STUDIES ON THE MIRIN (SWEET SAKE) I. ON THE SUGAR COMPOSITION OF THE MIRIN

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I. ON THE SUGAR COMPOSITION OF THE MIRIN*

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Mirin is a rebrewery produced by saccharification of enzyme of rice Koji under the existence of alcohol, from Shôchû, rice Koji and steamed waxy rice. In our country, the Mirin was separated into two types in the Liquor Tax Law, the one was alcohol over 13 per cent, Báume over 19° and the other was alcohol over 22 per cent, Báume over 2°. The former was called "Honmirin" and it was used for cooking and the latter was called "Honnaoshi".

Maruyama (1) has reported on the analyses of the sugar composition of Mirin. Kuriyama (2) has identified glucose and maltose as osazone. Tsukinaga (3) has reported on the analyses of Mirin and glucose, maltose, xylose and rhamnose were identified as osazone. Katô and Aoyagi (4) have reported that alcohol, glucose, dextrin, total acid, amino acid and Báume specific gravity in Mirin Moromi were analysed. Ômata *et al.* (5) have reported that alcohol, total sugar, reducing sugar and total nitrogen in Mirin were analysed.

We now report on the analyses of five kinds of Mirin produced from Shôchû, rice Koji and steamed waxy rice, paper chromatography (PPC) of sugars in Mirin, and separative determination of the sugars by the paper chromatographic method (Somogyi method), the separative determination of kojibiose, nigerose and maltose fractionated by carbon column chromatography (Carbon CC), compared the sugar composition with Saké (6, 7), rice Koji juice (8) and Amasaké (9) produced from rice.

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* The original Japanese report was published in Hakkō-Kōgaku Zasshi (J. Fermentation Technology **37**, 145–149 (1959).

Experimental

I. Analyses of Mirin.

The five samples of Mirin (Mirin A: two kinds of ordinary Mirin and one kind of Mirin made from only common rice, Mirin B: ordinary Mirin, Mirin C: ordinary Mirin) produced from Shôchû, rice Koji and steamed waxy rice were analysed. The results are shown in Table 1.

Table 1. Analyses of Mirin.

	Specific gravity	(Báume)	Total sugar (g/100*ml*)	Reducing sugar (g/100*ml*)	Totala cid (g/100*ml*)	Alcohol (%)	pH
No. 1	1.158(27.5)	20.41	47.33	44.80	0.049	14.1	—
No. 2	1.160(23.5)	—	45.00	38.25	—	14.6	5.5
No. 3*	1.099(27.5)	13.60	29.53	28.08	0.067	9.9	—
No. 4	1.163(15.0)	19.97	46.91	43.01	0.060	14.5	—
No. 5	1.152(25.7)	19.55	42.95	41.09	0.15	13.2	—

* No. 3: Mirin made from only common rice.

Analytical methods were as follows. Specific gravity: standard specific gravity meter and Báume specific gravity meter; total sugar: after heating with 2.27 per cent HCl on the boiling water bath for 2.5 hours followed by neutralization with NaOH, determined by the Bertrand-Henmi method (calculated as glucose); reducing sugar: Bertrand-Henmi method (calculated as glucose); total acid: titration acidity (calculated as lactic acid) with a mixed indicator of Brom-thymol blue and Neutral red; pH: Hitachi pH meter.

Table 2. Analyses of Mirin.

a) Maruyama (1898)

Productive place	Specific gravity	Alcohol (%)	Extract (%)	Glucose (%)	Dextrin (%)	Ash (%)
Nagareyama	1.136	13.79	40.70	38.38	1.17	0.08
Ôsaka	1.069	10.53	21.27	18.83	0.51	0.19
Aichi	1.102	16.07	32.10	30.03	0.66	0.08

b) Tsukinaga (1918)

Specific gravity	Alcohol (%)	Extract (%)	Sugars (%)	Dextrin (%)	Ash (%)	Total acid (as succinic acid) (%)
1.123	18.00	38.20	33.52	4.10	0.12	0.04

c) Ômata *et al.* (1954)

Sample	Alcohol (%)	Total sugar (%)	Reducing sugar (%)	Total nitrogen (%)	
No. 1	13.2	43.46	41.06	0.10	
No. 2	13.0	41.26	41.82	0.88	storage one years
No. 3	13.0	41.26	40.51	0.11	storage two years

In Table 2, the results of analyses by Maruyama, Tsukinaga and Ômata are shown for reference.

From the results of Table 1, the mean values were as follows: total sugar 45.55 g/100 *ml*, reducing sugar 41.79 g/100 *ml* as glucose, total acid 0.086 g/100 *ml* as lactic acid and alcohol 14.1 per cent.

Mirin produced from common rice only instead of waxy rice was not good in its quality, because the saccharification of common rice proceeded slower than that of waxy rice.

II. PPC of the sugars in Mirin.

Each Mirin was prepared by dilution with 10 fold water and spotted on the Tôyo filter paper No. 2. After irrigating the chromatogram with pyridine-butanol-water (4:6:3), ascending three times, the sugars were located by spraying with aniline hydrogen phthalate and resorcinol reagents. The results are shown in Fig. 1.

