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MOLECULAR CHANGE OF STARCH GRANULES WITH DRY/OIL HEAT TREATMENT AND ITS APPLICATION IN FOOD

Summary

Molecular change of starch granules and its reaction in the simple system with heat in the cases of 11 starch species (normal-, amylo-, waxy-maize, normal-, waxy-wheat, normal-, waxy-rice, potato, sweet potato, cassava, sago) were studied . Dry heat treatment of starch samples was carried out at 200°C for 0.5 h, 1 h and 2 h. Oil treatment involved heating of starch in soy bean oil, methyl laurate and methyl oleate and kept at 190°C. After heating, SEM showed no changes of the granule images but they became instantly water soluble after 2 h heat treatment. GPC studies revealed that every 2 h starch sample was largely disrupted and became smaller than amylose but fairly larger than oligosaccharide. Hence, one assumed that starches are disrupted to cluster unit. Decomposition ratio of amylose was different among plant origin. In general, tuber starch was far more resistant to heat than cereal starch. Oligosaccharides formed in this processing are all anhydro type. Heat treatment in oil gave almost same effect on starch and the decomposition took place more rapid than in air. However, treatment time did not bring increase of oil incorporation into starch granule and there was little difference among oil species.

Introduction

Many baked foods including bread, cookies and biscuit are very common all over the world. However, there are only limited studies on molecular change of their starches in the food on such processing. Because, foods are complex systems of several materials and processing, hence, situation of starch in a food is dependent on other residing with it components. As the result, molecular changes of all components are closely related to each other. Especially, behaviour of lipids is related to starch modification. At first, it is essential to recognize that starch in baked food ordinary exists in the granular state. Starch granule has the fine structure, multi-dimensional structure with radial direction. Also granule has a canal leading from surface to hilum. Naturally, these structures are related to gelatinization and formation of complex with other

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components in processing. For example, we reported that there are more saturated fatty acids incorporated into starch granule as inclusion complex than unsaturated fatty acids when starch is treated with fatty acid mixture under ultra high pressure (700 MPa) [1]. Probably this observation might be related to amylose situation in granule with relation to that of amylopectin. This fact might affect physical property of food. Hence, it is difficult to study properties and behaviour of starch in food.

We have begun studies of starch and lipid in food processing from simple system and results of this study are presented in this report.

Materials and methods

Materials

Ten species of starches were adopted, and they were, A) normal maize, B) amylomaize, C) waxy maize, D) wheat, E) normal rice, F) waxy rice, G) potato, H) sweet potato, I) cassava, J) sago.

Methods

Dry heat treatment: each starch sample (5g) was placed in Petri dish and covered with aluminum foil followed by maintaining samples at 200°C for 0.5 h, 1 h and 2 h.

Subsequently, samples in solution of 40% perchloric acid [2] were subjected to GPC analysis on Toyopearl HW-65 and HW-50 columns. The concentration of eluted saccharides in each fractionated tube was measured by means of the phenol-sulfuric acid method.

Iodine color reaction spectra patterns of the samples were also measured using the same solution.

Oil heat treatment was carried out as follows: Starch (300 mg) was suspended in a lipid (1 ml) (rape seed oil, methyl laurate and methyl oleate) in a small vials and ultrasonicated then maintained at 190°C in the oven. After such treatment, samples were centrifuged. Upper lipid layer was removed by decantation overnight, then, the incorporated amount of lipid was calculated by subtraction of starch weight from total weight. Lipid amount of inclusion complex in the sample was measured with gas-chromatography. After removing the incorporated lipid with diethyl ether, the inclusion complex of lipid in amylose helices was extracted with chloroform-ethanol mixture (1:1), followed by gas-chromatographic determination.

Glucoamylase sensitivity of the sample was measured as following: The sample (100 mg) was suspended in water (20 ml), then it was kept at 40°C with gently shaking and glucoamylase solution (1 ml) (10 unit) was added stepwise. Amount of liberated glucose in the suspension was measured by the Sumner method.

Microscopic observation was carried under birefringent light on samples suspended in water, and electron scanning microscopic (SEM) pictures were taken after platinum coating.

Matrix Assisted Desorption Ionization-Time of Flight Type-Mass Spectroscopy (MALDI-TOF-MS) was measured by means of Voyager DE PRO System (Biosystems) after dispersion of samplse in 2,5-dihydroxy benzoic acid and sodium iodide solution.

