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Title	On the Differences between Some Colloidal and Chemical Properties of Common and Glutinous Rice Starch. II
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Citation	Journal of the College of Agriculture, Hokkaido Imperial University, Sapporo, Japan, 16(2), 91-123
Issue Date	1926-09-28
Doc URL	https://hdl.handle.net/2115/12588
Type	departmental bulletin paper
File Information	16(2)_p91-123.pdf



On the Differences between Some Colloidal and Chemical Properties of Common and Glutinous Rice Starch. II.

By

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This report is an extension of the first report⁽¹⁾ by the author and S. Sato entitled "On the Difference between Some Colloidal Properties of Common and Glutinous Rice Starch." Some of the experiments described in the present report were undertaken using the same method as before but with different samples. Further new experiments were also added. Therefore, the same conclusion as before was arrived at; but new premises, and conclusions were added and also new summaries, were formulated from this as well as the first report.

The references already stated in the first report have been omitted this time and here only new ones are given. This experimental work was done from March 1922 until December 1925 in our laboratory by the author and the following collaborators, i. e. Seiji Wakasa, Teizo Takahashi, Yukihiro Nakamura, Makoto Abe, Hiroshi Sawai and Shukichi Watanabe.

I. SHORT REVIEW OF THE EXPERIMENTS DESCRIBED IN THE FIRST REPORT.

(1) The swelling of glutinous rice starch granules, in iodine-potassium-iodide solution is greater than that of common rice and in concentrations higher than N/25, the former swelled up two or three times its original volume.

(2) In the adsorption of iodine, by starch granules, the straight

(1) Tadokoro and Sato:—*Jour. Coll. Agric., Hokkaido Imp. Univ.*, 8, 1, 1923.

[*Jour. of the Collage of Agric., Hokkaido Imp. Univ., Sapporo Vol. XVI, Pt. 2, May, 1926.*]

line expression of the 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. The constant, obtained by calculation from the logarithmic equation, K of common rice starch is greater than that of glutinous, while $1/n$ of the former is smaller than that of the latter.

(3) The adsorption power of charcoals, prepared from glutinous rice starch is greater than that prepared from common rice starch. The same is also true in comparing the starch charcoals of the glutinous and common varieties of both millet and Italian millet.

(4) Common rice starch has a greater resistance against sulphuric acid than glutinous rice starch.

(5) In 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 result by glutinous rice starch is less than in the case of common rice starch. With excess of starch, the same blue color is also observed in both kinds of starch solution, the intensity of which however is deeper in common starch than in glutinous starch solution.

(6) In the spectroscopical investigation of these color reactions, it was observed that the red color reaction of glutinous starch solution by iodine is caused by the presence of a greater quantity of iodine than with that of common rice starch solution.

(7) By X-rays 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 fact that in the decoloration of iodine rice starch solution by X-rays, 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, while the same blue color as iodine common starch solution remains instead.

(8) In the decoloration of iodine starch solution by chemicals, it was observed that common starch solution needs a greater quantity of the decolorizing agents than does glutinous starch solution.

(9) The viscosity of glutinous rice starch solution is higher than that of common rice starch and its difference is strongly marked in the higher concentrations of starch paste.

(10) In the syneresis of rice starch solution, the water retention power of glutinous rice starch is stronger than that of common rice starch.

(11) The coagulation of glutinous starch solution by hydrogen ion or metal salts is very difficult, while common starch solution is easily coagulated by them.

(12) In the gel-formation, a greater quantity of water was separated from glutinous rice starch sol than from common starch sol. The water content of glutinous gel is less than that of common starch gel, and the dehydration velocity of the former is greater than that of the latter.

(13) 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 characterised by a solid phase. On the contrary, the structure of common starch gel makes a foamy appearance, constructed with thin walls, the spaces of the large cavity being characterised by water phase.

(14) In the experiment with starch gels which were formed by freezing, the author found a clear difference between glutinous and common starch in solidification, water retention, and resistance against diffusion. The glutinous starch solution formed a greater mass of more solidified gel, was less diffusible and less water retentive than that of common rice.

II. SAMPLES OF STARCH AND THEIR MINERAL CONSTITUENTS.

The following materials which were used in the manufacture of starch are of unhulled and hulled rice, produced in different parts of Japan from 1922 to 1924. With the glutinous rice was mixed 0.15-2.0% common rice, which was separated carefully from the former before the experiment was proceeded with. The manufacture of starch was carried out mainly according to John's method as already reported in our first report. The starches obtained were entirely white and their water suspensions and paste were neutral to litmus paper as well as to phenolphthalein. The contents of water and ash in per cent of starches were determined with the following results.

TABLE I.

Showing the per cent of starch in common and glutinous rice produced from different localities.

Kinds of starch	Com-mon	Gluti-nous	Com-mon	Gluti-nous	Com-mon	Gluti-nous	Com-mon	Gluti-nous	Com-mon	Gluti-nous	Com-mon	Gluti-nous
Place of Production	Chiba		Miye		Hokkaido		Akita		Akita		Hokkaido	
Water%	3.93	8.38	8.57	8.92	10.98	11.11	13.38	12.24	10.56	10.44	11.80	11.74
Ash %	0.10	0.12	0.16	0.10	0.18	0.13	0.11	0.08	0.12	0.10	0.15	0.13
Place of Production	Hyogo		Ibaragi		Tochigi		Mino		Shiga		Average	
Water%	7.62	8.21	7.81	8.01	10.41	11.02	11.06	10.50	7.66	8.05	—	—
Ash %	0.13	0.06	0.10	0.04	0.09	0.05	0.20	0.15	0.12	0.10	0.13	0.09
Place of Production	(The following samples are all common starch)											
	Higo	Hiuga	Shikoku	Shonai	Kumamoto	Formosa	Siam	China				
Water%	9.60	8.74	7.80	10.20	7.50	7.28	9.58	8.98				
Ash %	0.06	0.09	0.08	0.10	0.06	0.09	0.09	0.04				

From the above results the author observe that the ash content of glutinous rice starch is always less than that of common rice.

It is a well known fact that the mineral constituents of starch are potassium, calcium, phosphoric acid, and silica. Samec⁽¹⁾ stated that 100 g. of starch ash contain 19.4 g. of silica and 46.6 g. of phosphoric acid which predominates in amylopectine and is very scarce in anylose.

The author collected 22 samples of different kinds of rice starch and determined the silica and phosphoric acid contents by the following operation. Starch was ignited in a platinum dish and digested with 5 ccm. of concentrated hydrochloric acid, evaporated and dried. This operation was repeated three times. Then the separated silica was filtered, washed, dried, ignited, and weighed.

The filtrate was evaporated, dried, and dissolved in nitric acid. The phosphoric acid was determined by the method stated by Hawk and the following results were obtained.

(1) Samec:—Koll. Chem. Beiheft, 8, 1916.

TABLE 2.

Showing the quantity of phosphoric acid and silica in the starches produced from both common and glutinous rice from different localities.

