34247 = 0 847
Substituting 1/n in one of the above equation
1.307412 = log k + 0.847 × 0.70535
k = 51.28

II) In the case of commom millet starch

α) Taking two values for log X/M and log C,

1.851476 = log k + 1/n 1.483500
1.754572 = log k + 1/n 1.006384

Subtracting 0.096904 = 1/n 0.477116
∴ 1/n = 0.096904/0.477116 = 0.203
Substituting 1/n in one of the above equation
1.851476 = log k + 0.203 × 1.4835
k = 35.51

β) Taking two values for log X/M and log C,

2.421355 = log k + 1/n 2.386590
2.067070 = log k + 1/n 1.935800

Subtracting 0.354285 = 1/n 0.450790
∴ 1/n = 0.354285/0.450790 = 0.786
Substituting 1/n in one of the above equation
2.06707 = log k + 0.786 × 1.9358
k = 35.12

3. *The Adsorption of Sodium Hydroxide by Starch Granules.*

As stated above, we observed remarkable differences between glutinous and common rice starch granules in the adsorption of iodine as well as in the swelling phenomenon by iodine, and moreover, we observed that in the swelling phenomenon, alkaline solution causes rice starch granules to swell in a very marked degree. Therefore, we carried out the following experiments on the adsorption of sodium hydroxide by glutinous and common rice starch granules.

METHOD OF OPERATION.

The method of operation was almost the same as in the case of adsorption of iodine by starch granules. The only point of difference was that various concentrations of sodium hydroxide, such as N/200, N/100, N/50, N/25, N/10, were used instead of various concentrations of iodine.

In subsequent tables, the results obtained from the above experiment are given where, C=concentration of NaOH solution at equilibrium. X/M=amount of NaOH adsorbed by 1 gr. of starch granules.

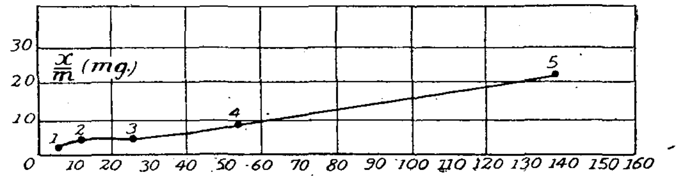
TABLE 7.

Concentr. of NaOH used in the reaction	Common and glutinous rice starches			
	X/M (mg)	C (mg)	Log X/M	Log C
N/200	1.6872	6.3048	0.22717	0.779676
N/100	3.5520	12.4320	0.55047	1.094540
N/50	4.4440	25.7520	0.64777	1.410814
N/25	7.9920	54.1680	0.90266	1.733744
N/10	21.3120	138.5280	1.32862	2.141543

If we take C on the abscissa and X/M on the ordinate, the curve shown in *Fig. 6* is obtained.

Fig. 6.

Adsorption Curve of NaOH. by Rice Starch Granules.

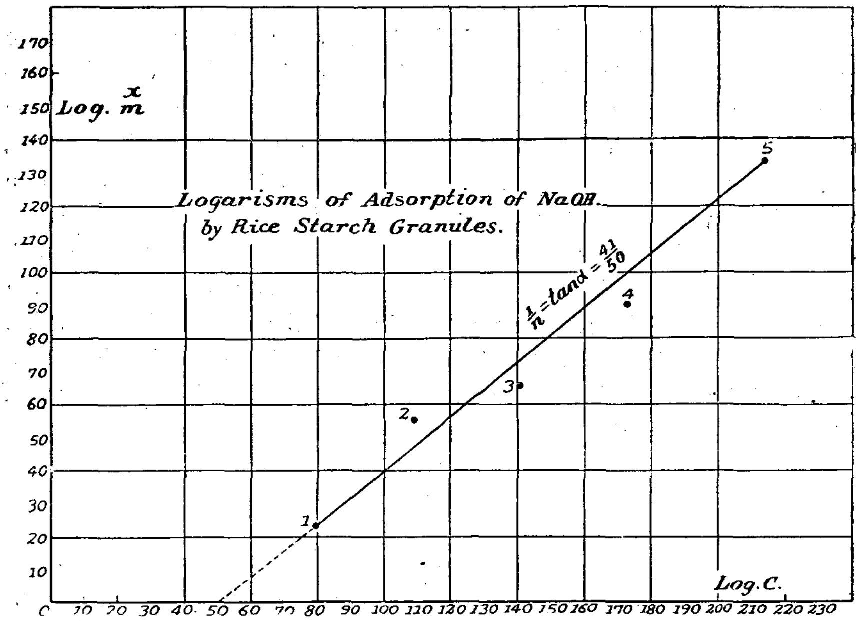


CONCLUSIONS.

1) As will be seen from the above table, concerning curve and logarithms, no noticeable difference between glutinous and common rice starch granules could be observed in the adsorption of NaOH, and moreover, the adsorption phenomenon of NaOH was exactly the same in both the kinds of starch granules.

2) The corresponding values for log X/M and log C were also plotted, taking log X/M on the ordinate and log C on the abscissa and the straight line was obtained as shown in *Fig. 7.* Thus, it was ascertained that the adsorption of NaOH by rice starch follows quite closely Freundlich's adsorption law.

Fig. 7.



3) If we show the constants (k and 1/n) in Freundlich's adsorption formula, the following are observed. (a) Constants obtained from the straight line is expressed by logarithms of adsorption.

TABLE 8.

Constants	Glutinous rice starch	Common rice starch
log k	−0.42	−0.42
1/n	$\frac{41}{50}$=0.82	$\frac{41}{50}$=0.82

(b) Constants obtained by calculation.

Taking two values for log K/M and log C,

$$1.328622 = \log k + 1/n\ 2.141543 \ldots\ldots\ldots\ldots a$$
$$0.227170 = \log k + 1/n\ 0.799676 \ldots\ldots\ldots\ldots b$$

subtracting $1.101452 = \qquad 1/n\ 1.341867$

$$1/n = 1.101452/1.341867 = 0.82$$

substituting 1/n in one of the above equations,

$$0.22717 = \log k + 0.82 \times 0.799676$$
$$k = 0.372766$$

4. Separation of Adsorbed Iodine from Starch Granules.

As already stated, it is admitted by many authors that iodine starch is an adsorption compound of iodine and starch. We also discovered by the above experiment the great difference between the adsorption quantities of iodine of common and glutinous starch granules, proving the above theory. Therefore we desired further to ascertain the difference between the combinations of iodine of these two kinds of starch granules. Thus 10 grs. of starch granules were treated with excess of iodine solution and free iodine was filtered off after standing for a few days. The residue was dried at 60°C and milled to powder. With these samples, we determined the distribution of iodine in starch by the following different processes and calculated the quantities of iodine in % of starch.

TABLE 9.

	Common starch		Glutinous starch	
	The quantity of iodine in % of original	The quantity of iodine in % of dry matter	The quantity of iodine in % of original	The quantity of iodine in % of dry matter
Moisture	7.96	—	7.44	—
Soluble iodine in hot alcohol.	3.61	3.91	2.93	3.16
Soluble iodine in cold alchol.	3.05	3.31	2.58	2.76
Soluble iodine in cold N/10 HCL alcohol.	3.28	3.56	3.20	3.45
Soluble iodine in cold N/10 HCL.	0.41	0.44	0.32	0.35
Soluble iodine in hot N/10 HCL.	0.96	1.04	0.32	0.35
Soluble iodine in cold water.	0.91	0.66	0.51	0.55

The separation of adsorbed iodine from starch granules showed no remarkable difference between common and glutinous starches.

5. On the Resistance of Starches against Sulphuric Acid.

Wolff and Fernbach (1903) discovered an amylo-coagulase, an enzyme which causes the soluble starch to coagulate, and Maquenne observed that the coagulate by that enzyme is the same substance as the retrogradation product i.e. the flocculent coagulate which is produced by allowing the starch paste to stand.

According to Roux, the starch granules consist of two distinct substances :—

a) An inner material or granulose (amylose) which is not viscous, its saccharification is very easy and produces easily 96–98 % of maltose when decomposed. Partly soluble in hot water and completely soluble at 150°C. Its solution gives a blue color with iodine;

b) An outer layer named amylopection which is the main substance which gives starch its viscosity. Its saccharification is very hard and hardly gives maltose but gives dextrine when decomposed. It does not give a characteristic color reaction with iodine.

Fernbach found that the saccharification of starch by diastase proceeds very rapidly but completely when the primary phosphates in the starch granules are changed into the secondary phosphates by the addition of a small quantity of acid. Beside this, Fernbach and Wolff discovered that the complete saccharification can also be proceeded when the saccharification is carried out for a long time at 50° C. and 100 % of maltose can be obtained even without the addition of a small quantity of acid. These discoveries were also admitted by Roux and Maquenne and the existence of a special substance such as amylopectin became very doubtful. Therefore Fernbach declared that the existence of amylopectin is to be abandoned and by most investigators, it is also admitted that amylopectin is only a polymerisation product of amylose and is not a special substance which is entirely different from amylose.

But Roux and Maquenne held still the theory of the existence of amylopectin owing to the special property that, in the saccharification of starch, though the saccharification is very rapid till 70–80 % of starch is decomposed, but after which, the saccharification becomes very slow. Thus they gave the following definition :—

'Amylopectin is a substance in the starch granules which is very hard to be saccharified.' And though there are some methods which were devised in order to determine the quantity of amylopectin, all of them are incomplete and can not be relied upon.

Recently, Fouard, investigating starch as colloids, explained that starch must consist of only one substance and that inorganic ingredients in the starch granules must play an important role on the viscosity of starch. Wolff also admitted these facts. But here, in order to examine the resistance of glutinous and common rice starch against sulphuric acid, the following experiment was carried out on the saccharification of starches, by means of sulphuric acid instead of diastase.

METHOD OF OPERATION.

Into a bottle, 2 grs. of starch were introduced, and mixed thoroughly with 50 cc. of water, to which was added sulphuric acid of various concentrations, such as 1 cc. of 1/100 conc. H_2SO_4, 1/10 conc. H_2SO_4, etc. and boiled on the water bath with a long glass tube as a condenser for 2–4 hours. Each digested solution was filtered and the remaining precipitate was washed with water till the filtrate gave no acid reaction. Then the precipitate as well as the filter paper were introduced into a drying tube and dried in a water even till the constant weight was obtained. The results obtained are given in the following table.

TABLE 10.

Treatment of starches	Residue in % of air dry substance (average of 5 samples)		Residue in % of air dry substance (average of 5 samples)	
	Glutinous rice starch	Common rice starch	Glutinous rice starch	Common rice starch
2 gr. rice starch No. 1. +50 cc. H_2O+1 cc. H_2SO_4 (1/100 conc.) boil for 2 hr.	0.7250	0.4600	0.8258	10.6406
2 gr. rice starch No. 1. +50 cc. H_2O+1 cc. conc. H_2SO_4 boil for 2 hours.	0.3250	0.7050	0.3702	0.7930
2 gr. rice starch No. 1. +50 cc. H_2O+1 cc. conc. H_2SO_4 boil for 4 hours.	0.1950	0.4350	0.2221	0.4893
2 gr. rice starch No. 1. +50 cc. H_2O+1 cc. conc. H_2SO_4 boil for 6 hours.	same as above	same as above	same as above	same as above
2 gr. rice starch No. 1. +50 cc. H_2O+2 cc. conc. H_2SO_4 boil for 4 hours.	0.1850	0.4300	0.2107	0.4837
2 gr. rice starch No. 2. +50 cc. H_2O+1 cc H_2SO_4 (1/100 con.) boil for 2 hours.	0.1950	11.3000	0.2178	12.8006
2 gr. rice srarch No. 2. +50 cc. H_2L+1 cc. H_2SO_4 (1/10) boil for 2 hours.	0.1500	1.0350	0.1675	1.1724
2 gr. rice starch No. 2. +50 cc. H_2O+5 cc. H_2SO_4 (1/10) boil for 2 hours.	0.1200	0.7950	0.1340	0.9005

Treatment of starches	Residue in % of air dry substance (average of 5 samples)		Residue in % of air dry substance (average of 5 samples)	
	Glutinous rice starch	Common rice starch	Glutinous rice starch	Common rice starch
2 gr. rice starch No. 2. $+50$ cc. H_2O+1 cc. conc. H_2SO_4 boil for 2 hours.	0.0700	0.6000	0.0782	0.6797
2 gr. millet starch $+50$ cc. H_2O+1 cc. H_2SO_4 (1/100) boil for 2 hours.	0.8900	13.9200	0.8944	15.6224
2 gr. millet starch $+50$ cc. H_2O+1 cc. conc. H_2SO_4 boil for hours.	0.0750	0.6150	0.0830	0.6902

CONCLUSION.

From the above table, the following conclusions are drawn:—

1) The resistance of glutinous rice starch as well as common rice starch is very strong against sulphuric acid.

At the first period, though the saccharification is very easy and rapid, yet at the final period, the saccharification becomes very hard. Thus, in order to obtain a complete saccharification a great deal of conc. sulphuric acid as well as considerable length of time are required for disgestion.

2) In every case, the resistance of common rice starch is stronger than that of glutinous rice starch.

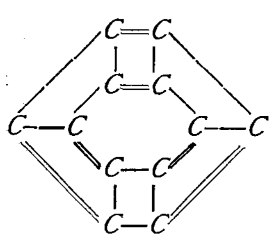
3) According to Roux's definition, "Amylopectin is a substance in the starch granules which is very hard to be saccharified," and is the main substance which gives the starch its viscosity. But here, we observed that the glutinous rice starch (the viscosity of which is higher than that of common rice starch), has a less quantity of the substance which corresponds to "Amylopectin."