Results and Discussion

SEM images of all species suggested that starches did not change after dry/oil heat treatment except random, small cracks on surface of some granules.

Microscopic observation of dry heated starch samples are diversified. Relatively many species have dark cross until 1 h treatment except waxy type, but after heating for 2 h, all specimens but these of cassava lost this cross. In contrast samples treated for 2 h in oil retained this cross.

Fig. 1 shows the result of glucoamylase sensitivity of samples. All species but waxy type starches showed increasing with heating time sensitivity to such treatment whereas waxy type starches showed opposite behaviour.

It is known that glucoamylase acts from non-reducing end of glucan chain. Hence, if the end moiety of its chain changes to non-glucose, the chain can not be hydrolysed and remains in intact. Reduced ability to amylolysis, remarkable in waxy type starches resulted probably from its sensitivity to thermolysis. Because, amylopectin has a cluster structure forming crystalline regions, amorphous regions in amylopectin bound two or more clusters. When heat is applied to starch, the water (including bound water) in granule is removed. As the result, stress should occur in structure-forming material. The stress might especially occur in the part between crystalline region, namely in amorphous region, because, the crystalline region is well organized and rigid. Disruption of starch in food processing is due to hydrolysis with water, but this disruption by dry/oil heating is rather a pyrolysis, hence, it induces anhydro-type or double bond formation at the scission part.

Fig. 2 shows MALDI-TOF-MS of fragments formed in the sample on the treatment. This figure suggests that they are dehyroxy substances, but it is not certain which type of anhydro or double bond it presents. This result strongly supports former explanation of the reason of heat-induces decrease of waxy starches to amylolysis.

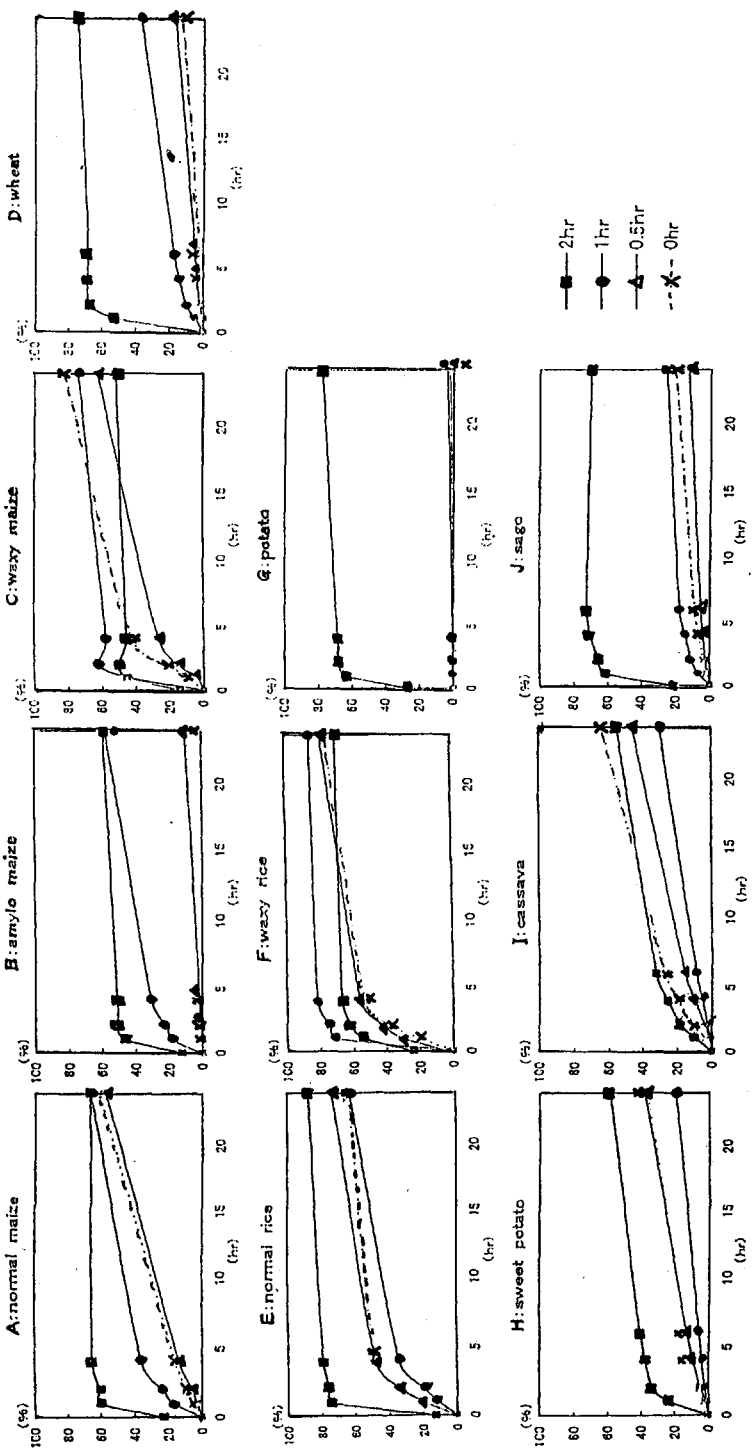
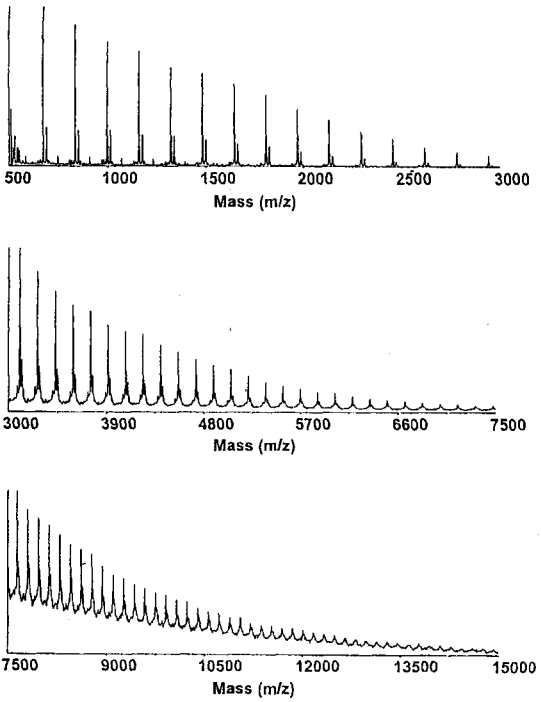