	P ₂ O ₅ (mgr.) in N/10HCl-sol.	SiO ₂	Mg- phosphate	% of ash		
				P ₂ O ₅	SiO ₂	
Hokkaido	7.4	0.0007	2.287	13.858	4.241	Common
Akita	8.0	0.0022	2.472	3.341	29.729	"
Miye	7.0	0.0017	2.163	8.011	5.925	"
Hyogo	4.7	0.0015	1.452	8.542	8.823	"
Hokkaido	3.3	0.0014	1.020	6.708	9.210	"
Shonai	6.4	0.00152	1.978	22.473	17.273	"
Higo	5.5	0.00482	1.699	7.357	77.584	"
Saitama	3.7	0.00512	1.142	6.608	29.525	"
Etchu	1.8	0.00152	0.556	4.635	11.667	"
Saitama	—	0.00502	—	—	29.017	"
Kyushu	—	0.00592	—	—	19.158	"
Ibaragi	4.9	0.00512	1.514	5.150	17.415	"
Tochigi	—	0.00222	—	—	8.222	"
Higo	2.55	0.00312	0.788	5.470	21.666	"
Niigata	2.7	0.01172	0.834	4.130	58.020	"
Hokkaido	2.7	0.01120	0.834	16.716	19.672	Glutinous
Kyushu	1.3	0.00620	0.402	1.141	17.614	"
Shiga	2.2	0.01670	0.680	2.105	51.702	"
Shiga	2.6	—	0.803	4.366	—	"
Miye	3.5	0.00552	1.081	5.783	29.519	"
Ibaragi	3.8	0.00482	1.174	7.575	77.548	"
Etchu	10.7	0.00512	3.306	3.210	14.485	"

Average:—Common...P₂O₅ 9.265, SiO₂...18.138, Glutinous...P₂O₅ 7.760, SiO₂ 35.791.

In the above table, the average phosphoric acid contents show a higher ratio in common starch than in glutinous, while with silica contents it is vice versa. But the quantities of both constituents showed no regular ratio and their contents are very divergent, therefore it was supposed that they make no definite compound with the (C₆H₁₀O₅)-radical in starch.

III. ADSORPTION OF IODINE BY STARCH GRANULES.

In his first report, the author stated that the adsorption of iodine by starch granules is expressed by the logarithmic equation (log. X/M

= $\log.K. + 1/n.\log.C$) of Freundlich's formula, and the constant obtained by calculation from this equation, $K.$ of common rice starch is greater than that of glutinous, while $1/n$ of the former is smaller than that of the latter. In this case, the adsorption of iodine by starch granules was examined with the following additional samples and the constant calculated using the same operation as stated in the first report.

TABLE 3.

Showing the adsorbed and the unadsorbed quantity of iodine in starch mixture produced from both common and glutinous rice from different localities,

Kinds of starch	Potassium iodide and iodine solution								
	N/200	N/150	N/100	N/75	N/50	N/25	N/20	N/15	N/10
Chiba-common X/M C	29.865	37.159	51.610	60.482	77.335	156.390	180.152	235.067	302.780
	1.864	5.105	11.849	24.172	49.584	102.449	137.147	187.956	331.819
glutinous X/M C	23.134	29.922	44.558	53.840	84.193	201.809	238.769	267.776	304.707
	8.595	12.342	18.901	30.815	42.727	51.806	78.661	155.248	341.892
Miye-common X/M C	30.678	39.285	55.164	60.943	90.230	106.152	199.120	233.211	305.306
	1.0514	2.979	8.295	23.712	36.689	93.687	118.179	189.813	329.103
glutinous X/M C	24.665	32.099	46.474	53.372	84.607	200.059	274.675	274.674	302.086
	7.065	10.164	16.985	31.284	43.321	53.782	73.437	73.437	331.513
Hokkaido-common X/M C	28.633	33.218	47.047	57.014	83.289	147.454	172.992	222.089	299.408
	3.096	9.044	16.410	27.640	43.530	106.365	143.308	200.927	335.192
glutinous X/M C	22.566	29.298	42.835	52.401	83.242	199.896	235.453	265.434	296.561
	9.179	12.965	20.629	32.254	43.877	54.033	81.845	177.717	338.038

TABLE 4.

Showing the constant of the adsorption formula calculated from the above results.

	Chiba		Miye		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
1/n	0.4406	0.7907	0.4021	0.7452	0.5460	0.7936
K	19.0523	4.7211	25.4965	6.01413	11.3900	4.3936

The results are very similar to those of the first report, i.e. K of common starch is greater than that of glutinous, while with 1/n it is the opposite.

In all the above adsorption experiments, use was made of a water solution of iodine which has many defects, caused by its colloidal nature, and when alcohol solution of iodine was used instead, one straight line resulted, expressed by the logarithmic equation of Freundlich's adsorption formula, while in the former case it was composed of two straight lines which showed different inclinations to the abscissa.

One g. of water-free starch was taken in each bottle and to it were added 30 ccm. of iodine alcohol solution of various concentrations, such as N/100, N/75, N/50, N/20, 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. Ten ccm. of each supernatant liquid was titrated with sodium thiosulphate solution and this experiment was controlled with a blank test, to correct the loss of evaporated alcohol solution in centrifuging.

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 g. starch.

TABLE 5.

Showing the adsorbed and the unadsorbed quantity of iodine in starch mixture produced from both common and glutinous rice grown in different localities.

Iodine-solution Rice	Glutinous				Common			
	X/M	C	log. X/M	log. C	X/M	C	log. X/M	log. C
N/100-Akita	4.0551	14.9748	0.6079	1.1752	4.6356	14.5943	0.6661	1.1580
Etchu	3.6738	15.3561	0.5651	1.1861	4.1821	14.8478	0.6214	1.1716
Hokkaido	3.1285	15.9014	0.4953	1.2014	3.4889	15.5410	0.5426	1.1914
N/75-Akita	4.6419	20.7313	0.6666	1.3166	5.6345	19.7387	0.7508	1.2953
Etchu	4.2577	21.1155	0.6291	1.3245	5.0166	20.3566	0.7004	1.3087
Hokkaido	3.7753	21.5979	0.5769	1.3344	4.2693	21.1039	0.6302	1.3246
N/50-Akita	6.0731	31.9867	0.7834	1.5049	7.3898	30.6700	0.8686	1.4869
Etchu	5.6050	32.4548	0.7485	1.5112	6.9254	31.1344	0.8902	1.4929
Hokkaido	4.7022	33.3576	0.6723	1.5232	5.6427	32.4171	0.7514	1.5107
N/25-Akita	8.9453	67.1743	0.9515	1.8272	12.3478	63.7718	1.0912	1.8046
Etchu	7.7514	68.3682	0.8893	1.8348	10.9383	65.1813	1.0386	1.8141
Hokkaido	0.7943	69.3253	0.8321	1.8409	8.3735	67.7461	0.9229	1.8308
N/10-Akita	15.3177	174.8915	1.1850	2.2452	22.756	67.5421	1.3570	2.2240
Etchu	13.2521	177.0471	1.1222	2.2480	20.3936	69.9056	1.3094	2.2302
Hokkaido	11.3870	178.9122	1.0625	2.2526	15.1803	175.1189	1.1812	2.2433

TABLE 6.

Showing the constant of the adsorption formula calculated from the above result.

	Akita		Etchu		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
1/n	0.5412	0.6666	0.5425	0.6644	0.5344	0.6124
K	0.9192	0.7452	0.8307	0.6863	0.7524	0.7524

The value of K of common rice starch is also greater than that of glutinous, while 1/n of the former is less than that of the latter.

IV. ADSORPTION OF IODINE BY STARCH CHARCOALS.

As stated in our first report, a difference of the power to adsorb iodine was observed between the charcoals of common and glutinous starch. The value of the constant K of common starch charcoal is greater than that of glutinous, while 1/n of the former is less than that of the latter. So the relation of the constant is just the same as the adsorption of iodine by starch granules.

The following experiment, the same as described in the first report, was undertaken with new, different samples. The results obtained in this experiment are given, as well as examples for calculation of the adsorption constant.

TABLE 7.

Showing the adsorbed and the unadsorbed quantity of iodine in starch charcoal mixture produced from both common and glutinous rice grown in different localities.