This may be due to the fact that the results obtained from the saccharification of starch by sulphuric acid is somewhat different from that obtained by diastase. But at any rate, the existence of amylopectin is very doubtful.

6. *Charcoals from Starch Granules.*

It is a well known fact, that charcoal has a strong adsorbing power of gas, electrolytes and colloids and also has a catalytic action like the powder of platinum. Up to the present time a great many authors have reported their experimental results on the action of charcoals from many different points of view. HUNTER[1] investigated the adsorption of gases by charcoals from 14 kinds of wood and reported that the cocoanut charcoal has the greatest adsorbing power and that each kind of wood charcoal has a different adsorbing power, owing to its affinity with gasses. DESAUSSURE[2] reported that charcoals which have many minute pores are best adsorbers because they present the largest surface for condensation. CHANEY[3] explained that the adsorbing power of charcoal is a function of the heat treatment applied in its preparation and also depends upon the hydrocarbons which are produced intermediately and have a different degree of easiness in decomposition. DEWAR[4] supposed a graphical formula of a fundamental charcoal molecule containning a large number of latent valences available for chemical or physical combination, (*Fig. 8.*) and stated that this structure might have some thing to do with general adsorbing power of charcoal. We have also investigated the difference between the activities of charcoals of common and glutinous starches and obtaine the following results. As the experimental details have already been reported in Journ. biol. chem., Tokyo, Japan, Jan. 1923, here we intend only to abstract, the resumé of those results. The adsorbing power of charcoals were determined with iodine potassium iodide solution and the const. 1/n of Freundlich's adsorption formula was calculated applying the method of least squares as follows:—

Fig. 8.



Charcoal from rice starch...Common (1/n) 0.1892–0.1663–0.1776
,, ,, ,, Glutinous ,, 0.2564–0.2210–0.2676–0.2660
,, ,, millet starch...Common ,, 0.306......Glutinous... 0.3544
,, ,, italian millet starch......Com. (1/n) 0.3181...Gluti. 0.3648

1) HUNTER:—Jour. chem. Soc., **24**, 76, 1871; **25**, 649, 1872.
2) DESUSSURE:—Proc. Roy. Inst., **18**, 180, 1905.
3) CHANEY:—Chem. Neros. News Des., 1919.
4) DEWAR:—Chem. News.

The values of $1/n$ of glutinous starches which indicate the tangents of the linear adsorption curves were greater than those of common starches in every case. If we accept Dewar's supposition of a graphical formula of a fundamental charcoal molecule, we must conclude that this difference is caused by the latent valences in the charcoal molecule available for chemical or physical combination.

III. STARCH SOLUTION WITH IODINE.

On the reaction of starch and iodine, a great many authors have discussed until, quite recently under the following different points of view. Padoa and Savare investigated the reaction of iodine potassium iodide solution to starch paste, and confirmed the MYLIUS[1] theory and concluded that the iodine starch is a compound of potassium iodide or hydrogen iodide and starch in the ratio of I : $(C_6H_{10}O_5) = 1 : 4$ and they rejected the adsorption theory. KATAYAMA[2] reported on the iodine color reaction of starch as follows:— "The iodine color reaction is produced by the equilibrium of iodine, starch and starch iodide in the presence of potassium iodide; the concentration of the blue color increases proportionally to the increase of the concentration of starch; but it is not clear whether the concentration of the blue color increases in proportion to the concentration of iodine. Against the former opinions COSTORE[3] confirmed that iodine coloration of starch in perfect soluion is wine-violet, in pseudo-solution is blue and in insoluble particles is bluish violet and concluded that this color reaction depends upon the size of colloidal particles. HARRISON[4] stated also on this color reaction that the presence of KI is not necessary but he could not deny the acceleration of iodine color reaction by weak acids or salts. Treating it with alcohol, he observed that the color of iodine-starch gradually changes just as in the case of Zsigmondy's gold colloidal solution. He concluded therefore that the color reaction of

---

BIBRIOGRAPHY.

1) MYLIUS:—Ber. deuts. Chem. Ges., **20**, 688, 1887.
2) KATAYAMA:—Zs. Anorg. Chem., **56**, 209–17, 1907.
3) COSTORE:—Gazz. Chim. Itali., **39**, I, 603–7, 1910.
4) HARRISON:—The Analyst, **28**, 1911.

iodine and starch is governed by its colloidal state only. From another point of view, BARGER[1] stated that the blue color of pure iodine solution with saponarin hydrosol is increased by potassium iodide as well as by other salts and temporarily destroyed by heating as in the case of starch. This report gave also very important suggestions for the following investigation by HARRISON.[2] He proved that the iodine color reaction of starch is always changed by the factors which change the colloidal state of starch, i.e., by the presence of salts and alcohol or by heating and boiling. He also explained that the change of color at high temperature or by the presence of alcohol is caused by the decreasing solubility of the iodine. BERZELLER[3] proved also that the reaction of starch with iodine is an adsorption phenomenon in which the equilibrium of reaction is readily obtained in dilute solution and the starch adsorbes much greater quantities of iodine in low temperature. Recently LANGE[4] also denied the opinion that iodine-starch is a chemical compound or solid solution and believed it to be an adsorption compound, formed by the precipitation which is caused by the two colloidal solutions of iodine and starch.

Now we must pay more attention to the latter opinion which is probably true, but it is not the principal object of our investigation, therefore we must also seek other literature which is concerned with the difference between common and glutinous starch. As is well known, the glutinous starch gives a red color with iodine whereas the common starch gives a blue color. On the color reaction of glutinous starch, Tanaka has investigated already and denied Dafert's erythrodextrine theory, Atkinson's albuminoid theory and Shimoyama's amylodextrine theory and concluded that the red color reaction of glutinous starch with iodine is a characteristic property of the starch granule itself. But he gave no explanation of this characteristic property. Therefore, the following experiments were undertaken.

1. Color Reaction of Pseudo-solution of Starch to Iodine.

The color of pseudo-solution of starch with iodine is variable

1) BARGER:—Chemical News **194**, 139, 1912.
2) HARRISON:—Zs. Chem. Ind. Kolloide, **9**, 5–9, 1913.
3) BERZELLER:—Biochem. Zeitschr., **84**, 106–17, 1917.
4) LANGE:—Biochem. Zeitschr., **95**, 46, 1919.

according to the ratio between adsorbed and remaining quantities of iodine. The following experiments were undertaken to prove how this color may be changed by the concentration of iodine in the starch solution, comparing common with glutinous starch. For the operation of our experiment, we took 5 cc. of starch solution of different concentrations, to which the different quantities of iodine potassium iodid solution were added. (The iodine potassium iodide solution was prepared by mixing 2 grs. of iodine, 6 grs. of potassium iodide and 100 cc. of water.) Then each mixture was diluted to equal total volume and the following colors were observed. In the following table, "D" expresses the original concentration of iodine potassium iodide solution.

TABLE II.

Iodine solution cc.	Common starch solution			
	0.05 %	0.1 %	0.2 %	05 %
0.1 D/4	blue	blue	blue	blue
0.1 D/2	brownish-blue	blue	blue	blue
0.5 D/2	brown	bluish-green	blue	blue
1.0 D/2	greenish-brown	brownish-green	blue	blue
1.0 D	reddish-brown	greenish-brown	brownish-green	greenish-blue
Iodine solution cc.	**Glutinous starch solution**			
	0.05 %	0.1 %	0.2 %	0.5 %
0.1 D/4	reddish-purple	violet-purple	light-purple	pink
0.1 D/2	brown	purple	purple	purple
0.5 D/2	brown	reddish-brown	brownish-purple	reddish-purple
1.0 D/2	brown	brown	reddish-brown	purple
1.0 D	—	—	—	—

By the above table, the same brown or the same reddih brown color was observed in two kinds of starch solution though it did not appear in the same concentration of iodine. In the glutinous starch solution, the reddish brown color appeared more clearly in dilute solution of iodine than in the case of common starch. This may be due to the fact that in glutinous starch solution, the quantity of iodine remaining unadsorbed was greater than in the case of common starch.

Next, we intended to examine the iodine color reaction of starch, when the starch content is in excess to the iodine content and we obtained the following results. In this experiment, we took 5 cc. 0.5 % starch solution and to each sample, the following different small quantities of iodine solution were added.

TABLE 12.

No. of experiment	Conc. of iodine solution	cc. of iodine solution added to starch sol.	Color of common rice starch solution	Color of glutinous rice starch solution
1	N/4000	0.4 cc.	no color	no color
2	N/4000	0.3 cc.	light purple	no color
3	N/4000	1.5 cc.	*deep blue	*light blue
4	N/2000	1.0 cc.	*deep blue	*light blue
5	N/2000	2.0 cc.	deep blue	purple
6	N/2000	3.0 cc.	deep blue	red

By the above table, almost the same blue color was observed in both, common and glutinous starch solutions. From these results (Table 11 & 12), we observed that, even in the case of glutinous starch, almost same blue color appears when the iodine content is in excess to the starch content and even in the case of common starch, practically the same reddish brown color appears when the starch content is in excess to the iodine content.

Concerning the intensity of the above same color in both starch solutions we obtained the following results using Duboscque's colorimeter.

TABLE 13.

No. of above experiment	Color of solution	Thickness of common rice starch sol. (mm.)	Thickness of glutinous rice starch sol. (mm.)	% of color intensity
3	blue	3.6	12.4	29.03
4	blue	2.0	11.1	18.01
7*	purple	11.0	7.0	63.63

In experiment No. 7, different quantities of iodine solution were added to the two starch solutions, i.e. 0.8 cc. to common and 4.6 cc. to glutinous starch solution. This was due to the fact that the purple color of the glutinous starch solution was more intense than that of common rice starch though the blue color in experiment No. 3 and No. 4 was more intense in common than in glutinous rice starch.

Here it was necessary to make further investigation on this color reaction and we thought it best to examine it with a spectroscope and we undertook the following experiments. At first we examined three different colors of iodine starch solution to know the change of the absorption band according to the colors; i.e. brown, green and blue. Thus we took 5 cc. of common starch solution, mixing with the following quantities of iodine potassium iodide solution which we used in the former investigation. For the operation of the spectrography[1], we used a quartz-cell of 10 mm. thickness filled with solution to be tested and, as an illuminating source, an electric lamp of 100 candle power, regulating the intensity with a photometer. Here we obtained the following numbers of wave-length of the boundary lines of the absorption bands which were measured on the photographic plates.

TABLE 14.

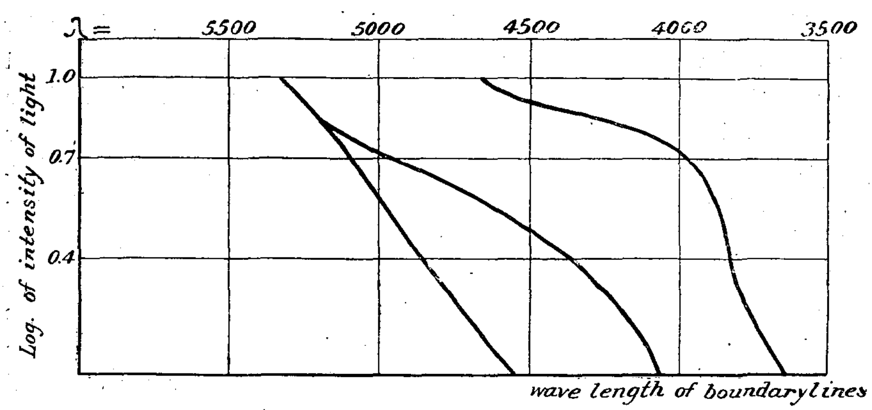
Exposure = 60 sec.	brown color	green color	blue color
Starch solution	5 cc. of 0.05 %	5 cc. of 0.1 %	5 cc. of 0.1 %
Iodine solution	1 cc. of 1/2 conc.	1 cc. of 1/2 conc.	1 cc. of 1/4 conc.
Secter of photometer	Wave-length of boundary line	Wave-length of boundary line	Wave-length of boundary line
1.0	4550	4105	3660
0.4	4850	4345	3835
0.7	5100	4990	3965
0.0	5325	5325	4650

From the above results we traced three curves, taking the log. of intensity of light on the ordinate and the wave-length of boundary lines of the absorption bands on the abscissa (*See photo. IV.*)

By these three curves we could observe that the absorption of the spectrum of brown was greater than that of blue which contained excess of starch. Next, further investigation was needed to compare the absorption of the color of common and glutinous starch in the same concentration of iodine mixture. Therefore we examined the solution of 10 mm. thickness by a quartz-spectroscope (D. I. Adam Hilgard, made in London), using a hydrogen tube of 7 cm. capillary, charging

1) TADOKORO:—Jour. Coll. Agr. Hokkaido Imp. Univ., X, 3, 1921.

Fig. 9.



ca. 15000 volts A. C. and took photographs with 6 minutes exposure.

Before the comparison of color reaction of both starches, we examined the change of absorption-bands on the spectrum of different iodine color reactions of soluble starch solution, during digestion by Takadiastase, and obtained the following results. We took 30 cc. of soluble starch solution and after digestion by 2 cc. of 1 % Takadiastase at 45° C, took out samples at different periods and examined them by spectrography with the same treatment as above mentioned.

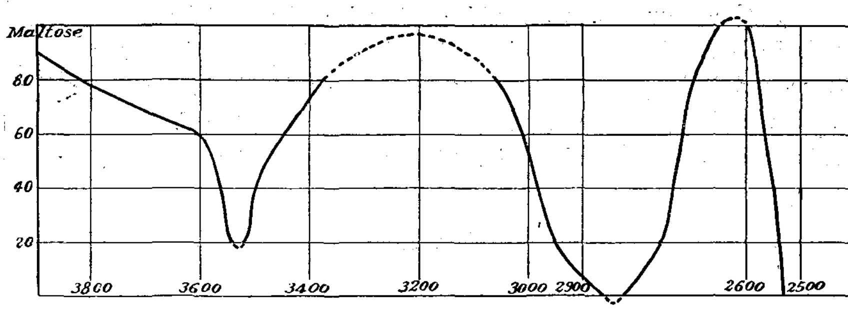
TABLE 13.