Fig. 1. Glucoamylase sensitivity of dry heated starch.



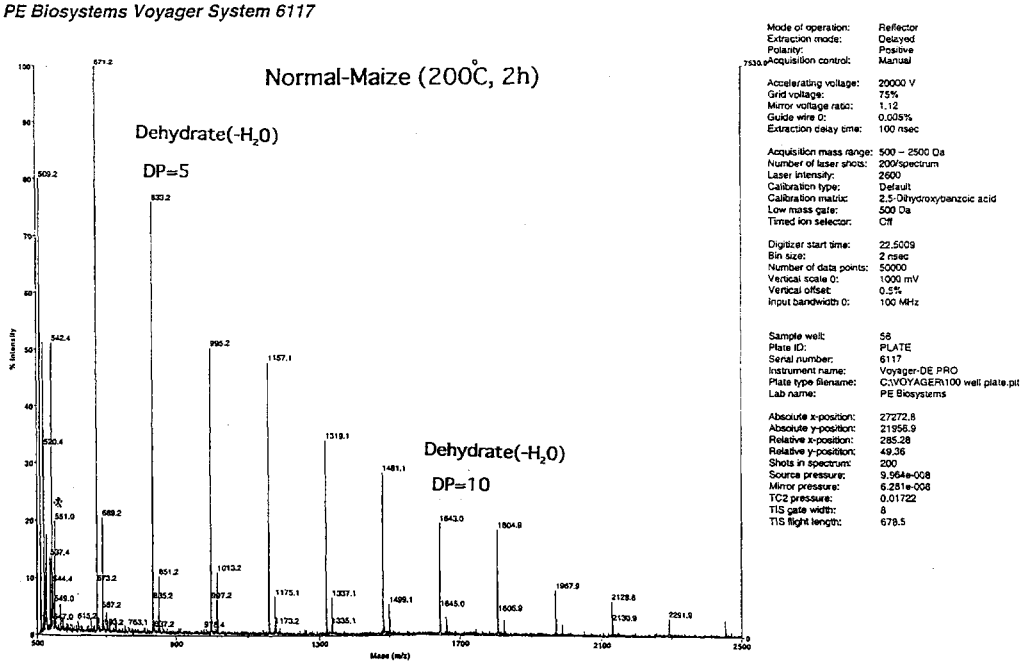


Fig. 2. MALDI-TOF-MS Spectra of dry heated starch (normal maize):
A: Wide range spectrum, B: Detail spectrum of small size fragment.