Iodine-solution	Common starch charcoal				Glutinous starch charcoal			
	C	X/M	log. C	log. X/M	XC	X/M	log. C	log. X/M
N/200	1.5865	14.2785	0.20045	1.15470	3.4903	12.3747	0.54281	1.09255
N/100	7.6152	24.1148	0.88168	1.38229	12.3747	19.3553	1.09255	1.28680
N/75	13.9612	28.3667	1.14492	1.45282	17.2929	25.0037	1.23786	1.39800
N/50	32.0473	31.4127	1.50507	1.49711	32.6819	30.7781	1.51430	1.48824
N/25	87.5748	39.3452	1.94238	1.59489	85.9883	40.6144	1.93444	1.60868
N/15	163.7268	47.5950	2.21412	1.67757	158.9192	49.4988	2.20390	1.69460
N/10	266.8493	50.4504	2.42627	1.70728	261.4552	55.8448	2.41740	1.74698

The constant was calculated by the method of least squares as follows :—

Common :—

$$\begin{aligned} \log. K + 1/n(0.20044) - 1.15470 &= 0 \\ \log. K + 1/n(0.88168) - 1.38229 &= 0 \\ \log. K + 1/n(1.14492) - 1.45282 &= 0 \\ \log. K + 1/n(1.50579) - 1.49711 &= 0 \\ \log. K + 1/n(1.94238) - 1.59489 &= 0 \end{aligned}$$

Glutinous :—

$$\begin{aligned} \log. K + 1/n(0.54287) - 1.09255 &= 0 \\ \log. K + 1/n(1.09255) - 1.28680 &= 0 \\ \log. K + 1/n(1.23786) - 1.39800 &= 0 \\ \log. K + 1/n(1.51430) - 1.48824 &= 0 \\ \log. K + 1/n(1.93444) - 1.60868 &= 0 \end{aligned}$$

Common :—	Glutinous :—
$\log. K + 1/n(2.21412) - 1.67757 = 0$	$\log. K + 1/n(2.20390) - 1.69460 = 0$
$\log. K + 1/n(2.42627) - 1.70286 = 0$	$\log. K + 1/n(2.41740) - 1.74698 = 0$
\therefore	\therefore
$7 \log. K + 1/n(10.31560) - 10.46224 = 0$	$7 \log. K + 1/n(10.94332) - 10.31685 = 0$
$19.3156 \log. K + 1/n(18.95774) - 16.31117 = 0$	$10.94332 \log. K + 1/n(19.75484) - 17.04134 = 0$
$1/n = 0.1999$	$1/n = 0.3448$

TABLE 8.

Showing the constant of the adsorption formula calculated from the above results.

	Chiba		Miye		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
1/n	0.2830	0.3095	0.1999	0.3448	0.2560	0.3108
K	11.9039	10.4429	15.4848	8.6060	11.6271	9.4378

The above results show that the charcoal of common rice starch has a greater K and a smaller 1/n value than that of glutinous.

V. HYDROLYSIS OF STARCHES WITH SULPHURIC ACID.

In his first report, the author stated that the resistance of common starch against sulphuric acid is stronger than that of glutinous, and that after digestion the quantity of insoluble residue of the former was greater than that of the latter. This difference is increased in a short time with dilute sulphuric acid solution. The same experiment was undertaken with new samples.

One g. of water free starch was introduced into a bottle and mixed thoroughly with 50 ccm. of water, to which was added 1 ccm. of concentrated sulphuric acid and this was boiled for two hours in a water bath (98°–100°C.) with a long glass tube as a condenser. Each digested solution was filtered and the remaining precipitate was washed with water until the filtrate gave no acid reaction. The dried precipitate was weighed and the filtrate neutralised and made up to 100 ccm. The reducing power of a definite quantity of the solution was determined by Bertrand's method. The results obtained are given in the following table :—

TABLE 9.

Showing the quantity of insoluble residue and reducing sugar in the starches produced from both common and glutinous rice grown in different localities.

Kind of starch	Akita		Etchu		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
Insoluble residue (mg.)	4.05	1.25	4.30	2.40	6.15	3.80
Per cent of starch	0.405	0.125	0.430	0.240	0.615	0.380
Ratio	100.0	ca. 30.8	100.0	ca. 55.8	100.0	ca. 61.7
Copper (mg.) in 20 ccm. of solution	333.113	349.059	356.631	350.274	362.249	358.341
As glucose (mg.)	186.068	183.735	187.738	184.316	191.249	189.071
Sugar % of starch	93.03	91.87	93.86	92.15	95.62	94.54

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

- (1) After hydrolysis with sulphuric acid, the common starch leaves a greater insoluble residue than does that of glutinous.
- (2) The hydrolytic products of common starch contain a greater quantity of reducing sugar than do those of glutinous.

VI. METHYLATION OF STARCH.

Denham and Woodhouse⁽¹⁾ succeeded in the methylation of cellulose and starch, and Denham⁽²⁾ and Irvine and Hart⁽³⁾ intended to determine the molecular structure of cellulose from the methylation products. Recently Komatsu, Inoue and Nakai⁽⁴⁾ determined the molecular structure of xylan from the methylation products. The author proposed to distinguish common and glutinous starch by their methylation products according to the following operation.

(1) Denham & Woodhouse:—*Jour. Chem. Soc.*, **103**, 1735, 1913; **105**, 2257, 1914; **111**, 244, 1917.

(2) Denham:—*Jour. Chem. Soc.*, **119**, 78-81, 1921.

(3) Irvine & Hart:—*Jour. Chem. Soc.*, **123**, 518, 1923.

(4) Komatsu, Inoue and Nakai:—*Memoirs: Coll. Sci. Kyoto Imp. Univ.*, VIII, A, 1923.

Ten g. of starch were boiled with 75 ccm. of water and this paste was mixed with NaOH solution (45 g. NaOH in 75 ccm. of H₂O) until a good paste resulted. 100 g. of dimethylsulphate were added drop by drop to the paste and the mixture was shaken for a few hours, then the methyl starch was separated by boiling in the presence of water. The methyl starch was washed with hot water, dialysed with parchment paper for one week and after all the sulphate and alkali had been washed out, it was taken up on a watch glass and dried in a sulphuric acid desiccator.

Both kinds of methyl starch are hygroscopical white masses soluble in water and 80 % alcohol but insoluble in hot water. The methoxyl group in methyl starch was determined by the process of Zeisel⁽¹⁾ modified by Hewitt and Moore.⁽²⁾ A clear difference between the methoxyl contents of glutinous and common methyl starch was obtained by the author.

TABLE 10.

Showing the methoxyl contents of the methyl starches produced from both common and glutinous rice grown in different localities.

Kind of starch	g. of sample	Ag-iodide (g.)	Methoxy (mg.)	%	Average
Akita common	(1) 0.2244	0.0413	5.4620	2.429	2.446
	(2) 0.2431	0.0453	5.9910	2.464	
glutinous	(1) 0.2159	0.0136	1.7950	0.832	0.834
	(2) 0.4748	0.0301	3.9730	0.837	
Etchu common	(1) 0.3427	0.0407	5.3720	1.568	1.561
	(2) 0.3644	0.0429	5.6630	1.554	
glutinous	(1) 0.3162	0.0135	1.7820	0.560	0.563
	(2) 0.3660	0.0164	2.0650	0.561	
Hokkaido common	(1) 0.4164	0.0403	5.3196	1.277	1.291
	(2) 0.5453	0.0539	7.1148	1.305	
glutinous	(1) 0.3956	0.0129	1.7028	0.430	0.434
	(2) 0.2835	0.0094	1.2408	0.438	

(1) Zeisel:—Monatshefte f. Chemie **6**, 989, 1885; **7**, 406, 1886.

(2) Hewitt & Moore:—Jour. Chem. Soc., **81**, 318, 1903.

From the above table, it is observed that the methoxyl group content of glutinous starch is less than that of common, the former corresponding to 34-36 % of the latter.