No.	Minutes of digestion	Color with iodine solution	Wave-length of boundary lines of absorption bands				
			(3700—3300)		(3100—2600)		<2600
1	0	blue	—	—	2824	2835	2535
2	20	reddish violet	3555	3545	2965	2745	2545
3	40	brownish violet	3555	3525	2975	2745	2555
4	60	reddish brown	3570	3430	3020	2720	2560
5	80	brown	3610	3395	3050	2700	2560
*6	maltose	brown	3810	—	—	2650	2520

Comparing with the photograph (I), we traced also the following curves, taking minutes of digestion on the ordinate and wave-length on the abscissa.

By this curve we observed that on the absorption bands of iodine color reaction of starch, during dextrination, there are different types of bands, i.e. the first is in part of 3750–3300 $\mu\mu$, the second is in part

Fig. 10.



of 3100–2600 and the third is in part of $<2600\ \mu\mu$. From these we knew that the blue color which is caused by the predomination of starch in solution shows greater transparency in the spectrum than that of violet or brown color which shows a larger absorption band.

In our last experiment on iodine color reaction of pseudo-solution of starch, the following spectrographyical operation was carried out to find the exact difference between the absorption bands of common and glutinous starches, by using the same quartz-spectroscope. All photographs were taken under 6 minutes exposure through 10 mm. thickness of liquid, illuminated by a hydrogen tube of 7 cm. capillary, charging ca. 15000 volts A. C. For this object, we prepared the following starch solutions of different concentrations as samples and 30 cc. of each sample were mixed with 2 cc. of 1 % iodine solution, and after operation the following results were obtained.

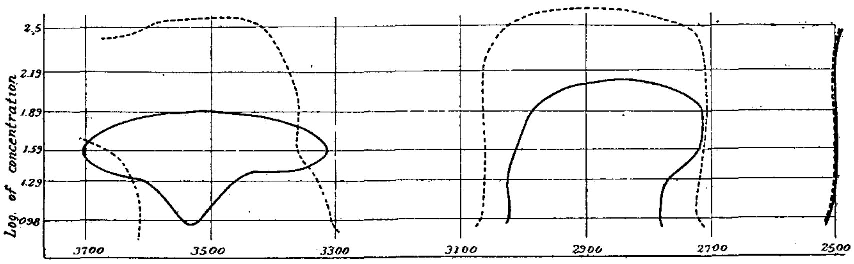
TABLE 16.

Concentration of starch solution	Wave-length of boundary lines of absorption bands	
	in common rice starch	in glutinous rice starch
0.0312 %	— — — — — 2510	3600–3420, 3035–2755, 2500
0.0156 %	— — — — — 2490	3750–3320, 3085–2705, 2505
0.0078 %	% 3520, 3000–2770, 2505	3750–3320, 3085–2705, 2505
0.0039 %	3725–3330, 3085–2775, 2507	3680–3340, 3070–2705, 2710
0.00199 %	3590–3460, 3025–2780, 2500	3650–3350, 3070–2715, 2500
0.00097 %	— 3520, 3010–2790, 2490	3650–3360, 3050–2720, 2500

Comparing with photographs (II & III) we traced also the following curves taking log. of concentration of starch solution on the ordinate and the wave-length on the abscissa.

By these curves we could distinguish three different absorption bands in both kinds of starch. The first is in part of 3800–3200 $\mu\mu$, the second is in part of 3000–2700 and the third is in part of $<$2500 $\mu\mu$ of wave-length. In common starch solution, the first and second bands were not observed in the higher concentration of starch while

Fig. 11.



in glutinous, they were clearly observed. If we consider the difference between these two kinds of starch, comparing with the former experimental results, we come to the following conclusion :— That the iodine adsorption of common starch solution is more powerful than that of glutinous, that is to say, in iodine mixture, the common starch solution contains less quantity of free iodine than glutinous. This conclusion can be confirmed also by a review of the results of the adsorption experiments.

2. *Decoloration of Iodine Starch Solution by X-ray.*

The action of ultraviolet ray on the colored products which starch and glycogen give with the iodine potassium iodide, was investigated by GAUTIER and NOGIER[1], they reported that starch blue in solution, when exposed to the ray of a mercury lamp become colorless. Recently Bordier (19) stated the X-ray has a bleaching action on starch blue solution and its action is more intense than that of ultraviolet rays. He explained that it is caused by change of iodine to hydrogen iodide in solution because after decoloration of starch solution it shows

1) GAUTIER and NOGIER :—Compt. rend. Soc. Biol., **69**, 156–7; 1911.

acid reaction. We therefore intended to determine the difference between the degree of decoloration of common and glutinous iodine starch by X-ray. We prepared the same blue solution with common and glutinous starch by the following treatment. Five cc. of 0.5 % starch solution was poured into a glass tube of ca. 12 mm., in diameter, and mixed with 1.5 cc. of N/4000 iodine potassium iodide solution and exposed under the X-ray of 2 miliamps. and 5 Benoist of hardness, using ca. 35000 volts A.C. The light blue solution of glutinous starch was easily bleached after exposing for ca. 10 minutes while the deep blue color of common starch solution still remained and after exposing for ca. 45 minutes this color entirely disappeared.

Next, we compared the resistance of the color of iodine and iodine-starch against the X-ray which was illuminated in the same way as before mentioned. In this experiment we took 5 cc. of 0.5 % starch solution and added 1.0 cc. of N/600 iodine solution, comparing it with iodine solution without starch. After 45 minutes exposure, the iodine solution became completely bleached, while iodine-starch solution still retained its color. It is a very curious fact that glutinous rice starch solution changes its color from red to blue, under the X-ray though this blue color is far lighter than that of common starch solution. After 2.5 hour exposure, the blue color of the glutinous starch solution faded away while that of the common starch solution still remained. If we compare these facts with the above experimental results, it is apparent that the excess of iodine in glutious starch is more quickly bleached and the remaining iodine starch solution shows a blue color like that of common starch. The bleaching of the color of common starch solution is very difficult because it contains a greater quantity of iodine-starch which has more resistance against the X-ray than free iodine.

3. Decoloration of Iodine Starch Solution by Chemicals.

It is well known that iodine-starch solution is decolorized by sodium thiosulphate. Clementi (17.) stated that iodized starch paste is decolorized not only by albumin, but also by many different types of proteins, also by tyrosin and furfural. We confirmed the bleaching actions of those substances and at the same time, observed that nitrobenzen, formalin, pyridin and alcohol have also the same bleaching action. Among them, pyridin has a very powerful bleaching action and it is easily soluble in water. When we considered this phenomenon regarding the difference in the properties of common and glutinous rice starches we supposed that there must be some difference between the decoloration of the two iodinestarch solutions. In the following experiment we used 5 % fresh starch solution mixing with 1/100ծ normal iodine solution as a sample and prepared 1 % sodium thiosulphate and 5 % pyridin solution as decolorizing reagents. Thus we took 5 cc of the starch solution, adding the following quantities of the iodine solution and this mixture was titrated instantly with both decolorizing reagents and the following results were obtained.

TABLE 17.

Iodine solution added to starch	Average of titration number (cc.) of pyridin solution				
	in water only	in common starch solution	(difference)	in glutinous starch solution	(difference)
0.5 cc.	0.6 cc.	1.9 cc.	1.5 cc.	1.4 cc.	0.9 cc.
0.8 cc.	0.85 cc.	3.4 cc.	0.7 cc.	2.3 cc.	0.7 cc.
1.0 cc.	1.2 cc.	4.1 cc.	2.6 cc.	3.0 cc.	0.8 cc.
1.25 cc.	1.45 cc.	6.7 cc.	1.6 cc.	3.8 cc.	1.3 cc.
1.5 cc.	2.0 cc.	8.3 cc.	2.8 cc.	5.1 cc.	2.2 cc.
2.0 cc.	2.7 cc.	11.1 cc.	2.4 cc.	7.3 cc.	1.2 cc.
2.5 cc.	3.2 cc.	13.5 cc.		8.5 cc.	
	(Average of titration numbers (cc.) of Na-sulphate solution)				
0.5 cc.	0.02 cc.	1.3 cc.	1.6 cc.	0.05 cc.	0.0 cc.
1.0 cc.	0.03 cc.	2.9 cc.	0.6 cc.	0.05 cc.	0.05 cc.
1.5 cc.	0.10 cc.	3.5 cc.	0.4 cc.	0.10 cc.	0.0 cc.
2.0 cc.	0.15 cc.	3.9 cc.	1.2 cc.	0.10 cc.	0.0 cc.
2.5 cc.	0.20 cc.	5.1 cc.		1.00 cc.	

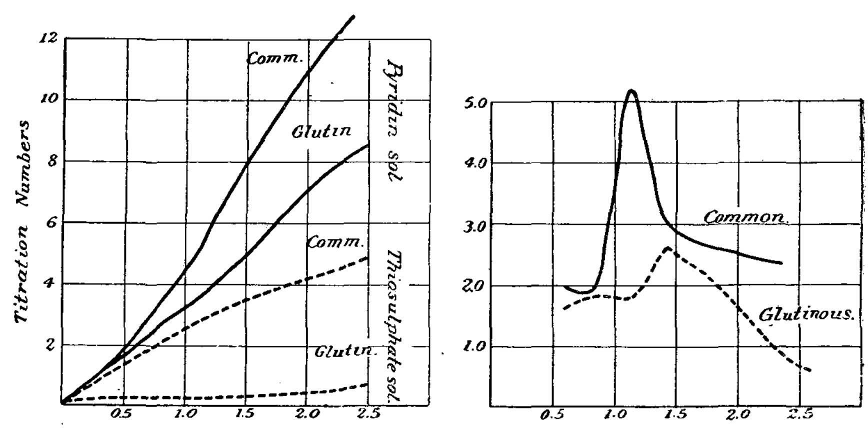
From the above results, we traced the following curves, taking the titration numbers on the ordinate and cc. of iodine solution on the abscissa (see *Fig. 11*). We traced two more curves from the following table in which the differences of the titration numbers of pyridin solution per 0.5 cc. of added iodine solution were calculated from the above difference and from these figures we observed the relative value of difference of the titration numbers in different concentration of iodine. That is to say, we observed the relative firmness of adsorption of iodine by starch which is indicated by the above relative value.

TABLE 18.

Iodine solution added to starch	Difference of titration numbers of pyridin solution			
	Common starch solution		Glutinous starch solution	
	of original	per 0.5 cc. of iodine	of original	per 0.5 cc. of iodine
0.5 cc.				
0.8 cc.	1.5 cc.	2.5 cc.	0.9 cc.	1.5 cc.
1.0 cc.	0.7 cc.	1.7 cc.	0.7 cc.	1.8 cc.
1.25 cc.	2.6 cc.	5.2 cc.	0.08 cc.	1.6 cc.
1.5 cc.	1.6 cc.	3.2 cc.	1.3 cc.	2.6 cc.
2.0 cc.	2.8 cc.	2.8 cc.	2.2 cc.	2.2 cc.
2.5 cc.	2.4 cc.	2.4 cc.	1.2 cc.	1.2 cc.

In the second curves (*Fig. 12*) we took the difference of the titration numbers per 0.5 cc of iodine solution on the ordinate and concentration of iodine solution on the abscissa.

Fig. 12.



Quantity of iodine solution.

Before drawing any conclusion, the following numbers as in the table 19 were calculated and a very interesting fact was observed that there are certain definite proportions between them as below.

TABLE 19.

cc. of iodine solution	Difference of titration numbers between common and glutinous rice starch solutions		Difference of titration numbers between pyridine and thiosulphate solutions	
	with pyridin solution	with thiosulphate	in common rice starch solutions	in glutinous rice starch solutions
0.5 cc.	0.5 cc.	1.2 cc.	0.6 cc.	1.3 cc.
1.0 cc.	1.1 cc. (0.5 × 2)	2.8 cc.	1.2 cc. (0.6 × 2)	2.9 cc.
1.5 cc.	3.2 cc. (0.5 × 6)	3.4 cc.	4.8 cc. (0.6 × 8)	5.0 cc.
2.0 cc.	3.8 cc. (0.5 × 8)	3.8 cc.	7.2 cc. (0.6×12)	7.2 cc.
2.5 cc.	5.2 cc. (0.5×10)	5.0 cc.	8.4 cc. (0.6×14)	8.2 cc.

From all of these results, the following conclusions were obtained, concerning the decoloration of iodine starch solution.

(1) The decolorizing action of sodium thiosuphate is far stronger than that of pyridin solution, the action of both is decreased in definite proportions by the increase of iodine concentration. Their decreasing ratio is very similar in both decolorizing reagents and in both starch solutions. These facts show that the reaction of glutinous rice starch with iodine as well as the reaction of common starch with iodine are the same kind of reaction, though there is a great difference quantitatively.

(2) The common starch solution has a greater affinity with iodine than that of glutinous and this difference is increased to a certain extent in proportion to the concentration of iodine solution.

(3) Their affinity with iodine has a maximum point in certain correlation of iodine and starch. In the above experiments this point is in concentration of N/5000–N/7500 iodine in 0.5 % starch solution.