Table 1

Decomposition rate of amylose in starch granule with dry heat treatment

normal maize		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
A	0hr	0.284	100	595.0~605.0	0.344	100
	1hr	0.078	27(73)	590	0.105	30(70)
	2hr	0.062	22(78)	475	0.024	7(93)

amylo maize		ε680	Ratio (%)	λmax	ελmax	Ratio(%)
B	0hr	0.495	100	605	0.588	100
	1hr	0.08	16(84)	575	0.127	21(79)
	2hr	0.047	9(91)	565	0.091	15(85)

waxy maize		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
C	0hr	0.056	100	450	0.174	100
	1hr	0.015	28(72)	535.0~540.0	0.042	24(76)
	2hr	0.01	18(82)	530.0~535.0	0.033	19(81)

wheat		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
D	0hr	0.309	100	610.0~615.0	0.345	100
	1hr	0.091	29(71)	595	0.118	34(66)
	2hr	0.073	23(77)	585	0.105	30(70)

normal rice		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
E	0hr	0.172	100	590.0~605.0	0.211	100
	1hr	0.048	28(72)	570	0.077	36(76)
	2hr	0.032	18(82)	565.0~570.0	0.058	27(73)

waxy rice		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
F	0hr	0.059	100	450	0.144	100
	1hr	0.015	25(75)	540.0~545.0	0.035	24(76)
	2hr	0.009	15(85)	520	0.34	23(77)

potato		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
G	0hr	0.295	100	600	0.351	100
	1hr	0.128	25(75)	595	0.159	45(55)
	2hr	0.069	15(85)	580	0.107	30(70)

sweet potato		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
H	0hr	0.234	100	605	0.275	100
	1hr	0.106	45(55)	595.0~600.0	0.132	48(52)
	2hr	0.06	25(75)	580	0.089	32(68)

cassava		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
I	0hr	0.221	100	600.0~605.0	0.257	100
	1hr	0.083	37(63)	590.0~595.0	0.107	41(59)
	2hr	0.071	32(68)	590	0.095	39(64)

sago		ε680	Ratio(%)	λmax	ελmax	Ratio(%)
J	0hr	0.295	100	605.0~610.0	0.323	100
	1hr	0.075	25(75)	585	0.099	30(70)
	2hr	0.047	16(84)	580	0.072	22(78)