VII. ACETYLATION OF STARCH.

Acetylation of starch was first successfully performed by Pregl⁽¹⁾. His preparate was stained blue by iodine and showed a specific rotatory power of +191.5°. Pringsheim and Eissler⁽²⁾ obtained the same acetyl starch and assumed that it contained a trisaccharide which corresponds to iso-tri-amylose.

Boeseken⁽³⁾ succeeded in the acetylation of cellulose and starch with acetic anhydride, using HCl, HBr, HI, H₂SO₄, ZnCl₂, AlCl₃, and Na-acetate as catalysers. Randall⁽⁴⁾ used the starch solution dissolved in alkali, adding CaO. Meyer⁽⁵⁾ classified the acetylation methods according to 5 kinds of reagents, i. e. acetylchloride, acetic anhydrid, Na-, K-acetate, acetic acid, chloroacetylchloride and thioacetic acid, etc. Lassar-Cohn⁽⁶⁾ added the following method to Meyer's classification and divided the acetic anhydride method into seven divisions, i. e. "Acetyl-nitrat Essig säure Anhydride (1. Verdünnt, 2. Allein, 3. mit Alkalilauge, 4. mit Na-Acetate, 5. mit Phosphorsäure, 6. mit Schwefelsäure, 7. mit Zink Chlorid.)" Miyake⁽⁷⁾ obtained acetylmannan using acetic anhydride and ZnCl₂ so the author used the same method as described in the following. Five g. starch were mixed with 40 g. of acetic anhydride and 0.2 g. of ZnCl₂ and heated gently for 4 hours with a reflux condenser. When all combined starch became a transparent, dark brown solution, it was poured into water and acetyl starch was precipitated. The precipitate was washed many times with water until the wash water had no reaction of acetic acid, and the precipitate was washed with alcohol, and ether and dried in a sulphuric acid disiccator.

(a) *Contents of acetyl group in acetyl-starch.*

The acetyl group of acetyl-starch was determined by Wenzel's

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- (1) Pregl:—Monatsch. Chem. **22**, 1049, 1901.
 - (2) Pringsheim & Eissler:—Ber. d. Chem. Ges.; **46**, 2959, 1913.
 - (3) Boeseken:—Rec. Tran. Chim., **35**, 320-415, 1916.
 - (4) Randall:—Chem. Abst., **14**, 1835, 1920.
 - (5) Meyer:—Lehrbuch d. Organische Chemische Methodik, **1**, 3658, 1922.
 - (6) Lassar-Cohn:—Arbeitsmethoden d. Organisch-chemische Laboratorium **2**, 1923.
 - (7) Miyake:—Jour. Soc. Agr. & Forest., Sapporo, **16**, 307-320, 1924.

method⁽¹⁾. 0.2 g. of each sample was saponified with 0.5 normal sulphuric acid and after addition of metaphosphoric acid Na-phosphate solution, the distilled acetic acid was collected in standard NaOH solution and titrated with standard H₂SO₄ solution, using phenolphthalein as indicator.

TABLE II.

Showing the acetyl contents of the acetyl starches produced from both common and glutinous rice grown in different localities.

Acetyl-starch	ccm. of H ₂ SO ₄ -sol. not titrate	Acetyl-radicle (g.)	%	Ratio
Akita common	5.90	0.116934	58.46	100.00
Akita glutinous	5.80	0.114953	57.47	98.30
Hokkaido common	5.50	0.109007	54.50	100.00
Hokkaido glutinous	5.42	0.107421	53.71	98.91
Etchu common	5.75	0.113962	56.98	100.00
Etchu glutinous	5.45	0.108892	54.44	95.89
Hyogo common	5.85	0.115944	57.97	100.00
Hyogo glutinous	5.76	0.114160	57.08	98.46
Chiba common	5.83	0.115548	57.77	100.00
Chiba glutinous	5.65	0.111980	55.99	96.91

The above results show that the acetyl group content of common acetyl-starch is always greater than that of glutinous acetyl-starch. This is caused by the greater number of OH-groups in the former molecule.

(b) *Melting point and specific rotatory power of acetyl-starch.*

The melting point of acetyl-starch was determined by ordinary methods with the following results:

TABLE 12.

Showing the melting point of the acetyl-starches produced from both common and glutinous rice grown different localities.

Acetyl-starch	Akita		Hokkaido		Etchu		Hyogo		Chiba	
	common	glut.	common	glut.	common	glut.	common	glut.	common	glut.
Melting-point	157-8°	149°	164°	148°-150°	158°-9°	151°	158°-160°	150°-152°	159°-160°	149°
Difference	ca. 8.3		ca. 15.0		ca. 7.5		ca. 8.0		ca. 11.0	

(1) Meyer:—Lehrbuch d. Organische Chemische Methodik, 1, 3658, 1922.

As shown in the above table, the melting point of common acetyl-starch is always higher than that of glutinous.

The specific rotatory power of acetyl-starch, dissolved in pyridin solution, was determined by a Schmidt-Haensch half-shadow polariscope at 15°C. and the following results obtained.

TABLE 13.

Showing the specific rotatory power of the acetyl starches produced from both common and glutinous rice grown in different localities.

	Common acetyl-starch	Glutinous acetyl-starch
Akita	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+7.50 \times 0.346 \times 25}{0.2 \times 2} = +156.04$	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+6.9 \times 0.346 \times 25}{0.2 \times 2} = +148.78$
Etchu	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+7.05 \times 0.346 \times 25}{0.2 \times 2} = +152.46$	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+6.7 \times 0.346 \times 25}{0.2 \times 2} = +144.02$
Hokkaido	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+6.8 \times 0.346 \times 25}{0.2 \times 2} = +147.05$	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+5.8 \times 0.346 \times 25}{0.2 \times 2} = +125.42$
Hyogo	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+7.0 \times 0.346 \times 25}{0.2 \times 2} = 151.37$	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+6.6 + 0.346 \times 25}{0.2 \times 2} = +142.73$
Chiba	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+3.6 \times 0.346 \times 25}{0.1 \times 2} = +160.89$	$\frac{[\alpha]_{D}^{20}}{d} = \frac{+6.5 \times 0.346 \times 25}{0.2 \times 2} = +140.56$

TABLE 14.

A comparison of the above values showing the difference of two kinds of acetyl-starch.

	Akita	Etchu	Hokkaido	Hyogo	Chiba
Common	156.04	152.46	147.05	151.37	160.89
Glutinous	148.78	144.02	125.42	142.73	140.56
Difference	7.26	8.44	21.63	8.64	20.33

The specific rotatory power of common acetyl-starch is higher than that of glutinous.

(c) Solubility, reducing power and iodine reaction of acetyl-starch.

Acetyl-starch whether from common or glutinous starch showed no difference in solubility, reducing power nor iodine reaction. Neither kind of acetyl-starch has any reducing power. They do not dissolve in cold water, alcohol or ether but they do dissolve easily in chloroform, acetic ether and pyridine.

(d) Iodine adsorption by acetyl-starch.

Bergmann and Ludwig⁽¹⁾ reported that iodine potassium iodide solution, starch and acetyl-starch adsorbed not only iodine but also potassium iodide and that their ratio is definite, i. e. 2 mols. of cyclo-acetal adsorbed 1 mol. each of iodine and potassium iodide. The ratio of iodine to potassium iodide adsorbed by acetyl-starch is always constant for the definite acetyl-starch. Two grams of acetyl-starch, obtained by the above operation, were added to 20 ccm of N/10 iodine solution (12.7 g. of iodine and 20 g. of potassium iodide were dissolved in 1 liter of water), shaken for 4 minutes, centrifuged for 5 minutes and 10 ccm and 5 ccm of the clear liquid were separated. The iodine in 10 ccm of the solution was determined, by titrating with N/10 Na-thiosulphate solution, and iodic acid was reduced with sulphurous acid by Volhard's⁽²⁾ method. The following ratios of adsorbed iodine and potassium were calculated.