4. *Alteration of Affinity of Starch Solution with Iodine by Age.*

Many authors have reported on the alteration of some properties of starch pseudosolution by age, for instance, on the alteration in viscosity and hydration degree. Samec (10.) concluded that the alteration of starch solution is observed in the decrease of viscosity, in its transparency and also in its sensibility to electrolytes. Here, in order to determine some differences between the alterations of the properties of common and glutinous starches the following experiments were carried out.

In this investigation we chose the decoloration method by pyridin solution which was used in the above experiment.

Five cc of 0.5 % starch solution were mixed with 2 cc of N/1000 iodine solution and titrated with 5 % pyridin solution until the iodine starch color become bleached.

TABLE 20.

Titration numbers (% of titration numbers to those of the fresh solutions)				
Age of solution	1 hour	2 days	4 days	6 days
Common starch solution	100	147.5	161.7	164.2
„ „ boiled for 1.5 hrs. at 95°C	100	116.0	116.0	126.0
Glutinous starch solution	100	103.0	119.0	124.0

For the determination of the reaction velocity of iodine with starch, we titrated the iodine starch solution with the pyridin solution at different periods after the mixing of both solutions, i.e. 5 cc. of 0.5 % starch solution and 2 cc. of N/1000 iodine solution and obtained the following difference between common and glutinous starch. All samples were kept in a water bath at 18°C during the process of their reaction and the following titration numbers were expressed in % of those which were instantly titrated.

TABLE 21.

Time	instantly	after 5 minutes	after 10 minutes	after 15 minutes	after 30 minutes
Common starch solution	100	121.5	128.0	133.0	151.0
Glutinous starch solution	100	106.8	112.0	112.0	113.5

From these results (table 20 & 21), we could observe that the affinity of common starch solution with iodine was increased daily until the 4th day while that of the same solution after long boiling increased very little as in the case of glutinous starch solution. In the case of common starch, the affinity with iodine increased minute by minute during the first 30 minutes, after mixing it with iodine solution, but in the case of glutinous rice starch, the affinity with iodine become almost constant after 10 minutes.

5. *Intensity of Iodine Color Reaction of Starch.*

The iodine color reaction of starch has been discussed by many authors, most of whom believed that the reaction is not a chemical but a physical reaction in which the solution of iodine is adsorbed by the starch. HARRISON[1] stated that this color which is produced by the color reaction of starch is formed with pure iodine and the intensity is increased by the presence of any salts or weak acids. Castore gave the conclusion that coloration of iodine starch is governed by the size of particles and the structure of the colloidal solution. CASSAL[2] reported that the intensity of this color reaction was interfered with by many factors, especially, temperature and turbidity. Harrison investigated the interfering factors thoroughly and concluded that the color reaction was always influenced by the degree of dispersion of starch and iodine in solution. LORENZ[3] proved that the sensibility of iodine starch reaction is increased by the presence of HI or iodide. Recently Lange (l.c.) also stated that the intensity of iodine color reaction of the electronegative colloid complex (starch iodide) depends on the degree of its solubility or its gelatination; an increased degree of solubility lessens the color intensity while a change towards precipitation increases the color. Therefore we undertook the following experiments in order to compare the intensity and the sensibility of iodine color reaction in common and in glutinous rice starch solution. For this purpose we took 5 cc of 0.25 %, 0.50 %, or 1.0 % starch solution in a test tube, titrated them with the following iodine solution until the color appeared in the mixture. The quantity of iodine solution which forms the first color in starch solution was determined as in the following table.

1) HARRISON:—Proc. Chem. Soc., 26, 252, 1911.
2) CASSAL:—Chem. Eng. and Works Chemist, I, 68, 1912.
3) LORENZ:—Chem. Analyst, 19, 20, 1916

TABLE 22.

Concentration of starch solution	0.25 %		0.50 %		1.0 %	
Concentration of iodine solution	Common	Glutinous	Common	Glutinous	Common	Glutinous
N/10000	1.4 cc.	2.7 cc.	2.5 cc.	3.8 cc.	2.5 cc.	2.7 cc.
N/5000	0.6 cc.	1.6 cc.	1.7 cc.	2.8 cc.	2.2 cc.	2.5 cc.
N/1000	0.25 cc.	0.30 cc.	0.20 cc.	0.30 cc.	—	—

(The above titration numbers are the average of five samples).

By this table we observed that the common rice starch solution reacts with iodine in more dilute solution than that of glutinous and this difference becomes greater in very dilute starch solution, that is to say, this difference is greater in higher dispersed colloidal starch solution.

6. Adsorption of Iodine by Starch Solution.

In the previous experiment, we investigated the adsorption phenomenon of iodine by starch granules and observed that there are remarkable differences between glutinous and common rice starches as well as in the case of millet. Therefore, in order to examine the adsorption phenomenon of iodine by starch pastes, the following experiment was undertaken with glutinous und common rice starch pastes.

METHOD OF OPERATION.

Into each bottle, was put 0.5 gr. of starch, to which 50 cc of water were added and heated by steam in the autoclave under 2 atmospheric pressure for 15 minutes, when the pseudo solution of starch was obtained. To each bottle was added the following cc. of N/10 iodine solution such as 1 cc., 2 cc., 3 cc., 4 cc., 6 cc., 7 cc., 9 cc., 10 cc., and brought to an equal total volume by addition of water. Each bottle was shaken on the shaking apparatus for 30 minutes when the equilibrium of adsorption of iodine by starch paste was obtained. The solution in each bottle was mixed thoroughly with 70 cc of 95 % alcohol, filtered and the precipitate on the filter paper was washed twice with 10 cc of 95 % alcohol, and then the whole filtriltrate was titrated with N/10 sodium thiosulphate solution and the amount of iodine adsorbed by starch paste from the various concentration of iodine was determined as follows.

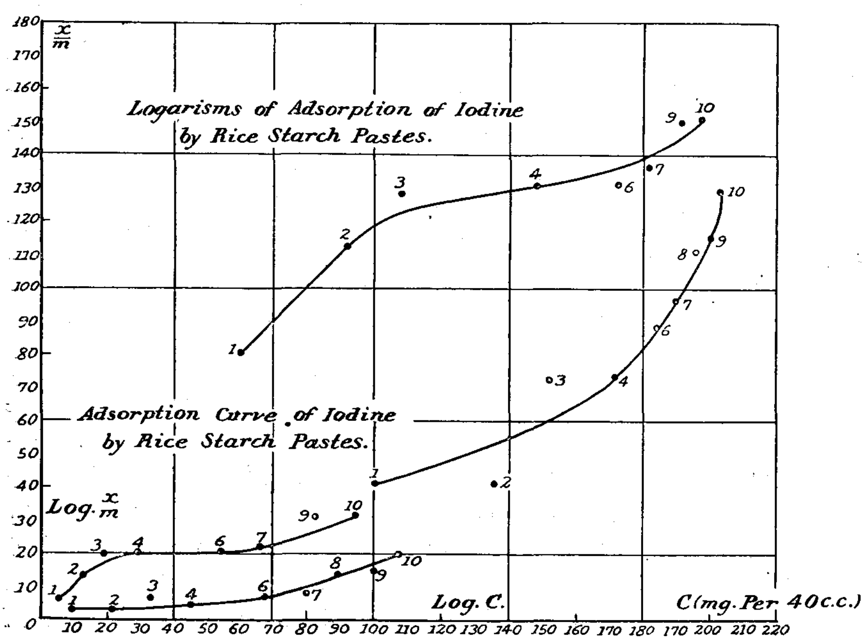
In subsequent tables, the results obtained from the above experiment are given where, C= concentration of iodine solution at equilibrium. X/M=amount of iodine adsorbed by 0.5 gr. of starch.

TABLE 23.

cc. of N/10 iodine solution	Glutinues rice starch paste				Common rice starch paste			
	X/M (mg.)	C (mg.)	Log X/M	Log C	X/M (mg.)	C (mg.)	Log X/M	Log C
1 cc.	2.5370	10.1480	0.40432	1.0063840	6.3425	6.3425	0.802260	0.8022600
2 cc.	2.5370	22.8330	0.40432	1.3585670	12.6850	12.6850	1.103290	1.1032900
3 cc.	5.0740	32.9810	0.70535	1.5182630	19.0275	19.0275	1.279394	1.2793940
4 cc.	5.0740	45.6660	0.70535	1.6595940	20.2960	30.4440	1.307412	1.4835000
6 cc.	7.6110	68.4990	0.88144	1.8356684	20.2960	55.8140	1.307412	1.7467420
7 cc.	8.8795	79.9155	0.94835	1.9026360	22.8330	65.9620	1.358567	1.8119294
9 cc.	13.9535	100.2115	1.14470	2.0009130	31.7125	82.4250	1.501239	1.9167350
10 cc.	19.0275	107.8225	1.27939	2.0327000	31.7125	95.1375	1.501239	1.9783520

By taking C on the abscissa and X/M on the ordinate, the following curves were obtained. (*Fig. 13*). The corresponding values for log

Fig. 13.



X/M and log C were also plotted, taking log X/M on the ordinate and log C the abscissa and the following figures were obtained (*Fig. 13*).

From the above tables and figures, we can observe that :—

(a) The adsorption phenomenon of iodine by glutinous and common starch pastes does not follow Freundlich's adsorption formula. But as the concentration of iodine increases, the amount of iodine adsorbed by starch pastes also increases.

(b) The amount of iodine adsorbed by glutinous starch paste is far smaller than that adsorbed by common starch pastes.

(c) The amount of iodine adsorbed by starch granules is far larger than that adsorbed by starch pastes. By comparison of the above result, the following is found.

TABLE 24.

Adsorbents	Amount of iodine adsorbed (mg.)
by 1 gm. of common rice starch granules	From 24.3552 to 262.8332
by " " " paste	From 12.6850 to 63.4250
by 1 gm. of glutinous rice starch granules	From 19.2812 to 262.8332
by " " " paste	From 5.0740 to 38.0550

IV. SOME COLLOIDAL PROPERTIES OF STARCH SOLUTION.

1. On the Viscosity of Starch Solution.

Glutinous rice is used in the preparation of "Mochi," a kind of Japanese food and characterised by its viscosity being much higher than that of common rice. Therefore, in order to examine whether its high viscosity is due to its characteristic property i. e. to the high viscosity of the glutinous rice starch or not, we carried out the following experiments with the glutinous and common rice starches. Since the age of the pseudosolution and the temperature as well as the presence of even a small quantity of acid, alkalies or other chemicals which give electric charge to the colloidal particles, have much influence on the viscosity, we considered those factors very carefnlly in its determination.

(a) *100 cc of 0.25, 0.5, 0.7 and 1.0 % starch solutions were taken,* and the viscosity of those solutions was measured by a MacMichael viscosimeter, at 16.5°C.(*) From the average numbers of three samples we calculated the following relative viscosity (water = 1) at this temperature.

TABLE 25.

Concentration of starch solution	Rice starch		Millet starch		Italian millet starch	
	Common	Glutinous	Common	Glutinous	Common	Glutinous
0.25 %	2.25	2.43	2.28	2.55	1.78	2.07
0.50 %	2.50	3.78	2.88	3.71	2.28	2.65
0.70 %	2.78	4.27	3.82	5.18	2.56	3.28
1.00 %	2.93	10.57	7.42	11.00	3.21	5.35

(b) 10 cc of 1 % or 2 % starch solution were introduced into an Ostwald's Viscosimater and after cooling at 20° C, the flowing time was determined. The time(t) required for the outflow of starch solution was noted and compared with that of water(to) at 20° C. The ratio t/t_0 was used to compare the viscosity of glutinous and common rice starches and the results are given in the following table.

TABLE 26.

Flowing time	Glutinous rice starch (1 %)	Common rice starch (1 %)	Glutinous rice starch (2 %)	Common rice starch (2 %)
t	21″1/5	14″0	25″3/5	17″3/5
to	8″3/5	8″3/5	8″3/5	8″3/5
t/to	2.465	1.628	14.605	2.047

By the above tables, the viscosity of glutinous starch solution is higher than that of common starch solution and its difference is strongly marked at the higher concentration of the starch paste.

(c) The following amounts of starch such as 1 gr., 0.875 gr., 0.750 gr., 0.625 gr., 0.5 gr., 0.375 gr., were dissolved in 100 cc of alkali solution(5 cc of N/10 NaOH + 95 cc H_2O) 10 cc of each solution were introduced into an Ostwald viscosimeter and the time of outflow

*) The MacMichael's viscosimeter was made in Eimer and Amend Co., New York City, U.S.A. In this viscosimeter, a plunger was suspended in a cup of fluid. The force exerted on the plunger by the rotation of the fluid, was measured and this force was proportional to the viscosity.

was determined in the same manner as above(b). The results obtained are given in the following table, $t_0 = 8'' \ 3/5$, where, t_0 is the time required for the outflow of 10 cc of alkaline water (5 cc of N/10 NaOH + 95 cc H_2O).

TABLE 27.

Amount of starch (%)	Glutinous rice starch		Common rice starch	
	t	t/t_0	t	t/t_0
1.000	52″	6.05	40″	4.65
0.875	42″	4.88	27″	3.14
0.750	35″	4.07	25″	2.91
0.625	23″	2.67	19″	2.21
0.500	18″	2.09	15″2/5	1.91
0.375	15″	1.74	13″3/5	1.58

According to the above table, the viscosity of glutinous rice starch in such a concentration or alkali as above is also greater than that ot common rice starch. And similary with the case of water solution, its difference is strongly marked at the higher concentration of starch solution.

(d) The viscosity of starch solution was determined in the presence of tannin solution by the following treatment. Each 40 cc of the same starch solution was mixed with the following quantities of tannin solution and the change of the viscosity of the mixture was determined by the MacMichael viscosimeter at 16–17° C. The relative viscosity was calculated as in the case of(a) ($H_2O = 1$)

TABLE 28.