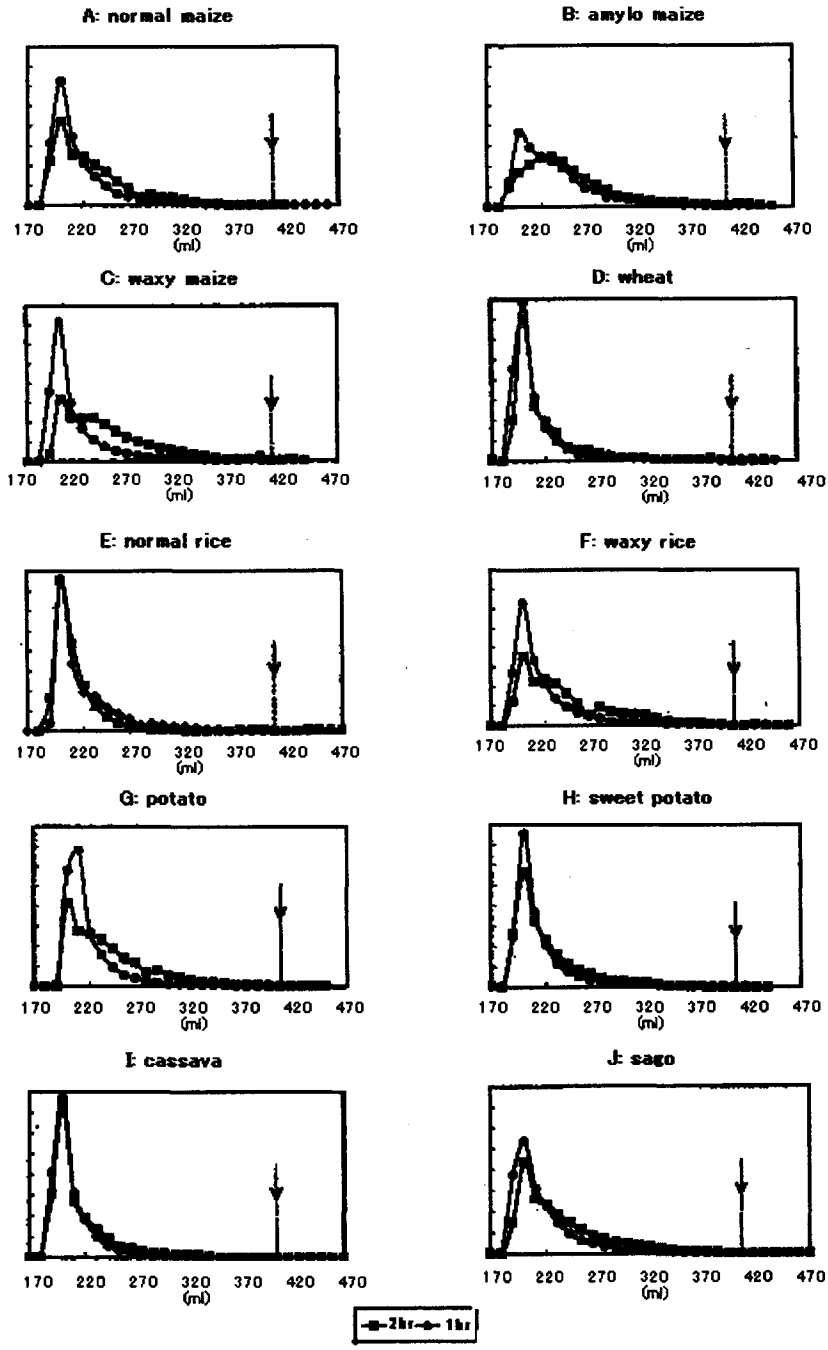


Fig. 3. GPC Profiles of dry heated starches on Toyopearl HW-65.

Table 1 shows amylose decomposition rate estimated with iodine color reaction. Amylose in root starches is more resistant to heat than that in cereal starch, and amylo maize starch is the most sensitive to the heat treatment. It is well known that there is more lipids included in amylose of cereal starch than in amylose of root starches and lipids readily form peroxide with heat in open air. Hence, it is suggested that amylose in cereal starches decompose more readily from amylose of root starches.

Fig. 3 shows GPC profiles of dry heated starches on Toyo-pearl HW-65. Decomposition of starch progressed with the heating time, and peaks finally converged to one peak at the end of elution pattern indicating that its molecular size corresponds to a species of lower molecular weight than amylose.

Table 2-A

Incorporation amount of lipid to starch granule suspended in lipid with heat treatment (soybean oil)

heating time(min)		0	20	40	60	120
Normal maize	weight(mg)	144	126	109	85	97
heating time(min)		0	20	40	60	120
Amylo maize	weight(mg)	178	110	90	95	106
heating time(min)		0	20	40	60	120
Waxy maize	weight(mg)	203	141	122	110	94
heating time(min)		0	20	40	60	120
Wheat	weight(mg)	125	84	74	71	79
heating time(min)		0	20	40	60	120
Normal rice	weight(mg)	276	281	123	198	131
heating time(min)		0	20	40	60	120
Waxy rice	weight(mg)	305	209	204	207	228
heating time(min)		0	20	40	60	120
Potato	weight(mg)	54	13	-8	1	17
heating time(min)		0	20	40	60	120
Sweet potato	weight(mg)	158	127	91	79	100
heating time(min)		0	20	40	60	120
Cassava	weight(mg)	107	142	108	107	114
heating time(min)		0	20	40	60	120
Sago	weight(mg)	159	44	43	41	66

starch: 300 mg

Table 2-B

Incorporation amount of lipid to starch granule suspended in lipid with heat treatment (methyl oleate)