TABLE 15.

Showing the iodine adsorption of the acetyl-starches produced from both common and glutinous rice grown in different localities.

Acetyl-starch	Akita		Chiba		Etchu	
	common	glutinous	common	glutinous	common	glutinous
% of acetyl group	58.467	57.476	57.774	55.990	56.981	54.447
The ratio	18 : 1	7 : 1	9 : 1	7.8 : 1	7.6 : 1	5 : 1

(1) Bergmann & Ludwig:—Ber. d. Chem. Ges., **57**, 961-963. 1924.

(2) Treadwell:—Lehrbuch d. Analytischen Chemie, **2**, 537. 1907.

From the above table, it will be seen that the ratio of iodine adsorption by common acetyl-starch is greater than that by glutinous.

IX. HEAT OF COMBUSTION OF STARCH.

It is well known that the heat of combustion of starch is on the average 4.18 Cal. but it is not the same for different kinds of starch in the strict sense. In the heat of combustion there should be also some difference between common and glutinous starch. The heat of combustion of both pure starches was determined by Atwater and Benedict's Bombcalorimeter with the following results:—

TABLE 16.

Showing the small calories of the starches produced from both common and glutinous rice grown in different localities.

	Sample (g.)	Small calorie per 1 g. starch	Small calorie per 1 g. H ₂ O free starch	Average
Etchu- common glutinous	(1) 0.8929 (2) 0.9158	(1) 3674.12 (2) 3692.20	(1) 4107.64 (2) 4127.99	4117.8
	(1) 0.6868 (2) 0.9842	(1) 3582.20 (2) 3638.90	(1) 4001.32 (2) 4064.63	4033.0
Akita- common glutinous	(1) 0.8815 (2) 0.6702	(1) 3547.60 (2) 3574.20	(1) 4093.93 (2) 4124.63	4109.3
	(1) 0.7479 (2) 0.7050	(1) 3511.30 (2) 3570.90	(1) 3999.37 (2) 4067.26	4033.3
Chiba- common glutinous	(1) 0.6733 (2) 0.8848	(1) 3704.20 (2) 3707.30	(1) 4016.70 (2) 4019.95	4018.3
	(1) 0.8896 (2) 0.9732	(1) 3663.20 (2) 3663.40	(1) 3998.25 (2) 3998.47	3998.4
Hyogo- common glutinous	(1) 0.9824 (2) 1.1365	(1) 3766.40 (2) 3751.10	(1) 4077.39 (2) 4060.82	4064.1
	(3) 1.3878	(3) 3745.20	(3) 4054.44	
	(1) 1.2900 (2) 1.0105 (3) 0.7680	(1) 3718.80 (2) 3732.90 (3) 3727.30	(1) 4051.44 (2) 4066.81 (3) 4060.70	4059.7
Hokkaido- common glutinous	(1) 1.3002 (2) 0.6888	(1) 3769.80 (2) 3747.90	(1) 4274.05 (2) 4250.12	4262.5
	(1) 0.7365 (2) 1.0303	(1) 3762.70 (2) 3649.50	(1) 4263.14 (2) 4134.88	4199.0
Hokkaido- common glutinous	(1) 1.0517 (2) 0.8278	(1) 3587.50 (2) 3597.40	(1) 4029.88 (2) 4041.11	4033.4
	(3) 0.9194	(3) 3586.80	(3) 4029.21	
	(1) 0.8722 (2) 0.8486 (3) 0.6836	(1) 3455.60 (2) 3487.00 (3) 3439.60	(1) 3887.50 (2) 3922.83 (3) 3839.50	3893.3

From the above table, it was observed that the heat of combustion of common starch is greater than that of glutinous.

X. ADSORPTION OF IODINE BY STARCH SOLUTION.

Starch pseudosolution was prepared with 2 g. of water-free starch and 100 ccm of water, boiling 15 minutes in a water bath. Twenty ccm of this pseudosolution were poured into a cylinder of parchment paper and this cylinder was placed in a glass cylinder which contained 100 ccm of 1/200 normal iodine potassium iodide solution. The diameter of the two cylinders which were used for common and glutinous starch solution were the same. The quantity of iodine diffused into the inner cylinder and adsorbed by starch solution was measured.

TABLE 17.

Showing the quantity of iodine (mg.) adsorbed by starches produced from both common and glutinous rices grown in different localities.

Starch sol.	Time					
	.24 hrs.	64 hrs.	96 hrs.	120 hrs.	144 hrs.	168 hrs.
Akita common	36.9980	44.5296	46.9081	48.0312	49.0882	49.6829
„ glutinous	30.0391	39.1120	42.6136	44.2653	45.3884	46.4135
Etchu common	33.0340	41.8208	44.7738	46.4786	48.0642	48.5588
„ glutinous	26.4272	36.4693	41.2263	43.4725	45.0581	46.0491
Hokkaido common	35.6767	43.2082	45.5866	46.7098	47.7669	48.2622
„ glutinous	33.0340	42.4822	44.9268	46.0500	47.1070	48.0980

From the above table, it was observed that the iodine adsorption of common starch solution is greater than that of glutinous.

XI. DIFFUSION OF IODINE FROM STARCH SOLUTION.

The diffusion velocity of iodine from iodine starch solution to water was determined by the following operation. Two per cent starch solu-

tion was prepared as above mentioned and 20 ccm of the solution were mixed with the same volume of 1/50 normal iodine potassium iodide solution; then the mixture was poured into a cylinder of parchment paper which was immersed in 150 ccm of water. After a given time the cylinder was taken out, and the quantity of iodine in the water was determined. The same volume of fresh water was used for the successive repetitions of the experiment at the different time periods.

TABLE 18.

Showing the quantity of iodine diffused from the iodine starch solutions of common and glutinous rices grown in different localities.

Iodine starch sol. mg. \ Time	24 hrs.	48 hrs.	72 hrs.	96 hrs.	144 hrs.
Akita-common	3.964	2.775	2.511	2.180	1.982
„ glutinous	5.814	4.360	3.699	3.302	3.039
Etchu-common	4.757	3.699	3.436	3.171	2.907
„ glutinous	6.342	5.650	4.757	4.360	4.096
Hokkaido-common	6.078	4.889	4.230	3.899	3.701
„ glutinous	7.567	5.556	5.021	4.492	4.228

The author observes that the diffusion velocity of iodine from iodine common starch solution is less than from glutinous.

XII. VISCOSITY OF STARCH SOLUTION.

In his first report, the author stated that the viscosity of glutinous starch solution is greater than that of common. Here the viscosity of both kinds of starch solution is again examined with different samples.

TABLE 19.

Showing the specific viscosity of starch solutions calculated from the time required of flowing, measured with Ostwald's viscosimeter at 18°C.

	Chiba		Miye		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
0.5 % starch solution	1.226	1.797	1.063	1.725	1.114	1.543
1.0 % " "	1.669	4.549	1.602	4.029	1.514	3.364
1.5 % " "	1.797	18.075	2.239	13.696	1.879	11.421

The viscosity of starch solution was changed somewhat by the preparation method. The following samples were prepared by another treatment, i. e. at first starch was converted to a paste with water by heating 4 minutes on a water bath, and the paste was made up to 100 ccm and boiled 20 or 40 minutes in boiling water at 98°-100°C.

TABLE 20.

Showing the specific viscosity of the common starch solution determined by MacMichael's viscosimeter at 15°C.