% of starch solution	Added quantity of tannin sol.	Rice		Millet		Italian millet	
		Common	Glutinous	Common	Glutinous	Common	Glutinous
0.5 %	0.3 cc.	2.28	2.57	2.59	3.29	3.57	2.28
0.5 %	0.6 cc.	2.87	2.59	2.89	2.89	2.89	2.27
0.5 %	1.0 cc.	3.50	2.57	2.89	2.87	9.44	2.21
0.5 %	1.5 cc.	3.50	3.57	2.87	2.89	10.11	2.28
0.7 %	0.3 cc.	2.78	4.86	4.57	4.42	9.25	4.28
0.7 %	0.6 cc.	3.28	5.00	7.85	3.14	13.48	3.43
0.7 %	1.0 cc.	4.28	4.86	5.14	3.14	14.57	3.57

% of starch solution	Added quantity of tannin sol.	Rice		Millet		Italian millet	
		Common	Glutinous	Common	Glutinous	Common	Glutinous
0.7 %	1.5 cc.	5.00	4.71	4.42	3.57	14.00	3.71
1.0 %	0.3 cc.	2.71	9.86	7.57	6.14	5.28	5.28
1.0 %	0.6 cc.	9.14	9.71	12.28	7.00	16.28	5.42
1.0 %	1.0 cc.	19.28	9.86	11.57	6.85	17.14	5.28
1.0 %	1.5 cc.	16.77	7.28	7.71	5.88	14.71	5.57
1.0 %	2.0 cc.	15.28	6.28	—	—	—	—

By the above table we could observe that the viscosity of common starch solution was increased in the presence of small quantity of tannin solution and was decreased in the presence of large quantity of tannin solution. In the case of glutinous starch solution, there was not so great a change of viscosity as that of common starch solution.

2. *Syneresis of Starch Solution.*

Pseudo-starch solution on standing separates into two phases, a phase containing more solid and a liquid phase, containing very little starch. This phenomenon was called "syneresis" by Graham. This phenomenon is probably due to the aggregation of the molecular complex, the colloid becoming less dispersed and forming a phase containing more solid OSTAWALD[1)] stated that syneresis is caused not only by the change of dispersion degree but that it depends also upon the phenomenon of swelling. Here, we carried out the following experiments, concerning the velocity of syneresis as well as the change of viscosity according to the syneresis of glutinous and common starch solutions and obtained the following results.

The following % of starch solution such as 0.5,1.0,1.5,2.0,2.5 were prepared. 15 cc of each solution were introduced into a test tube and the velocity of syneresis of starch solution was determined by measuring, from time to time, the following ratio :—

$$\frac{a}{b} = \frac{\text{the length of clear liquid portion from the above surface}}{\text{the total length of the liquid and solid gel portion from the above surface}}$$

1)

The results obtained are given in the following table.

TABLE 29.

Time of observation	Common rice starch (a/b)					Glutinous rice starch (a/b)				
	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %	0.5 %	1.0 %	1.5 %	2.0 %	2.5 %
instantly	0	0	0	0	0	0	0	0	0	0
after 13 hours	0.185	0.085	0.020	0.015	0	0.032	0	0	0	0
after 23 hours	0.336	0.140	0.027	0.026	0	0.063	0	0	0	0
after 37 hours	0.540	0.248	0.036	0.035	0	0.083	0.012	0.012	0	0
after 47 hours	0.700	0.276	0.050	0.041	0	0.095	0.012	0.021	0	0
after 61 hours	0.810	0.402	0.058	0.053	0	0.107	0.013	0.021	0	0
after 69 hours	0.821	0.456	0.060	0.053	0	0.131	0.013	0.021	0	0
after 109 hours	0.840	0.602	0.078	0.188	0.023	0.191	0.023	0.037	0	0
after 133 hours	0.852	0.602	0.078	0.238	0.036	—	0.023	0.037	0	0
after 157 hours	0.859	0.622	0.078	0.290	—	—	0.037	0.056	0	0
after 253 hours	0.869	0.668	0.078	0.387	—	—	0.048	0.094	0	0

If we plot the curve, taking the ratio (=a/b) on the ordinate and % of starch solution on the abscissa, the following are obtained. (*Fig. 15*)

CONCLUSION.

From the above table, we can observe that (a) the velocity of syneresis of the rice starch is much quicker in the dilute solution of starch in the case of glutinous as well as in the case of common rice starch.

(b) The velocity of syneresis of the common rice starch is quicker than that of glutinous rice starch and its difference is very marked in the higher concentration of starch.

Next, to determine this difference, we took 1000 cc. of 1 % starch solution and transferred it into a cylinder of 20 cm height. After standing 24 hours, we observed three different layers in common starch solution, in which, the upper was clear, the middle was opaque and the lower was semisolid gel, while in the case of glutinous there were no separated layers. After 48 hours, ca. 2 cm of the upper layer of glutinous starch solution became clear. Therefore, we took out 50 cc of starch solution from the different layers of 15 cm, 5 cm and 1.5 cm height from the bottom and examined the iodine color reaction and measured the intensity by decolorization method with pyridin solution, as described in the above experiment.

The iodine color reaction was tested with 5 cc of starch solution, mixing 1 cc of N/1000 iodine solution. In the case of common starch solution, a blue color was observed in the upper layer and a purple or violet color in the lower layer. The same observation were also obtained in the case of glutinous. When we continued the syneresis for four days in the case of common and 6 days in the case of glutinous, we observed that in common, almost the whole of the solution became clear and starch subsided only in the part of 2 cm from the bottom, while in glutinous, the upper 5 cm became clear and the middle opaque layer occupied the larger part of the total volume. Here we separated the solution by the above difference and examined the following properties.

TABLE 30.

	Common rice starch solution		Glutinous rice starch solution		
	upper	lower	upper	middle	lower
Specific gravity	1.0008	1.0209	1.0015	1.0023	1.0055
Viscosity t/t_0	1.00	36.90	1.00	1.34	4.71

By the above results, we observed that in the case of common starch solution, syneresis occurred very quickly while in the case of glutinous starch solution, it could hardly be obtained even after long standing. Here, in order to know by what character of both kinds of starch solution, this difference would be caused, we examined the change of viscosity of the same rice starch solution by a MacMichael viscosimeter during a standing period and obtained the following results (100 cc of starch solution was transfered into the MacMichael viscosimeter and operated at 16–17°C).

TABLE 31.

% of rice starch solution	Standing period			
	The same day	After 2 days	After 10 days	After 20 days
0.5 % Common starch solution	1.88	—	1.80	—
0.5 % Glutinous starch solution	3.37	—	2.42	—
1.0 % Common starch solution	3.50	3.28	3.00	2.71
1.0 % Glutinous starch solution	10.42	9.00	3.71	2.28

Each 100 cc. of 1.5 % glutinous starch solution was taken and the viscosity was measured daily by the same viscosimeter and obtained the following results.

TABLE 32.

Date sample	Glutinous rice starch solution		Glutinous millet starch solution	
	A	B	A	B
12 December	33.42	39.57	42.71	40.41
13 "	31.42	33.00	30.28	34.59
15 "	22.57	14.71	14.57	16.00
17 "	19.71	9.71	11.01	14.71
19 "	16.88	8.14	8.00	10.14

By the above two tables, the viscosity of common rice starch solution was not changed during many days though the syneresis occurred very easily in the solution. But the viscosity of glutinous rice starch solution decreased very rapidly though syneresis was very hard to obtain. The daily decrease of viscosity of glutinous starch solution was very rapid and this decreasing was greater in the concentrated than in the dilute solution.

According to the above experimental results of the viscosity and syneresis of both kinds of starch solution, the following conclusions might be drawn for the difference between the characters of common and glutinous starch solutions.

(1) The viscosity and the hydration of the glutinous starch solution were greater than those of common starch solution. In the case of common starch solution, the viscosity was increased very rapidly by the addition of even a small quantity of tannin solution whereas in the case of glutionous starch solution, no great effect was obtained This is probably due to the fact that the degree of dispersion of the glutinous starch solution is greater than that of the common starch solution. And in the case of common starch solution, the degree of dispersion is increased by the increase of dissociation degree which is caused by the electric charge, obtained by the addition of tannin solution, but in the case of glutinous starch solution, no increase of the dispersion degree could be obtained by the above process.

(2) In the case of common starch solution, syneresis occurred very rapidly, while, in the case of glutinous starch solution, syneresis was

very hard to obtain, though a great change of viscosity occurred in course of time. This is probably due to the fact that in the common starch solution, aggregation occurred very rapidly, while in the glutinous starch solution aggregation was very hard to obtain. The great change of viscosity of glutinous starch solution in the course of time is probably due to the hydrolytic cleavage of molecules as in the case of Traube's β-gelatine which is produced from β-gelatine by the hydrolytic cleavage due to long heating.

3. Coagulation of Starch Solution.

The coagulation of pseudo-starch-solution is caused by the presence of H-ion and the coagulates thus produced can be dissolved again by the presence of OH-ion. Among many authors[1] Fouard[2] studied thoroughly this phenomenon, comparing the coagulating power which is caused by many kinds of acid is in the same H-ion concentration, and stated that the coagulation is accelerated by the presence of H-ion and the increase of temperature. He supposed that in the coagulation of pseudo starch solution, a complex of starch molecules combined with H-ion will be formed.

From these reports, we assumed that if there is any difference between the coagulating phenomenon of pseudo starch solution of common and glutinous rice, it must be caused by the difference of molecular affinity or combining power with cation. Therefore we carried out the following experiment with 1 % starch solution at 20°C, mixing with potassium iodide, hydrochloric acid alcohol, tannin, ferrous sulphate and lead acetate solution as coagulating reagents.

(a) Different quantities of N/1 solution of potassium iodide as in the following table were added, and after one hour, we examined whether coagulation had occurred or not.

(b) Five cc. of 95 % alcohol was added to 5 cc. of the samples and mixed with the different quantities of HCL solution of various concentrations such as N/10, N/100, N/500, N/1000. After mixing, we noted the coagulation in each sample.

1) WOLFF U. FERNBACH:—Compt. rend., 138–819. 1904; MALFITANO u. MOSCHKOFF: —Compt. rend. 150–710, 1904.

2) FOUARD:—Bull. assoc. Chim. Sucr. dist., **24**, 1007, 1907. Compt, rend., **144**, 501–03, 1366–68, 1907.

(c) Different quantities of 5 % tannin solution or 5 % ferrous sulphate solution were added to the samples and their coagulation at different periods was examined.

(d) Lead acetate solution, was prepared by dissolving 120 grs. of lead acetate and 60 grs. of lead oxide in 400 of water. The samples were mixed with the different quantities of this reagent and the coagulation of starch solution was observed.

TABLE 33.

Quantities of reagent	Coagulation by N/1 KI-solution 5 cc. of starch solution was taken Common	 Glutinous	Quantities of reagent	Coagulation by HCL-alcohol sol. 5 cc. of starch sol. was taken Common	 Glutinous
0.50 cc.	–	–	0.25cc. N/1000	–	–
1.00 cc.	+	–	0.10 cc. N/500	–	–
1.50 cc.	++	–	0.25 cc. N/500	–	–
2.00 cc.	+++	–	0.10 cc. N/100	+	–
2.50 cc.	++++	–	0.25 cc. N/100	++	–
3.00 cc.	+++++	–	0.10 cc. N/10	++	–
	Coagulation by tannin solution.			Coagulation by 5 % $F_e SO_p$ solution	
0.10 cc.	–	–	0.50 cc.	–	–
0.50 cc.	+(after 1 hr.)	–	1.00 cc.	–	–
1.00 cc.	+(after 30 min.)	–	1.50 cc.	–	–
1.25 cc.	+(after 20 min.)	–	2.00 cc.	+(after 10 min.)	–
1.50 cc.	+(after 15 min.)	–	2.50 cc.	++(after 10 min.)	–
1.75 cc.	+(after 10 min.)	–	3.00 cc.	+++(after 10 min.)	–
2.00 cc.	++(after 10 min.)	–	3.50 cc.	++++(after 10 min.)	–
	Coagulation by Pb-acetate solution				
0.10 cc.	+	–	0.75 cc.	++++	+
0.25 cc.	++	–	1.00 cc.	+++++	++
0.50 cc.	+++	–	1.25 cc.	+++++	+++

(Coagulation = +......++......+++ No coagulation = –)

From these results, we observed that, in the case of common starch solution, the coagulation was caused very easily by the presence of H-ion and of metal salts, while in the case of glutinous starch solution, the coagulation was very difficult and needed greater quantities of those reagents.

On the coagulation of rice starch solution by tannin, we examined the change of surface tension with the following treatment. 10 cc of 1.0 % or 2.0 % rice starch solution were mixed with following quantities of 5.0 % tannin solution and its surface tension was measured by NOUY's apparatus[1] which was calibrated to indicate the surface tension of water=75 dynes per sq. cm. The numbers in the following table are the averages of 5 samples.

TABLE 34.

Quantities of tannin solution	Common rice starch solution		Glutinous rice starch solution	
	1.0 %	2.0 %	1.0 %	2.0 %
Starch only	75.5	73.1	75.5	72.2
+0.5 cc. tannin	72.5	72.8	*66.9	*66.2
+1.0 cc. „	71.6	72.2	66.2	66.0
+1.5 cc. „	69.6	70.9	66.0	65.0
+2.0 cc. „	67.5	69.5	65.5	65.5
+2.5 cc. „	66.2	67.8	65.0	65.1
+3.0 cc. „	64.8	66.2	64.8	65.0
+3.5 cc. „	63.4	64.8	64.5	65.0
+4.0 cc. „	63.0	64.2	64.8	64.8
+4.5 cc. „	*62.0	*63.4	*62.0	*63.4

According to the above table, the following conclusion may be drawn. In the case of common rice starch solution, the change of the surface tension occurred very gradually and decreased according to the increase of the quantity of the tannin solution added. In the case of glutinous rice starch solution the change of the surface tension did not occur so gradually but quite suddenly at one point i.e. decreased suddenly with the first addition of a small quantity of tannin solution, though, after which, the decreasing degree of the surface tension was very slow.