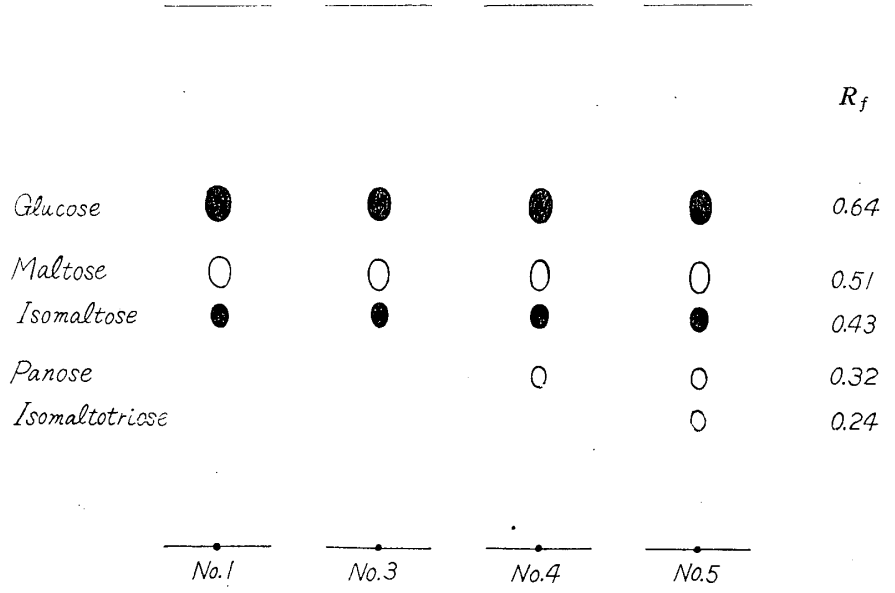

Fig 1. Multiple paper chromatogram of sugars in Mirin.

From the results of Fig. 1, glucose, isomaltose and maltose were detected in each samples, and in Mirin No. 4, panose was detected besides the above three sugars, in Mirin No. 5, panose and isomaltotriose were detected besides the three sugars.

The maltose fraction in Mirin was fractionated by Carbon CC followed by PPC in detail. The results are shown in Fig. 2.

From the results of Fig. 2, kojibiose and nigerose were detected in Mirin besides the above mentioned sugars. Glucose, kojibiose, nigerose, maltose, isomaltose, panose, isomaltotriose were detected.

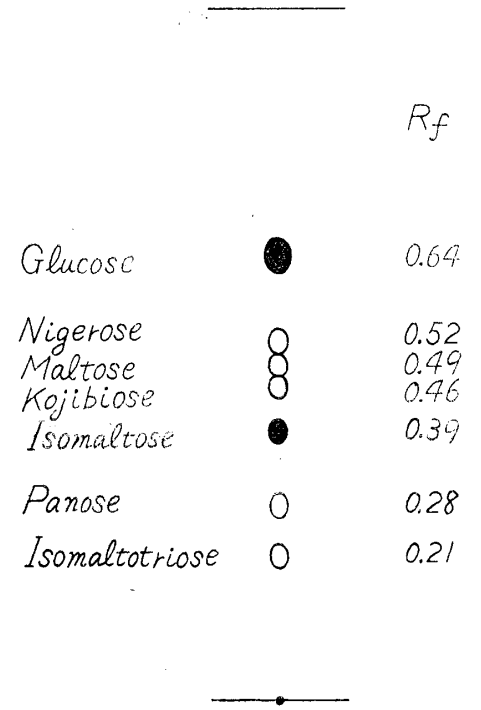

Fig 2. Multiple paper chromatogram of sugars in Mirin.

In Fig. 3 and Fig. 4, multiple paper chromatogram of sugars in Saké and Amasaké (sweet sugary liquor made from rice) are shown, and compared with the sugar composition in Mirin.

From the above results, it was recognized that Mirin and Amasaké contained maltose, while Saké did not contain maltose, because it was fermented by yeast.

III. Separative determination of sugars in Mirin.

Since glucose, kojibiose, nigerose, maltose, isomaltose, panose and isomaltotriose were detected in Mirin as mentioned above, these sugars were determined separately by PPC followed by the Somogyi method. Each Mirin was prepared by dilution with 10 fold water and

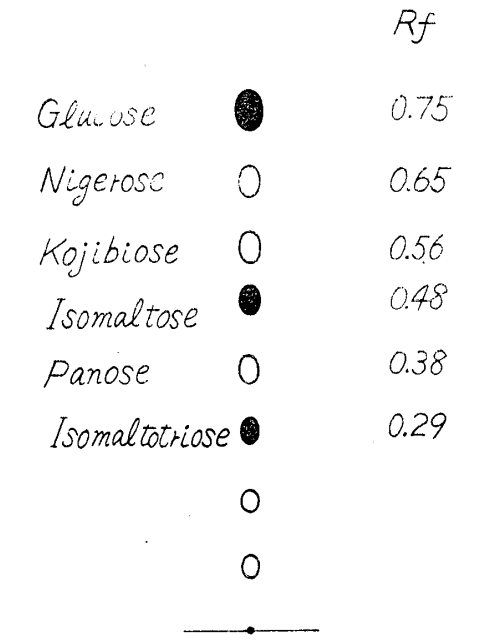

Fig 3. Multiple paper chromatogram of sugars in Saké.