Concentration of starch solution	Boiling 20 minutes			Boiling 40 minutes		
	1.0%	1.5%	2.0%	1.0%	1.5%	2.0%
Kind of starch						
Common-Saitama	18.5	38.0	91.0	18.5	37.5	98.0
" Tochigi	29.0	79.0	270.0	25.0	75.0	250.0
" Higo	21.0	47.5	138.0	20.0	51.0	147.0
" Hyuga	24.5	63.0	211.5	25.0	70.0	190.0
" Shikoku	26.0	82.5	137.5	26.0	82.0	290.0
" Niigata	23.5	45.5	122.0	22.0	48.0	185.0
" Shonai	19.0	37.0	91.0	17.0	43.0	112.0
" Chiba	26.5	66.0	201.0	23.0	62.0	192.0
" Miye	22.0	52.0	145.5	22.0	56.0	171.0
" Hyogo	25.5	61.0	175.0	23.0	62.0	199.0
" Ibaragi	21.0	46.0	135.0	22.0	55.0	131.0
" Manchuria	17.0	30.5	70.0	16.0	35.0	83.0
" Formosa	23.5	48.0	105.0	22.0	50.9	125.0
" Siam	19.5	47.5	141.5	20.0	45.0	159.0
" China	15.5	54.5	179.0	22.0	35.0	202.0

TABLE 21.

Showing the specific viscosity of the glutinous starch solution prepared by boiling 20 minutes. Determined by MacMichael's viscosimeter at 15°C.

	Etchu	Miye	Hyogo	Hokkaido	Ibaragi
0.5 % starch solution	17.0	16.5	16.0	16.5	25.5
0.75% ,, ,,	30.5	31.5	23.0	29.0	35.5
1.0% ,, ,,	56.0	47.0	45.0	44.0	64.0
1.25% ,, ,,	99.5	90.5	81.0	79.5	237.5

From the above tables, the author observes a remarkable difference between the viscosity of glutinous and common starch solution. The former always showed two or three times the viscosity of the latter. The viscosity changes according to the varieties or growing places of rices. Further investigation was undertaken to learn the influence of duration of boiling of starch solution on their viscosity. The viscosity of starch solutions, which were treated for the following intervals in a water bath at 98°-100°C., was measured with MacMichael's viscosimeter at 15°C.

TABLE 22.

Showing the change of the specific viscosity of glutinous starch solution, according to the duration of boiling.

Kind of starch	Concentr. of starch solution	Duration of boiling				
		3 minutes	7 min.	15 min.	30 min.	60 min.
Etchu-glutinous	1.0%	7.1	8.4	8.4	8.3	8.5
Akita-glutinous	1.0%	8.2	8.9	8.9	8.9	8.9
Hokkaido-glutinous	1.0%	6.3	6.2	7.4	7.2	7.5
Etchu-glutinous	1.5%	33.4	33.2	39.4	39.8	32.5
Akita-glutinous	1.5%	38.7	39.7	45.7	46.5	44.8
Hokkaido-glutinous	1.5%	24.2	25.9	28.5	20.4	19.2

From the above table, the author observes that the viscosity of glutinous rice starch was increased proportionately to the boiling time and reached a maximum point at a certain time after which it decreased again with a longer time of boiling. The boiling time which is needed to reach the maximum point of viscosity varied with the different kinds of glutinous starch.

Next the author examined the change of viscosity of glutinous starch solution according to hours of standing.

TABLE 23.

Showing the specific viscosity calculated from the results of 1.25-1.5% starch solution at 14°-18°C. (MacMichael's viscosimeter.)

1.25% glutinous starch solution	Instantly	After 2 days	After 4 days	After 8 days	After 10 days			
Chiba	18.08	14.28	11.85	9.34	8.65			
Miye	13.70	11.81	10.34	8.15	7.76			
Hokkaido	11.42	9.99	8.89	7.34	6.61			
1.5% glutinous starch solution	In-stantly	1.5 hrs.	2.25 hrs.	3.08 hrs.	4.5 hrs.	24.0 hrs.	48.0hrs.	190 hrs.
Etchu	100	98.5	91.6	84.2	75.0	23.8	4.4	2.3
Akita	100	96.5	94.0	87.5	79.0	24.0	7.8	2.9
Hokkaido	100	92.0	91.0	90.0	77.0	24.0	9.2	3.9
1.0% glutinous starch solution	Instantly	After 2 days	After 3 days	After 4 days	After 5 days	After 6 days	After 7 days	
Akita	(1) 100	99.8	75.0	—	69.5	—	22.3	
	(2) 100	99.7	—	59.7	35.1	19.7	—	
Hokkaido	(1) 100	99.2	73.0	—	39.5	—	25.5	
	(2) 100	99.8	—	59.2	43.4	27.5	—	
Chiba	(1) 100	99.5	94.8	—	66.1	—	42.5	
	(2) 100	99.8	—	93.5	74.1	16.2	—	
Hyogo	(1) 100	98.9	97.0	—	62.5	—	40.2	
	(2) 100	99.9	—	73.1	52.5	34.5	—	
Miye	(1) 100	99.2	89.0	—	63.5	—	42.5	
	(2) 100	99.5	—	88.5	78.5	50.6	—	
Hokkaido	(1) 100	98.0	89.5	—	76.0	—	34.5	
	(2) 100	99.7	—	81.5	68.5	29.2	—	
Etchu	(1) 100	99.0	77.0	—	31.5	—	19.3	
	(2) 100	99.0	—	47.1	24.7	14.9	—	

From the above table, the author observes that the viscosity of glutinous rice starch was decreased proportionately to the hours of standing.

XIII. PHYSICO-CHEMICAL CHANGES OF STARCH SOLUTION ILLUMINATED BY ULTRAVIOLET RAYS.

It is a well known fact that the physico-chemical properties of starch solution are changed by illumination with ultra-violet rays. The author intended to examine the physico-chemical changes of common and glutinous starch solution by illumination with these rays.

(a) *Change of viscosity of starch solution.*

One and a half per cent starch solution was illuminated with a quartz-mercury lamp from a distance of 1 foot during different hours. Its viscosity was compared with the control.

TABLE 24.

Showing the specific viscosity which was calculated from the value obtained by MacMichael's viscosimeter at 20°-30°C.

	Akita		Etchu		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
No illumination	2.0	41.2	1.7	50.8	1.9	38.5
Illumination	1.9	31.7	1.7	32.4	1.5	23.5
Difference	0.1	9.5	0	18.4	0.4	15.0
	Etchu glutinous		Akita glutinous		Hokkaido glutinous	
	ill.	no ill.	ill.	no ill.	ill.	no ill.
No illumination	64.8	62.6	37.6	42.4	28.6	28.6
45 minutes	41.6	61.5	24.7	41.6	23.4	25.4
Next 30 minutes	32.7	56.0	18.4	39.7	18.6	25.0
" " "	25.3	50.1	16.3	35.6	14.8	24.5
" " "	19.4	42.8	11.1	30.2	11.1	18.8

From the above table, the decrease of viscosity of glutinous starch

solution is observed to be greater than that of common. The rate of the change varied with the kinds of glutinous starch.

(b) *Change of iodine reaction of starch solution.*

One per cent starch solution was heated in an autoclave at 3.0-3.5 atmospheric pressure for 1 hour and 10 ccm of this solution was illuminated by a quartz-mercury lamp for 30 minutes at the distance of 1 foot. Its iodine reaction was examined with 1-2-3 drops of 1/200 1/100 and 1/10 normal iodine solution. The common and glutinous starch solutions which were illuminated by ultra-violet rays were more easily stained by iodine solution than those not illuminated.

Next 0.5 % starch solution was mixed with 1/2000 normal iodine solution and the time of illumination necessary to decolorize the iodine starch solution was determined. The author observed that the illuminating periods were less in the case of glutinous starch solution than in common.

Table 25.

Showing the illumination period needed to decolorize the iodine starch solution.