heating time(min)		0	20	40	60	120
Normal maize	weight(mg)	193	136	134	128	104
heating time(min)		0	20	40	60	120
Amylo maize	weight(mg)	183	128	112	121	116
heating time(min)		0	20	40	60	120
Waxy maize	weight(mg)	202	141	145	122	98
heating time(min)		0	20	40	60	120
Wheat	weight(mg)	159	121	112	112	107
heating time(min)		0	20	40	60	120
Normal rice	weight(mg)	260	203	217	237	198
heating time(min)		0	20	40	60	120
Waxy rice	weight(mg)	256	238	236	210	192
heating time(min)		0	20	40	60	120
Potato	weight(mg)	90	2	28	-22	41
heating time(min)		0	20	40	60	120
Sweet potato	weight(mg)	176	133	120	96	96
heating time(min)		0	20	40	60	120
Cassava	weight(mg)	144	134	89	109	89
heating time(min)		0	20	40	60	120
Sago	weight(mg)	88	59	66	35	25

starch: 300 mg

However, GPC profiles of samples on HW-50 shown in Fig. 4 show that some fragments of the samples eluted at top position of the pattern. This fact indicates that these fragments are not so small. Results observed in Fig. 4 and Fig. 3 imply the same conclusion that major fragmentation might occur at amorphous region in amylopectin. Localisation of amylose in starch granule is still uncertain. Therefore, the problem whether amylose might form crystalline regions can not be solved. If amylose might form such regions, decomposition should be affected by amylopectin decomposition. Incorporation amount of lipid into the oil heated starch sample is shown in Table 2. Initial water content in starch should change with heat and approaches zero. Hence, the starch weight at each stage should be corrected but it is impossible.