This is probably due to the difference between the dispersion degree of common and glutinous rice starch solutions.

4. *Starch Solution as a Protective Colloid.*

The protective action of starch solution is a well known fact. A

1) NOUY's:—Journ. General Physiology vol. I, No., 5, 1919.

few years ago, GUTBIER and WEINGARTNER[1] investigated starch as a protective colloid against the coagulation of silver and gold colloid solution. ZSIGMONDY[2] in his latest work stated its gold value comparing it with dextrine. In our experiment it is not our object to determine the gold value but to determine any difference between the protective power of common and glutinous starch sols.

In the comparison of protective action of common and glutinous starch sol, we used 2N-NaCL solution, 0.5 % starch solution and a colloid gold solution which was prepared by Zsigmondy's method. But, as we observed in the preliminary experiment that the difference was very small, we had to have recourse to more delicate method. Therefore we intended to determine their difference according to the change of color of 10 cc gold solution in the mixture of NaCL and starch sol and repeated the experiment, changing their concentrations.

TABLE 35.

cc. of 2N/1 NaCL	0.5 cc. of starch sol. (5 mm. after)		cc. of N2/1 NaCL	0.3 cc. of starch sol. (5 mm. after)		0.25 cc. of starch sol. (10 mm. after)		0.25 cc. of starch sol. (1 hour after)	
	Common	Glutinous		Common	Glutinous	Com.	Gluti.	Com.	Gluti.
0.0 cc.	−	−	2.5 cc.	+	−	+	−	++	+
1.0 cc.	−	−	3.0 cc.	+	−	+	−	++	+
2.0 cc.	−	−	3.5 cc.	+	−	+	−	++	++
3.0 cc.	+	−	4.0 cc.	+	−	+	−	++	++
4.0 cc.	+	−	4.5 cc.	+	−	+	−	++	++

In the above table, the violet color of the mixture was indicated by sign (†), more bluish violet color by (††) and red color by (–). From these results, we observed that the action of glutinous starch sol. against the coagulation of gold colloidal solution is stronger than that of common starch sol.

1) GUTBIER u. WEINGARTNER:—Koll & Beihf., **5**, 211–, 1914.
2) ZSIGMONDY:—Ein Lehrbuch Kolloidchemie, Leipzig, 1920, s 175.
3) „ „ „ „ „ s 150.

V. SOME PROPERTIES OF STARCH GEL.

1. *Dehydration of Gel.*

The dehydration of hydrogel is different according to its structure. Therefore if there is any difference between the gel structures of common and glutinous starches, their dehydration degree would be also different. In order to examine this, the following experiment was carried out. For the preparation of starch-gel we took 1000 cc of 1.0 % starch solution and added to it 5 % of tannin solution until starch was precipitated and observed the following difference between the powers of the gel of common and glutinous starches to contain water. The formation of starch gel by tannin took place with the separation of water from the hydrosol.

TABLE 36.

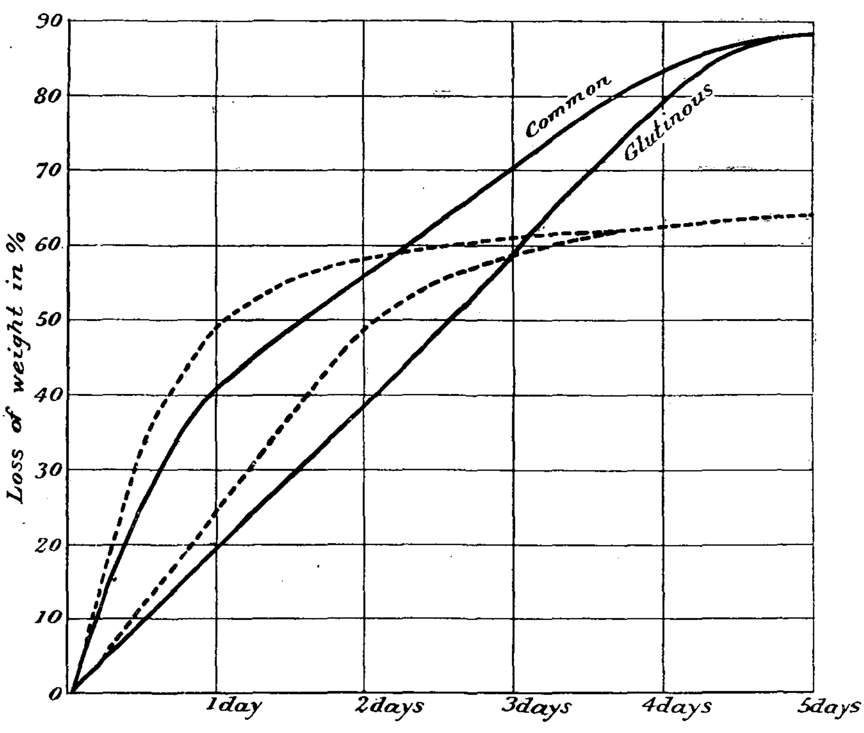
Starch	Wt. of samples	cc. of starch & tannin sol.	cc. of filtrate	Filtrate, % of original
Common	10.0 gr.	1600.0 cc.	1325.0 cc.	82.8 %
Glutinous	10.0 gr.	1850.0 cc.	1640.0 cc.	88.6 %

In the gel-formation of starch solution, the glutinous starch separates greater quantity of water than that of common rice starch. From this fact we expected to obtain the difference between the degrees of dehydration of the two kinds of gel and for this purpose we carried out the following experiment. 1 gr. of starch was mixed with 50 cc of water, formed into paste and precipitated by 5.0 % tannin solution. Those precipitates were put on a filter and left standing for 18 and 48 hours to drain off the excess of water. The definite quantity of gel was taken in a dish of dia. 47 mm and kept in a H_2SO_4 desiccator, weighed day by day to determine the loss of weight. Thus, the following results were obtained.

TABLE 37.

Period	Loss of weight in % of original weight			
	after standing for 18 hrs.		after standing for 48 hrs.	
	Common	Glutinous	Common	Glutinous
Original weight	5.6971 gr.	2.3464 gr.	6.8307 gr.	1.9173 gr.
after 1 day	43.5	49.1	19.5	23.3
after 2 days	54.7	58.0	37.4	49.2
after 3 days	70.5	60.3	58.8	59.7
after 4 days	83.7	61.0	79 9	62.8
after 5 days	86 6	61.8	—	—

Fig. 14.



Next, the same experiment was repeated with starch gel of salicylic acid, taking samples in a glass tube of dia. 12 mm. and following result was obtained :—

TABLE 38.

Starches \ Period	Loss of weight in % of original weight				
	after 3 days	after 7 days	after 10 days	after 15 days	after 22 days
Common	13.4	26.9	32.8	38.4	51.7
Glutinous	10.6	20.3	25.9	31.4	42.9

From the above numbers and figures we were able to observe that the water contents of the glutinous starch gel is less than that of the common and the dehydration velocity of the former is greater than that of the latter.

2. *Solubility of Starch Gel.*

The fresh gel. of common or glutinous starch had a different character in its solubility when separately treated with hot ferric chloride or calcium chloride or sodium hydroxide solution. When starch gel of tannin was boiled with ferric chloride or calcium chloride solution, it was partially reversed, but in the case of common starch large flocculent precipitates were formed and in the case of glutinous starch, only small precipitates were formed. When we boiled these two kinds of gel with 2.5–5.0 % of sodium hydroxide solution, they were also reversed and the common starch gel formed a viscous turbid solution while the glutinous starch all became transparent. The powder of these gels swelled up in boiling water and their iodine color reaction could be observed as in the case of ordinary starch solution.

3. *Viscosity of Reversed Gel.*

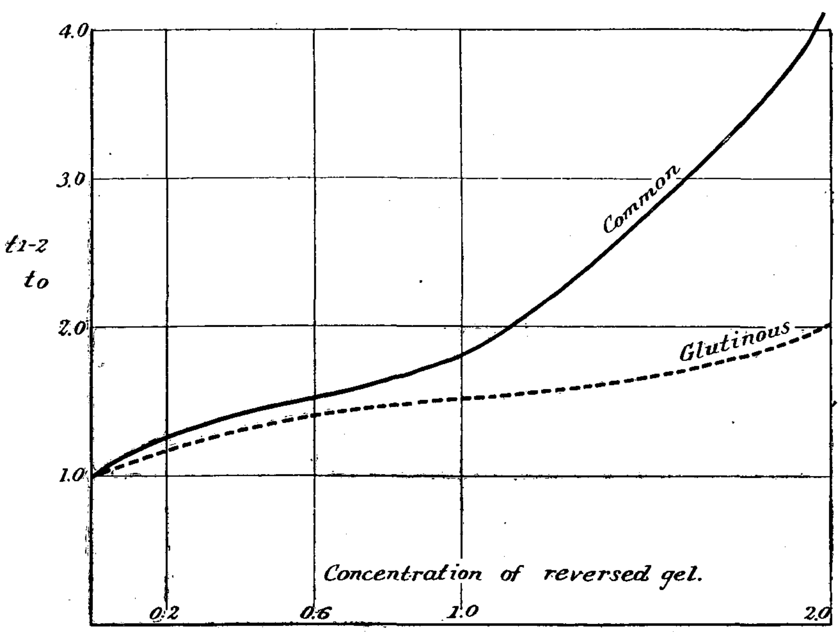
As we observed by the above experiment that the reversed tannin gel. of common starch seems to be more viscous than that of glutinous starch we examined its difference more exactly with Ostwald's viscosimeter. We prepared the following different solutions of reversed starch gels treating them with hot 1 % potassium hydroxide solution and after coolling at 17°C, we determined their viscosity with Ostwald's viscosimeter. For comparison of viscosity, we used the ratio t_1/t_0 and t_2/t_0, where " t_0 " being the flowing time of alkali solution only and " t_1 " and " t_2 " that of alkali solution of gel.

TABLE 39.

% of starch gel. in KOH-solution	Averages of 5 samples			
	1.1 %	1.0 %	0.6 %	0.2 %
t_0 of alkali solution only	8.80 sec.	8.80 sec.	8.80 sec.	8.80 sec.
t_1 of reversed common gel.	37.80 sec.	15.60 sec.	13.20 sec.	11.40 sec.
t_2 of reversed glutinous gel.	17.80 sec.	13.20 sec.	11.80 sec.	10.60 sec.
t_1/t_0 of reversed com. gel.	4.29 sec.	1.77 sec.	1.49 sec.	1.29 sec.
t_2/t_0 of reversed gluti. gel.	2.01 sec.	1.49 sec.	1.34 sec.	1.20 sec.

From these data we traced the following curves taking t_{1-2}/t_0 on the ordinate and concentration of reversed gel on the abscissa. Here we observed the difference between the viscosity of two kinds of reversed gel; i.e. the viscosity of the common starch gel was greater than that of the glutinous starch gel.

Fig. 15.



4. *Transparency for X-ray and Gelstructure under an Ultramicroscope.*

Recently, the X-ray has been used by many scientists[1] to investigate the inner structure of metals, woods or animal tissues and it is well known that their investigations produced much valuable information. Therefore we intended to investigate the gel structure of starch by means of X-ray. At first we examined the penetrating power of the X-ray through common and glutinous starch gels of the same thickness. Next, we determined the difference between the structures of their metal containing gels. In order to make the metal containing starch gel, tannin was added to a suspension of copper powder in starch solution. These gels had a strong preventive power against the penetration of the ray and had a very characteristic structure. A metal cylinder which had a bottom of very thin aluminium plate, was divided vertically into two parts and each part was filled with common or glutinous starch gel in the following thickness. The photographs were taken with Sherman's special sensitive plate under the following exposures, using 2 mili amps, 5-6 Benoist, 35000 volts A.C.

TABLE 40.

Starchgels	Time of exposure	Thickness of gels.	Intensity of penetiation	Preparation of starch gels.
Common	60 sec.	28 mm.	intenser than glutinous	7·5 gr. starch in liter, added with 5 % tannin solution
Glutinous	60 sec.	28 mm.	week penetration	" " "
Common	150 sec.	25 mm.	very intensive but figures are heterogeneous	7·5 gr. starch and 0.5 gr. copper powder in liter and added with 5 % tannin solution
Glutinous	150 sec.	25 mm.	very weak penetration, but figures are homogeneous	

From the results of the above experiment, we obtained the idea to distinguish the gel-structures of common and glutinous starches, therefore we examined more precisely their structure under an ultramicroscope. As shown by the following photographs (V & VI), the structure of common starch gel is rougher and more predominated by the water phase than the glutinous starch gel.

1) GOBY:—An. Rt. R. Dec., 1913. BORDIER:—Compt. rend., **163**, 205–6, 291–3, 1916.

5. *Charcoals from Starch Gels.*

As we observed that there was a marked difference between the adsorbing power of common and glutinous starch charcoals, we also carried out the following experiment in order to ascertain whether there is also a difference between the adsorbing powers of common and glutinous starch gel charcoals. As the experimental details have already been reported in Journ. biol. chem., Tokyo, Japan, Jan. 1923, here we intended only to abstract the resumé of those results.