	Chiba		Miye		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
Decoloration (min.)	110	40	130	40	95	30

(c) *Formation of reducing substance from starch solution.*

It is well known that when the starch solution contains AgNO_3 , on illumination by ultra-violet rays, the AgNO_3 solution is reduced. Thus the author proposed to determine the contents of reducing substance of the illuminated starch solution by the following operation. Using each starch sample 2 ccm of 0.1 % solution were mixed with 3 ccm 1/1000 normal AgNO_3 solution, illuminated with a quartz-mercury lamp in vessels of the same diameter, and the color intensity of common and glutinous starch solution was compared by Duboscq's colorimeter.

TABLE 26.

Showing the contents of reducing substance of the illuminated starch solution.

	Akita		Etchu		Hokkaido	
	common	glutinous	common	glutinous	common	glutinous
30 minutes (color)	no	violet	no	violet	no	violet
Intensity of color	0	1.00	0	1.39	0	1.34
60 minutes (color)	no	—	no	—	no	—
90 minutes (color)	light violet	—	light brown	—	yellowish brown	—
Intensity of color	1.00	—	1.12	—	3.75	—

The above results show that the color of glutinous starch solution was more intense than that of common, therefore the glutinous starch solution was changed easily to reducing substance by illumination of ultra-violet rays.

XIV. CONTENTS OF ALCOHOL SOLUBLE SUBSTANCE IN STARCH SOLUTION.

Samec and Haeftti⁽¹⁾ proposed a method for determination of amylose and amylopectine in starch, though the method has many defects in its operation. The author tried to determine the difference between common and glutinous starch solution by this method and operated as follows:—1 % starch solution was converted to paste in 4 minutes on a water bath and kept 20 minutes in boiling water (98°–100°C.). One hundred ccm of the solution were cooled to 80°C., stirred vigorously, cooled again and 200 ccm of 95 % alcohol added to make a precipitate. The precipitate was filtered off and the filtrate was evaporated, dried and weighed. Thus it was observed that the soluble substance of glutinous starch solution is always greater than that of common.

XV. DETERMINATION OF AMYLOSE AND AMYLOPECTINE OF STARCH.

There are many methods which have been proposed for the determination of amylose and amylopectine by many authors, viz. Maquenne and

(1) Samec & Haeftti:—Koll. Chem. Beiheft, 5, 16. 1913.

Roux's method⁽¹⁾, Gatin-Gruzewska's method⁽²⁾, Samec and Haefti's method⁽³⁾, and other's. But these are not adapted to exact determination of both constituents so Pringsheim⁽⁴⁾ recommended the following process⁽⁵⁾ as the best method. The author intended to determine the difference in amylose and amylopectine contents between common and glutinous starch by this method. By the ordinary method, 1 % starch solution was prepared and when it was frozen for 12 hours under -10°C ., the amylopectine appeared as a cloudy precipitate. The precipitate was separated from soluble amylose by filtration, washed with hot water at 80°C ., dried and weighed. The filtrate was concentrated on a water bath and alcohol used to precipitate the amylose which was then filtered, dried and weighed.

TABLE 27.

Showing the contents of amylose and amylopectine in starches produced from both common and glutinous rice grown in different localities.

	Hokkaido		Ibaragi		Kyushu		Miye	
	common	glutinous	common	glutinous	common	glutinous	common	glutinous
Amylo- pectine	72.49	20.68	81.09	28.53	80.98	28.78	72.00	25.49
Amylose	27.51	79.32	18.91	71.47	19.02	71.22	28.00	74.51

XVI. PREPARATION AND COMPOSITION OF SOLUBLE STARCH.

The soluble starch was prepared by the following operation. In 2 litres of 7.5 % HCl-solution, 500 g. of starch were soaked, shaken many times in a day and then kept for 10 days at 20°C . The soaked starch was washed with water until the wash water showed no chlorine reaction, then washed with 70 % alcohol and poured on a silk cloth which was placed on a filter. The washed starch was washed again

- (1) Maquenne & Roux:—Compt. rend., **140**, 1303. 1905.
- (2) Gatin-Gruzewska:—Compt. rend., **146**, 540. 1908.
- (3) Samec & Haefti:—Koll. Chem. Beiheft, **5**, 16. 1913.
- (4) Pringsheim:—Deuts. chem. Ges., **5**, 888. 1924.
- (5) Ling & Nanji:—Soc., **123**, 266. 1923.

with pure alcohol and ether and then dried for 2 days at 40°C. The contents of water and mineral substance were determined.

TABLE 28.

Showing the moisture- and ash-contents of soluble starches produced from both common and glutinous rice.

	Common		Glutinous	
	(1)	(2)	(1)	(2)
Moisture	7.67	12.87	5.96	11.98
Ash (dry matter %)	0.038	0.045	0.024	0.028

From this table, the author see that the above operation is a process of demineralization of starch, and that the content of mineral matter of glutinous soluble starch is less than that of common.

XVII. VISCOSITY OF SOLUBLE STARCH SOLUTION.

The viscosity of soluble starch solution differed much from that of the original starch solution. The viscosity of common and glutinous soluble starch solution was examined with Ostwald's viscosimeter at 15°C. Their specific viscosity is shown in the following table.

TABLE 29.

Showing the viscosity and the specific gravity of soluble starch solution.

Conc. of starch solution	common		glutinous	
	Viscosity (sp. gr.)	Viscosity (sp. gr.)	Viscosity (sp. gr.)	Viscosity (sp. gr.)
1.0%	1.3420(1.0040)	1.3204(1.0040)	1.1316(1.0041)	1.1401(1.0033)
1.5%	1.5296(1.0053)	1.4684(1.0053)	1.2431(1.0055)	1.3707(1.0053)
2.0%	1.6554(1.0076)	1.5712(1.0077)	1.4886(1.0076)	1.5189(1.0075)

The viscosity of glutinous soluble starch solution was lower than that of common, it being quite different from that of the original starch solution.

XVIII. SOLUBLE STARCH WITH ALKALI.

(a) *Alkali combined with soluble starch.*

In 20 ccm of 10 % NaOH solution, 0.5 g. of soluble starch was dissolved and a precipitate was formed by the addition of 30 ccm of 95 % alcohol. The supernatant alcohol which dissolved the excess of alkali was poured off and the precipitate was dissolved in 10 ccm of water and precipitate was formed again. The manipulation was repeated about 7 times and when the alcohol showed no alkali reaction, the precipitate was taken out and dried in a sulphuric acid desiccator. The ash content of glutinous alkali starch was less than that of common (0.37 % in the former and 0.83 % in the latter). Therefore glutinous soluble starch combines with a less quantity of alkali than that of common.

(b) *Solubility of alkali soluble starch.*

When the powder of alkali soluble starch was dissolved in water, shaking for 24 hours at 15°–20°C., the glutinous alkali soluble starch dissolved easily to a 1 % solution, while the common alkali soluble starch formed a saturated solution of 0.82 %.

(c) *Conductivity of alkali soluble starch.*

The alkali soluble starch is dissociated in water solution and when the same quantity of common and glutinous alkali soluble starch was dissolved in 25 ccm of water, the solution showed the following conductivity. So it is evident that the dissociated parts of glutinous alkali starch are far less in quantity than those of common.

TABLE 30.

Showing the conductivity of alkali soluble starch solution.

Concentration	0.82%	0.41%
Common alkali soluble starch	5.388·10 ⁻⁵ –5.363·10 ⁻⁵	1.010·10 ⁻⁵ –1.020·10 ⁻⁵
Glutinous „ „ „	1.968·10 ⁻⁵ –1.849·10 ⁻⁵	0.265·10 ⁻⁵ –0.213·10 ⁻⁵

(d) *Precipitate of alkali soluble starch with alcohol.*

When the soluble starch was dissolved in alkali solution, the precipitate decreased as time elapsed. Here 5 g. of soluble starch were taken, mixed with 100 ccm of 10 % NaOH solution and shaken for 2 hours. A definite quantity of this mixture was mixed with the same volume of 95 % alcohol and the precipitate was collected on a filter, dried and weighed.