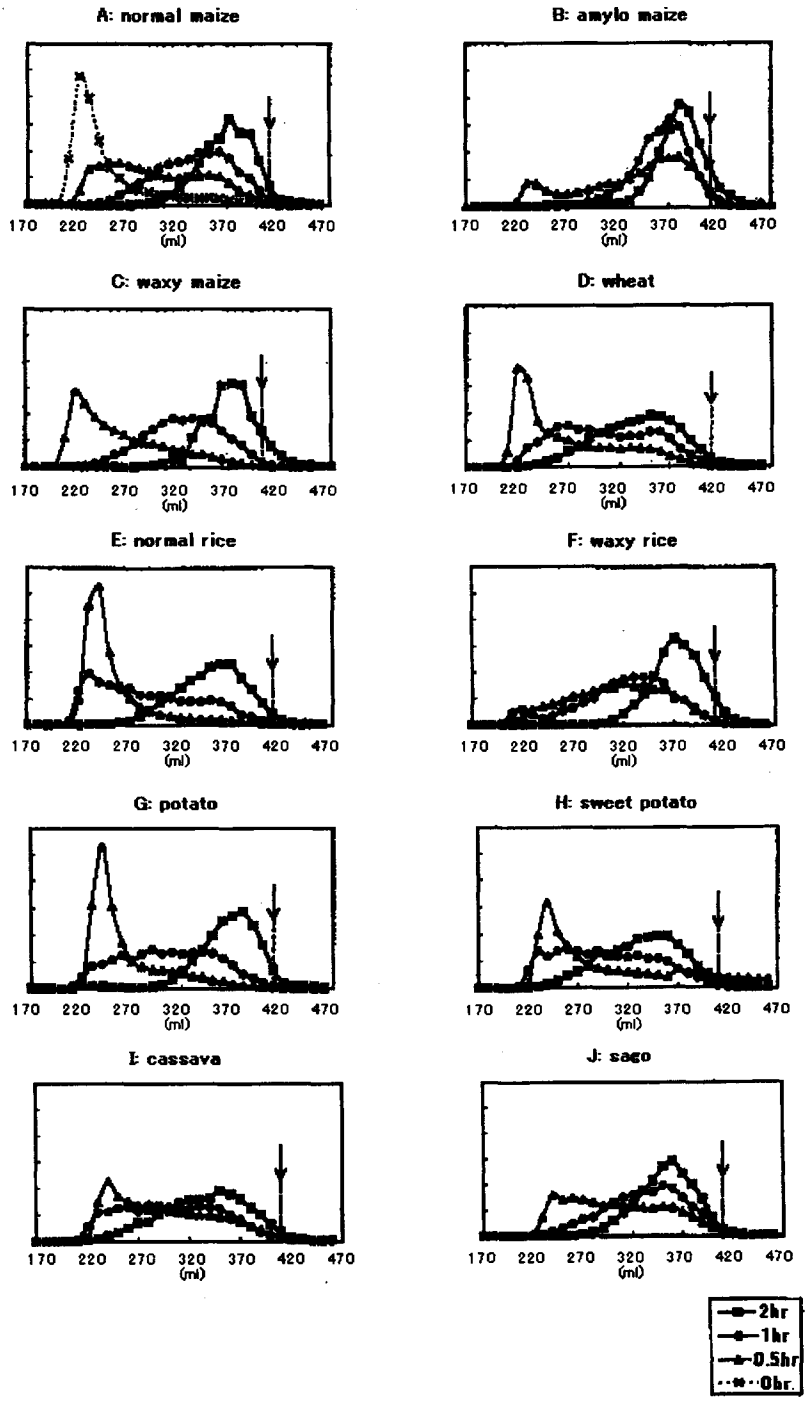


Fig. 4. GPC Profiles of dry heated starches on Toyopearl HW-50.

Ordinarily, the water content of starch is about 15%, hence it is equivalent to 45 mg in this case. This value does not contribute in any essential way to the total weight of the treated sample. However, one can say that lipid amount decrease with heat treatment time. This result is out of our expectation that vacant space in granule might increase by removing water, and lipid can easily penetrate into the space through fine cracks which might be formed with heat, and as the result, the incorporation amount of lipid might increase with the treatment.

In conclusion, baked food has fairly much water at initial stage of processing, hence on heating starch should be gelatinized to some extent. Amount of oil incorporated amount should be associated with this gelatinisation which contributes to expansion of starch granule and it adds a space for incorporation of lipids. Because of low water content in starch processed in our experiments, no increase in the oil amount in starch could be observed.

References

[1] Yamada T., T. Kato, S. Tamaki, K. Teranishi and M. Hisamatsu : Starch/Starke, 1998, **50**, 484-486.
[2] Tamaki S., M. Hisamatsu, K. Teranishi, T. Adachi and T. Yamada: Starch/Starke, 1998, **50**, 342-348.

ZMIANY NA POZIOMIE MOLEKULARNYM W GAŁECZKACH SKROBIOWYCH W CZASIE OGRZEWANIA ICH NA SUCHO ORAZ W OLEJU I ZASTOSOWANIE ZAOBSERWOWANYCH ZJAWISK W TECHNOLOGII ŻYWNOŚCI

Streszczenie

Na rynkach światowych powszechnie spotyka się szereg wypieków jak np. ciasteczka i biszkopty. Niewiele jednak pojawiło się w literaturze prac poświęconych zmianom na poziomie molekularnym w znajdującej się w tych produktach skrobi. Badania takie są utrudnione przez obecność lipidów, białek i innych składników.

Próbowano ustalić jakie zmiany zachodzą w gałeczkach skrobiowych 11 botanicznych odmian skrobi (kukurydziana zwykła, wysokoamylozowa i woskowa, pszenna zwykła i woskowa, ryżowa zwykła i woskowa, ziemniaczana, ze słodkich ziemniaków, tapioki i sago). Skrobie przetrzymywano w stanie suchym w 200°C przez 30 minut, jedną i dwie godziny. Ogrzewanie w oleju sojowym oraz estrach metylowych kwasu laurowego i olejowego prowadzono w 190°C w tych samych przedziałach czasowych. Ogrzewanie nie zmieniało obserwowanego pod skanningowym mikroskopem elektronowym wyglądu. Zmieniała się jednak rozpuszczalność gałeczek w wodzie. Po dwugodzinnym ogrzewaniu gałeczki niemal natychmiast się rozpuszczały.

Podatność na trawienie glukoamylazą zmieniała się w sposób zależny przede wszystkim od botanicznego pochodzenia gałeczek. Pod tym względem wpływ ogrzewania na skrobie woskowe był nieznaczny. Badania chromatograficzne (chromatografia żelowa) wskazują, że prawdopodobnie w wyniku ogrzewania doszło do zniszczenia klasterów, a nie samych cząsteczek polisacharydów. Skrobie bulw były odporniejsze na termolizę od skrobi zbożowych.