The common starch gel charcoal was inferior to the glutinous starch gel charcoal in the respect of adsorption capacity as was seen in the starch charcoal. The constant $1/n$ of the Freundlich's adsorption formula $X/M = k\, C^{1/n}$ was calculated applying the method of least squares as follows :—

The charcoal from common rice starch gel

$1/n$............0.2977–0.2996

" glutinous " " "

$1/n$............0.3802–0.3593

This difference is probably due to the difference of the structure of gels of common and glutinous starch gels.

6. *Starch Gel formed by Freezing.*

Ten years ago, Malfitano and Moschkoff[3] stated that when a starch solution is frozen the starch coagulates and after the ice has been melted, the greater part of the starch remains in the form of a coagulum surrounded by a perfectly clear liquid. Therefore we undertook to distinguish the gel of common starch from that of glutinous by freezing and carried out the following experiments. 200 cc of 1.0 % starch solution were frozen by standing over night out of doors under snow. Then frozen, samples were melted and, the coagulums were separated by a centrifugal machine and the gels of common and glutinous starches were obtained. Between the properties of these two kinds of gel, we found the following differences. (1) In the case of common starch solution a greater mass of more solidified gel was

1) HUNTER :—Jour. Chem. Soc., **24**, 76, 1871 ; 25, 649, 1872.
2) DEWAR :—Proc. Roy. Inst., **18**, 180, 1905.
3) MALFITANO & MOSCHKOFF :—Compt. rend., **150**, 710–1, 1910.

formed than in the case of glutinous starch solution and its volume was two or three times that of glutinous starch.

(2) The glutinous starch gel was a semi-fluid while the common starch gel was solid. But even in the case of glutinous starch, a solid gel was finally obtained by repeating freezing and thawing.

(3) The diffusion velocity of methylene blue into both kinds of gel was ascertained by pouring 5 cc of 0.005 % methylene blue solution upon gels which were taken in the test tubes 7.0 mm. diameter and the positions of the level of diffused colored layers were observed daily. In this experiment, we obtained the following results from the values of four samples of each kind of starch. In the case of glutinous starch gel, the colored layer diffused into the gel ca. 1.0–2.0 mm per day, and continued during one week, while in the case of common starch gel it diffused only 0.5 mm. per day and continued only for 3–5 days.

(4) The water retention power of those gels was examined by the following method. The glass tubes of the same diameter (12 mm.) were filled with the fresh gels and by keeping them in a H_2SO_4-desiccator, the loss of weight which is caused by the evaporation of water from the same surface was determined. The following results are the values obtained from the four samples.

TABLE 41.

Samples	Loss of weight in % of original weight			
	after 5 days	after 9 days	after 14 days	after 20 days
Common rice starch gel.	15.5–16.8	25.2–31.4	31.8–33.5	47.–55.36
Glutinous rice starch gel.	12.4–13.4	21.0–24.2	26.6–29.5	40.2–42.3

Therefore the following conclusion may be drawn from the precipitates of the frozen starch gels. The colloid solution of common starch forms a solid gel by the aggregation of particles while it is very difficult in the case of glutinous starch solution. Therefore the gel-structure of glutinous starch is more convenient for the diffusion of coloring matter than that of common starch gel. The water retention of glutinous starch gel is also greater than that of common starch gel.

SUMMARY.

The most important points resulting from our experiments may be summarized as follows :—

1) We find a great difference between the swelling of glutinous and common rice starch granules. The increased volume of glutinous starch in iodine solution is greater than that of common and in the concentration higher than N/25, the former swelled up two or three times their original volume.

2) In the adsorption of iodine, by starch granules, the straight line expressed by logarithmic equation ($\log X/M = \log k + 1/n \log C$) of Freundlich's adsorption formula shows a great difference between glutinous and common starch granules. Logarithms of adsorption by glutinous do not simply express one straight line but plainly express two straight lines of a markedly different direction from each other. While, in the case of common starch it seems to express almost only one straight (it is not exactly a straight line but two straight lines which have however only a slightly different direction from each other) line. The constants obtained by calculation from the logarithmic equation which was derived from Freundlich's formula are shown in the following table.

Lines	Common starch		Glutinous starch	
	k	1/n	k	1/n
α	15.66	0.5328	106.4780	0.1643
β	24.04	0.3400	4.9357	0.7543

In the case of millet starch, the same conclusion is also obtained as in the case of rice starch, the constants are as follows :—

α	35.510	0.203	59.840	0.270
β	3.512	0.786	5.128	0.847

The power of adsorbing iodine of glutinous rice starch is stronger, than that of common rice starch, in the concentration of iodine higher than about N/50. This is also due to the fact that in the case of glutinous rice starch, the degree of swelling increases more rapidly

in such a high concentration as above and its adsorption surface becomes much greater than that of common rice starch.

3) In the resistance of starches against sulphuric acid, common rice starch is stronger than that of glutinous.

4) The adsorption power of charcoals from glutinous rice starch is greater than that of common rice starch as well as the charocal of millet or Italian millet starch.

5) In the presence of excess of iodine, the same brown color is observed in both kinds of starch solution but the quantity of iodine required for this purpose by glutinous rice starch is less than in the case of common rice starch. In the excess of starch, the same blue color is also observed in both kinds of starch solution, the intensity of which is however deeper in common starch than in glutinous starch solution.

6) In the spectroscopical investigation of these color reactions, we observed that the red color reaction of glutinous starch solution by iodine (the reaction of which was believed to be the characteristic color reaction of glutinous starch solution) is caused by the presence of a greater quantity of iodine than in that of common rice starch solution.

7) By X ray the red color of iodine glutinous starch solution is more easily bleached than the blue color of iodine common starch solution. This probably is due to the following fact that (a) the power of glutinous starch solution of adsorbing iodine is weaker than that of common starch solution, and subsequently, in the case of glutinous, the quantity of the free iodine not being adsorbed is greater than the case of common starch. (b) In the decoloration of iodine rice starch solution by X ray, the color of free iodine is more easily bleached than the color of iodine starch. During the bleaching of iodine glutinous starch solution, it is also observed that the red color disappears whereas the same blue color as iodine common starch solution remains instead.

8) In the decoloration of iodine starch solution by chemicals, we observed that common starch solution has a stronger affinity with iodine than that of glutinous starch and their affinity with iodine has a maximum point in concentration of N/7500 iodine in 0.5 % starch solution. The affinity of common starch solution with iodine increases day by day while in the case of glutinous starch solution there is but a slight increase only. The reaction of starch solution with iodine is

completed after about 10 minutes in glutinous starch solution while in common starch solution, it continues even after 30 minutes.

9) The color reaction of glutinous starch solution with iodine is observed by the addition of a greater quantity of iodine solution than that of common rice starch solution.

10) The amount of iodine adsorbed by glutinous starch paste is much less than that of common starch paste.

11) The viscosity of glutinous rice starch solution is higher than that of common rice starch and its difference is strongly marked in the higher concentration of starch paste. In the alkallne solution, the same results are obtained. In the presence of tannin solution, the change of the viscosity of common starch solution is greater than that of glutinous starch solution.

12) In the syneresis of rice starch solution, the water retention power of glutinous rice starch is stronger than that of common rice starch. During the syneresis, the decrease of viscosity of glutinous starch solution is greater than that of common starch solution.

13) The coagulation of glutinous starch solution by H ion or metal salt is very difficult, while common starch solution is easily coagulated by them.

14) The protective action of glutinous rice starch solution against the coagulation of gold colloid solution by salts is little stronger than that of common starch solution.

15) In the gel-formation, glutinous rice starch sol separated a greater quantity of water than that of common starch sol, the water contents of glutinous gel is less than that of common starch gel and the dehydration velocity of the former is greater than that of latter The reversed gel of common rice starch in alkaline solution is viscous and turbid while that of glutinous starch is thin liquid.

16) The structure of glutinous rice starch gel shows a network appearance, constructed of thick walls i. e. in general the structure is more compact and predominated by the solid phase. On the contrary, the structure of common starch gel shows a foam like appearance, constructed with thin walls, the spaces of the large cavity being predominated by water phase. The former shows a weak penetration for X ray while the latter shows very strong penetration, this difference is clearly observable in the case of metal containing gels.

17) Between the adsorption power of two kinds of charcoal obtained from glutinous and common rice starch gels, a great difference

is observable, and that of glutinous starch gel is greater than that of common starch gel.

18) In the experiment with the starch gels which were formed by freezing, we find clear difference between glutinous and common rice starch in solidification, water retension and resistance against diffusion. The common starch solution formed a greater mass of more solidified gel, and is less diffusible and possesses less water retention than that of common.

DISCUSSION.

Our intention is to discuss only the most important points.

(1) On the iodine color reaction of starch.

The typical difference between glutinous and common rice starches is found in the iodine reaction, in which the glutinous rice starch shows a red color while the common rice starch shows a blue color. To explain this phenomenon, Tanaka concluded that the red coloration of the former is due to a characteristic property of the starch itself and not to the contamination of amylopectin, erythrodextrine or special albuminoids. But this explanation is incomplete, because he did not account for the fact why glutinous rice starch gives a red color, while common rice starch gives blue. Therefore, we intended to give some explanations according to the results which were obtained by our experiments as follows:—

(a) By the difference of the dispersity.

By our experiment, the iodine color reaction of glutinous as well as common rice starch solution varied very markedly according to the ratio $\frac{\textit{the quantity of idione added}}{\textit{the quantity of starch tested}}$ and even in the case of glutinous starch solution, the same blue color as in the case of common rice starch solution was observed, and even in the case of common starch solution, the same brown color as in the case of glutinous starch solution was present. *Therefore the different iodine color reaction of glutinous and common rice starch solution is probably due to the difference of their dispersity.* By our experiment, it was also proved that the glutinous starch solution was stronger than the common starch solution, in its viscosity, hydration power, water retention power and protective power against the coagulation of gold colloid solution etc. and these facts verify the above explanation on the difference of the color reaction of both starches, proving the high dispersity of glutinous rice starch.

(b) By the quantity of free iodine.

The difference of iodine color reaction of starch solutions is also probably due to the ratio $\frac{\text{the quantity of free iodine not being adsorbed}}{\text{the quantity of iodine absorbed.}}$. In the case of glutinous rice starch solution, the quantity of free iodine not being absorbed was far greater than in the case of common rice starch solution, owing to its adsorption power being very weak. This may be one of the principal reasons why glutinous starch solution shows a red color. This was also proved by the experiment of X-ray.

(c) By the affinity of starch solution with iodine.

The affinity of glutinous starch solution with iodine was weaker than that of common starch as was clearly proved by the experiment under the decolorization of starch iodine solution by X-ray, as well as by chemicals. This may be also one of the greatest reasons why glutinous starch solution shows a red color.

(2) On the adsorption of iodine by starch granules as well as by starch pastes.

(a) . . . . . *The reaction of starch to iodine is an adsorption phenomenon.* Though the strong power of starch in its affinity with iodine leads us to think "iodine starch" to be a chemical compound, yet the reaction of starch to iodine is an adsorption phenomenon and the substance produced is not a chemical compound but an additional product. This is easily proved by the fact that the quantity of iodine adsorbed by the starch increased as the concentration of iodine added in the reaction increased. The adsorption phenomenon did not closely follow Freundlich's adsorption formula but this slight deviation may be due to the fact that the diffusion of iodine into starch particles took place besides the adsorption phenomenon, subsequently, the swelling of the starch particles influenced the adsorption phenomenon to a certain degree.

(b) On the difference between the adsorption powers of iodine by glutinous and common starch.

The power of glutinous starch to adsorb iodine was markedly different from that of common starch. This is probably due, not only to *the difference of the extent as well as to the arrangment of surface but also to the difference between the gel structures of glutinous and common rice starches.* The proof of this was ascertained for verification under the ultramicroscope, and also by the experiment of absorption of coloring matter by charcoals from glutinous starch gel as well as from common starch gel.

(3) On the coagulation of starch solutions. By our experiment, (a) the coagulation of glutinous starch solution by H-ion or metal salt was very difficult while common starch solution was easily coagulated by them.

(b) In the case of gel formation by tannin solution, the glutinous starch needed more energy or a greater quantity of reagents than common rice starch. These facts are probably due to the difference between the quantities of their electric charge, as both are electronegative colloids.

CONCLUSION.

The most important points resulting from our experiments may be concluded as follws:—

(*1*) *On the suspensoids of starches.*

(a) The suspensoid of common rice starch had a less swelling power by iodine solution, a stronger resistance against sulphuric acid solution than that of glutinous starch.

(b) Strikingly marked differences were observed between the powers to adsorb iodine as well as between the iodine color reactions of the suspensoids of glutinous and common starches.

(c) The affinity of the suspensoid of glutinous starch granules with iodine was also much weaker than that of common starch granules.

(*2*) *On the starch pseudo solutions.*

(a) The power of glutinous rice starch solution to adsorb iodine was much weaker than that of common rice starch solution. The affinity of glutinous rice starch solution with iodine was also much weaker than that of common rice starch solution and decolorized easily.

(b) The coagulation of glutinous starch by H-ion or metal salt was very difficult while common starch solution was easily coagulated by them. i. e. the characters like emulsoid were more predominated in the former than in the latter.

(c) The hydration power, the water retention power, the viscosity and the protective power against the coagulation of gold colloid solution, were much stronger in the case of glutinous rice starch than in the case of common rice starch. i. e. the dispersity of glutinous starch was higher than that of common starch.

(3) *On the starch gels.*

(a) In the gel formation by tannin solution, the glutinous starch needed more energy or a greater quantity of reagents than common rice starch.
(b) In the case of glutinous starch, the gel structure was like a network, while in the case of common starch, it was a foam like structure.