TABLE 31.

Showing the precipitate of alkali soluble starch with alcohol.

%	After 2 hrs.	Difference	After 48 hrs.	Difference	After 96 hrs.
Glutinous	82.09	3.82	78.17	3.82	74.25
Common	99.84	4.09	95.73	4.73	91.02

The alcohol precipitate of glutinous alkali soluble starch was less than that of common.

(e) *Precipitate of alkali soluble starch with acetic acid.*

When the precipitate of alkali soluble starch was formed by the addition of acetic acid, the quantity varied with the different kinds of soluble starch. One half gram of soluble starch was dissolved in 5 ccm of 10 % NaOH solution and 20 ccm. of water added, then the solution was neutralised with acetic acid. In the case of common starch solution, the precipitate corresponded to 13.87-17.44 % of the original starch while in glutinous soluble starch solution no precipitate formed.

XIX. DETERMINATION OF AMYLOSE AND AMYLOPECTINE OF SOLUBLE STARCH.

One per cent soluble starch solution was prepared and the quantity of amylose and amylopectine was determined by the method described in section XV, supra. The following numbers represent the percentages of the soluble starch.

TABLE 32.

Showing the amylose and amylopectine contents of soluble starch.

%	Amylopectine		Amylose	
	Common	Glutinous	Common	Glutinous
Ibaragi	26.50	1.77	73.50	98.23
Chiba	24.64	1.04	75.36	98.96

From the above table the author observes that the amylopectine content of common soluble starch is greater than that of glutinous while the amylose is vice versa.

DISCUSSION.

In the colloidal and chemical structure, the ultimate difference between common and glutinous rice starch may be deduced by the results of the author's experiments, which are stated already in the author's first as well as in this report.

Strikingly marked difference was observed between the powers to adsorb iodine as well as the affinity for iodine in the case of both glutinous and common rice starch. The same difference was observed not only in the case of starch granules or solutions but also in the charcoals of both kinds. If the author supposes that the adsorption power of iodine by charcoal is caused by the latent valences in their molecule the same assumption would hold for the molecular structure of starch. This characteristic behavior of starch may be caused by higher polymerization degrees of molecules.

The common rice starch has a larger calorific value, i. e. heat of combustion, than glutinous, and after hydrolysis the former is richer in undigested residue as well as in reducing substance. Thus the lower decomposition velocity of common starch is caused by its higher polymerization.

The difference of polymerization degree between common and glutinous rice starch as well as between different varieties of both kinds would account for the difference in viscosity, number of boiling hours required for maximum viscosity of solutions, and also formation of reducing substance by the illumination with ultra-violet rays.

The difference of methylation and acetylation degree may be caused by the different position of OH-groups which are replaced easily or not in the molecular structure. The common rice starch has many OH-groups which are replaced by the acetyl or methyl radical.

In common rice starch, the quantity of amylopectine, which is rich in mineral substance, especially P_2O_5 is far more abundant than amylose, which is poor in ash contents, while in glutinous the relation of amylopectine and amylose is reversed. When the starch was treated with HCl to make soluble starch, P_2O_5 was dissolved out and its amylopectine be converted to amylose. The amylopectine of glutinous starch was almost all converted to amylose, while in common starch the quantity of amylopectine converted was very small.

Solubility and degree of dissociation of the sodium compound of soluble starch show a great difference between common and glutinous. The solubility of sodium compound of glutinous soluble starch, which was converted almost completely to amylose, is greater than that of common soluble starch. The dissociation degree of sodium compound of glutinous soluble starch is less than that of common, because the former is combined with a less quantity of sodium than that of the latter. Further we know that the common soluble starch is precipitated from NaOH-solution by neutralization with acetic acid, while the glutinous soluble starch formed no precipitate. These facts show that the amylopectine is precipitated by the above treatment, but the amylose is not.

SUMMARY.

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

(1) The ash content of glutinous rice starch is less than that of common, and the former is richer in SiO_2 -contents than in P_2O_5 , while the latter is richer in P_2O_5 than in SiO_2 . The ash content of both kinds of rice starch is very variable and it shows no definite ratio to the $(C_6H_{10}O_5)$ -group.

(2) In the results of adsorption of iodine-in-water-solution by rice starch, the constant K (Freundlich's formula) of common rice starch is greater than that of glutinous, while the constant $1/n$ is the contrary. The same relation of the constants was observed also in the adsorption of iodine in alcohol solution, and the logarithmic equation of adsorption was expressed by one straight line, while in the former case, the

equation was composed of two lines which showed different inclinations to the abscissa.

(3) In the adsorption of iodine by common starch charcoal, the constant K of Freundlich's formula is greater than that of glutinous. This relation is very similar to the results described in the author's first report.

(4) In the resistance of starch to sulphuric acid, common rice starch is stronger than glutinous and the former gives also a greater quantity of reducing substance than the latter.

(5) In the methylation of starches, the methoxyl-group content of common rice starch is greater than that of glutinous.

(6) In the acetylation of starch, the acetyl-group content of common rice starch is greater than that of glutinous and the melting point and the specific rotatory power of the former are higher than those of the latter. The two kinds of acetyl starch show a difference from each other in adsorption power of iodine and K -iodide.

(7) The heat of combustion of common rice starch is greater than that of glutinous, the latter corresponding to 96.0–99.8 % of the former.

(8) In the adsorption of iodine by starch solution which is separated by a wall of a parchment paper, the common rice starch solution adsorbed a greater quantity of iodine than did that of glutinous in a definite time. In the diffusion of iodine from iodine starch solution through a parchment paper, the velocity of diffusion from glutinous starch solution is greater than that of common. This is probably caused by the weakened adsorptive power of glutinous starch solution to iodine.

(9) The viscosity of glutinous rice starch solution is higher than that of common and the difference is strongly marked in the higher concentration of starch paste. The viscosity of both kinds of starch solution varied with the varieties of rice, place of production and also boiling time of their preparation. When the boiling time of the starch solution was lengthened, the viscosity was increased gradually and after reaching a maximum point, decreased by the further lengthening of the boiling time. The boiling time which is needed to attain the maximum viscosity of starch solutions varied with the varieties and production places of the rice. So the starch of rice should differ by its condensation degree.

(10) On illumination by ultra-violet rays the viscosity of glutinous

rice starch solution decreased more quickly than that of common and the former gave a greater quantity of reducing substance than did the latter.

(11) The quantity of alcohol-soluble substance of glutinous rice starch solution is greater than that of common, and the content of amylopectine of common is greater than that of glutinous. With amylose the contrary holds.

(12) The ash content of common soluble starch which was prepared by treating with HCl-solution is greater than that of glutinous, and the viscosity of the former is higher than that of the latter.

(13) The quantity of alkali combined with common soluble starch is greater than that of glutinous, i. e. 0.82 % of the former to 0.37 % of the latter. The solubility of alkali soluble starch is greater in glutinous than in common, i. e. the former formed a 1.0 % solution easily, while the latter become saturated at 0.82 %. The conductivity of the alkali soluble starch solution is greater in common than that in glutinous, though the concentration of both solutions was the same.

(14) When the soluble starch was treated with alkali solution, the quantity of alcohol precipitate decreased gradually as time elapsed and the quantity of alcohol precipitate of glutinous was less than that of common. The precipitate of alkali soluble starch which was formed by neutralization with acetic acid showed 13.8-17.5 % in common while glutinous gave no precipitate.

In the demineralization of starch, the amylopectine was converted to amylose, and in the case of glutinous soluble starch, the amylopectine was converted easily to amylose, while in common soluble starch, 1/3 part of the original amylopectine remained intact.