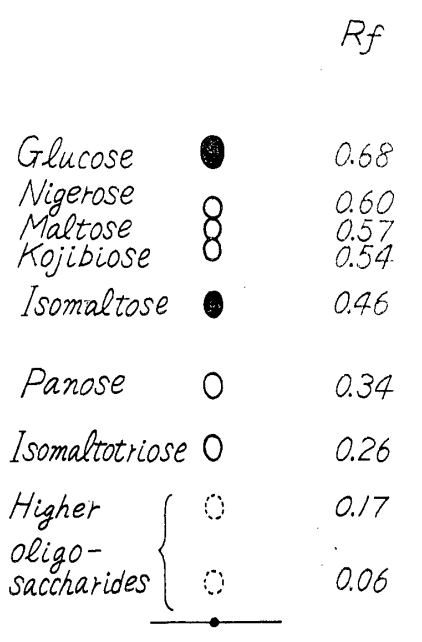

Fig 4. Multiple paper chromatogram of sugars in Amasaké.

spotted on the Tôyo filter paper No. 51. After irrigating the chromatogram with pyridine-butanol-water (4 : 6 : 3), ascending three times, guid strips were cut off from both sides of the chromatogram and the position of the sugars were located with aniline hydrogen phthalate. The zones corresponding to monosaccharides and oligosaccharides were cut off and eluted with water and oligosaccharides fraction were hydrolysed with acid, followed by neutralization with NaOH, and determined by the Somogyi method. The results are shown in Table 3.

Table 3. Separative determination of sugars in Mirin.

	Glucose (g/100 *ml*)	Nigerose (g/100 *ml*)	Isomaltose (g/100 *ml*)	Higher oligosaccharides (g/100 *ml*)
No. 1	36.50	3.22	5.57	2.04
No. 2	36.35	1.66	3.87	3.12
No. 3*	23.47	2.06	2.33	1.67
No. 4	42.76	1.34	1.87	0.94
No. 5	35.52	2.65	3.75	1.03

* Mirin produced from common rice only.

In Table 3, kojibiose and maltose were contained in nigerose fraction. The main sugar of Mirin was glucose and its content was 77~91 per cent (average 82.25 per cent) of the total sugar.

IV. Separative determination of sugars in maltose fraction (kojibiose, nigerose and maltose).

The maltose fraction in Mirin fractionated by Carbon CC was spotted on the Tôyo filter paper No. 51. After developing the chromatogram with pyridine-butanol-water (4 : 6 : 3), ascending three times, guid strips were cut off from both sides of the chromatogram and position of the sugars were located by aniline hydrogen phthalate. The zones corresponding to three sugars were cut off and eluted with water followed by hydrolysis with acid, neutralization with NaOH, and determined by the Somogyi method. The results are shown in Table 4.

Table 4. Separative determination of kojibiose, nigerose and maltose in Mirin.

	The ratio of three sugars in maltose fraction (Mirin) (%)	The content in Mirin (%)	The ratio of three sugars in maltose fraction (Saké) (%)	The content in Saké (%)
Nigerose	44.84	0.74	50.00	0.08
Maltose	37.30	0.62	—	—
Kojibiose	17.86	0.30	50.00	0.08
Total		1.66		0.16

From the results of Table 4, the content ratio of nigerose, maltose and kojibiose fractionated by Carbon CC was 44.84 : 37.30 : 17.86.

The content of nigerose was larger than kojibiose in Mirin, but nigerose was equal to kojibiose in Saké. Mirin contained maltose, while Saké did not contain maltose, because it was fermented by yeast.

Summary

Analyses of five samples of Mirin produced from Shôchû, rice Koji and steamed waxy rice were carried out. The mean values were as follows: total sugar 45.55 g/100 *ml*, reducing sugar 41.79 g/100 *ml* as glucose, total acid 0.086 g/100 *ml* as lactic acid and alcohol 14.1 per cent.

On the paper chromatogram of the sugars in Mirin, seven spots corresponding to glucose, kojibiose, nigerose, maltose, isomaltose, panose and isomaltotriose were detected and determined. The main sugar of Mirin was glucose and its content was 77~91 per cent (average 82.25 per cent) of the total sugar.

The content ratio of nigerose, maltose and kojibiose fractionated by Carbon CC was 44.84 : 37.30 : 17.86.

From the above results, it was recognized that Mirin contained maltose, while Saké did not contain maltose, because it was fermented by yeast.

Mirin produced from common rice only instead of waxy rice was not good in its quality, because the saccharification of common rice proceeded slower than that of waxy rice.

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