(4) Notwithstanding many characteristic differences between the colloidal properties of glutinous and common rice starches were observed as above, no noticeable differences could be discovered between their ordinary chemical properties. Therefore the following conclusion may be drawn :—

The glutinous rice starch as well as common rice starch are not necessarily of a different substance to each other but seem to be only different in the polymerization degree. This may be also true in the case of dextrines.

The authors wish to express their thanks to Prof. Miyabe, Prof. Oshima and Prof. Hatta, for the valuable suggestions they give in the publication of this papers.

Photo. I. (Iodine color reaction of soluble starch solution, during digestion by Takadiastase.)

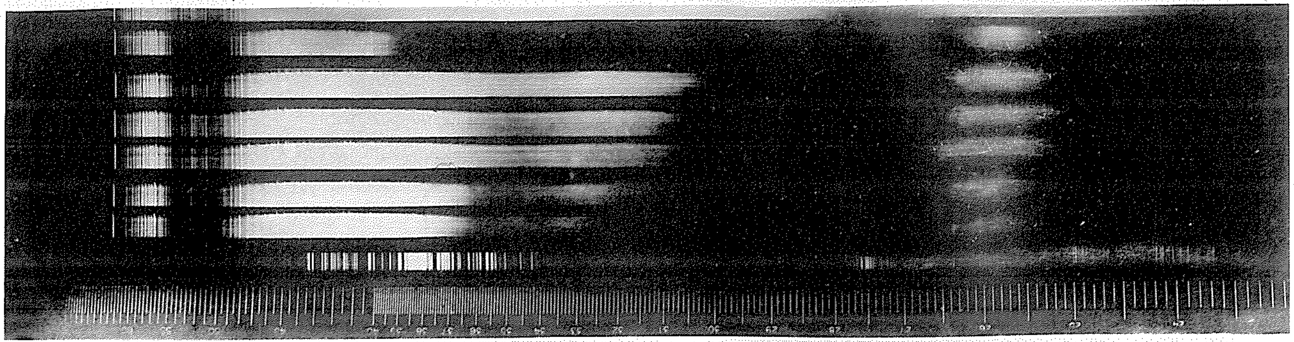


Photo. II. (Iodine color reaction of pseudo-solution of common rice starch.)

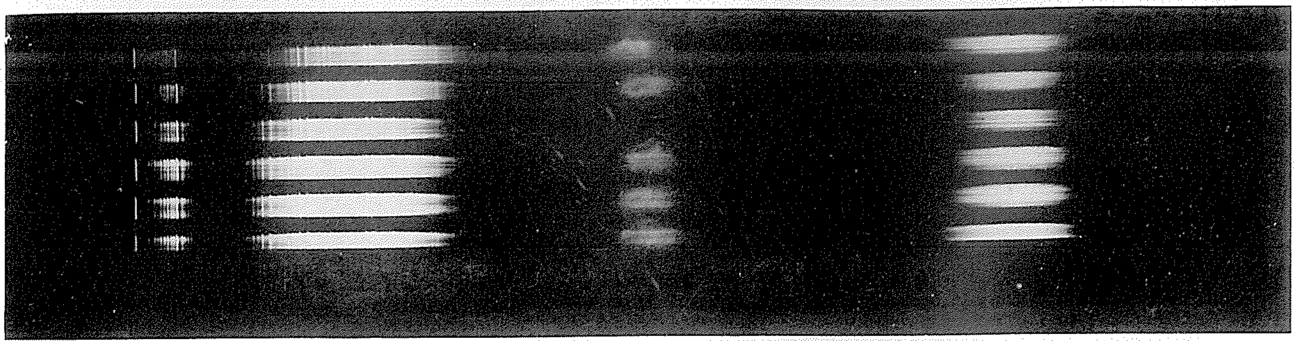


Photo. III. (Iodine color reaction of pseudo-solution of glutinous rice starch.)

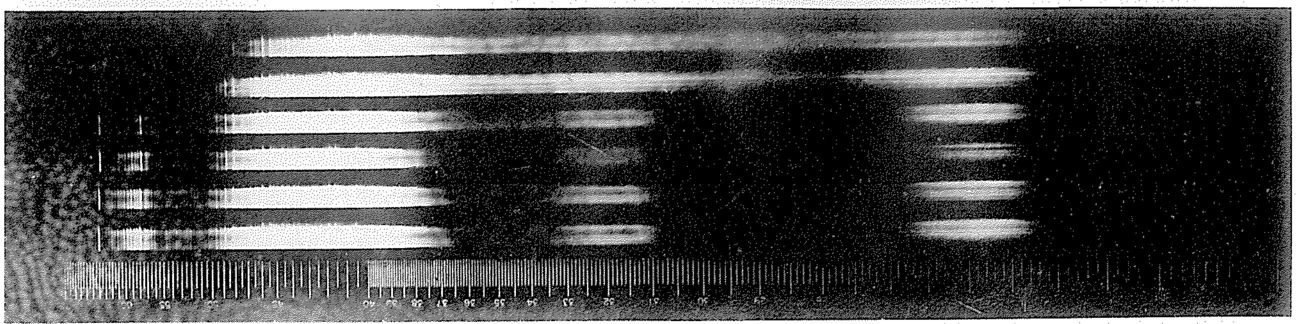


Photo. IV. (Iodine reactions . . . blue . . . brown . . . green.)

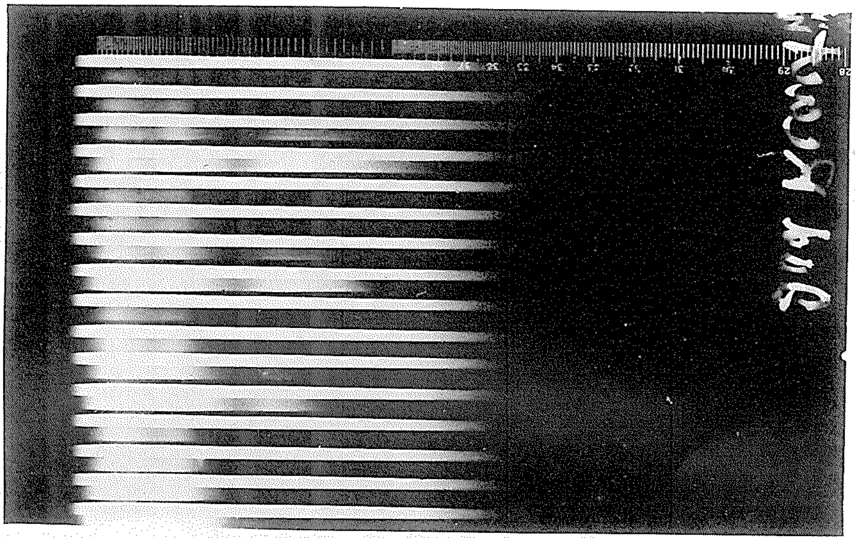


Photo. V.
(Foam-like structure of common starch gel.)

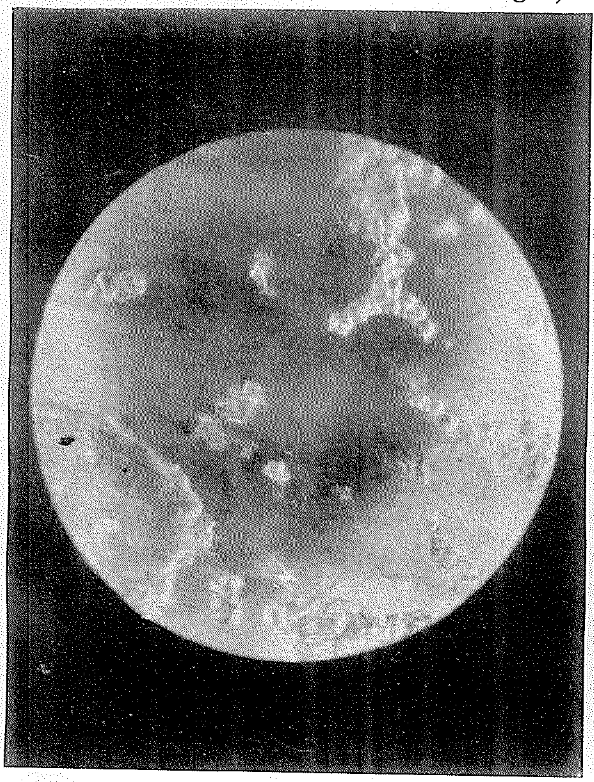
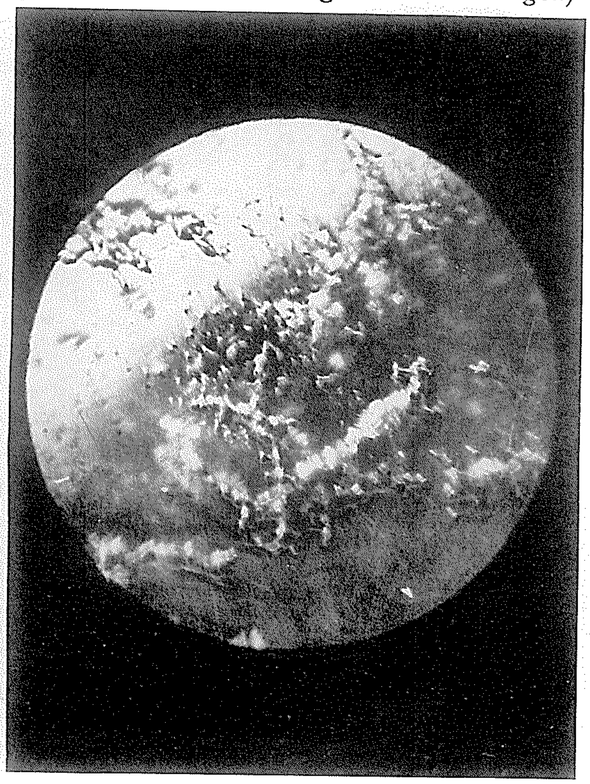


Photo. VI.
(Network structure of glutinous starch gel.)



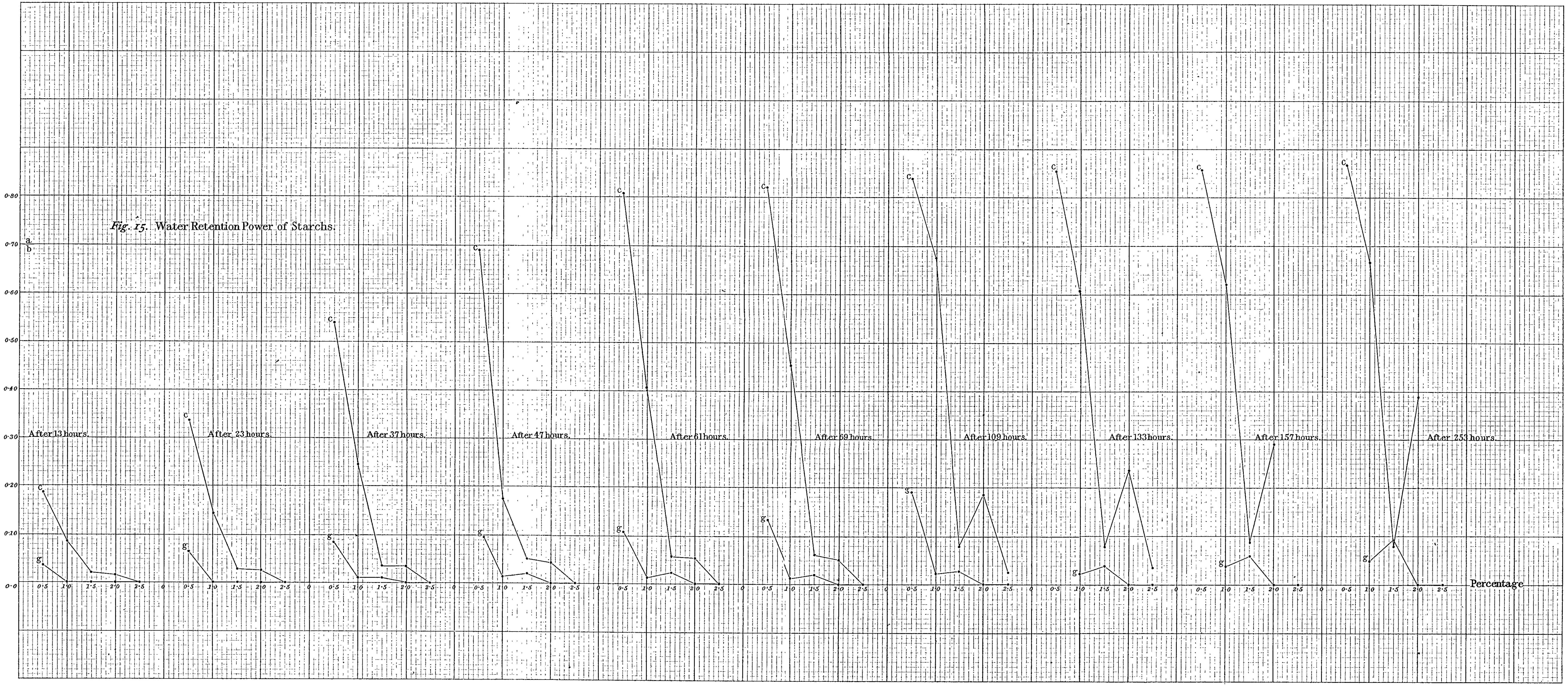


Fig. 15. Water Retention Power of Starchs.
a.
b.
0·80
0·70
0·60
0·50
0·40
0·30
0·20
0·10
0·0
After 13 hours.
After 23 hours.
After 37 hours.
After 47 hours.
After 61 hours.
After 69 hours.
After 109 hours.
After 133 hours.
After 157 hours.
After 253 hours.
c
g
0·5
1·0
1·5
2·0
2·5
Percentage