Molecular Structure and Pasting Properties of Normal Barley Starches

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The molecular structure and pasting properties of the starches from seven normal cultivars of barley were examined and compared with those of normal maize, rice and wheat starches. The barley starches had an actual amylose content of 24.3–27.9%. The starches had different pasting properties, such as maximum viscosity and breakdown, and different amylose gelatinization. A positive correlation was found between the maximum viscosity and the gelatinization degree of amylose, suggesting that low amylose gelatinization restrains the swelling of starch granules. The amylopectins had a low iodine affinity (0.42–0.70 g/100 g) and resembled each other in chain-length distribution with the individual peaks of B1 and A chains. The amyloses had DP_n of 810–1410 with 3.6–5.2 chains per molecule, indicating that barley amyloses differed in molecular structure with the cultivars. Among the cereal starches, barley starches were similar to wheat starch in amylose content and molecular structure, especially molecular size of amylose and chain-length distribution of amylopectin.

Barley is one of the major cereals along with maize, rice and wheat, and is mainly used for live-stock feed and raw material for the production of alcoholic beverages. Recently, barley has also been used as food, such as a rice substitute, and in breads and noodles. Starch is the main component of barley grains (65% by wet weight).¹⁾ However, structural characteristics of barley starches have been less well established compared with those of other major cereals such as maize,^{2,3)} rice^{4–6)} and wheat.^{7,8)} We recently examined the molecular structure of starches from some barley cultivars with different amylose content, one waxy (0% amylose), two low-amylose (2 and 11% amylose), two normal (23 and 25% amylose) and two high-amylose (33 and 41% amylose) barley starches.^{9,10)} The barley amylopectins from starches with different amylose content were similar in molecular structure, while the amyloses had different molecular structures. The amyloses from the normal cul-

vars were similar in size to those of high-amylose cultivars but smaller than those of low-amylose cultivars. To date there is only limited literature in which the molecular structure of normal barley starches is examined^{9–12)} although many varieties are cultivated. Moreover, in most studies,^{13–18)} their structural analyses were conducted using whole starch. In this study, seven normal barley starches were characterized in molecular structure of fractionated amylose and amylopectin and starch pasting properties in order to elucidate both similarities and differences among the normal varieties.

MATERIALS AND METHODS

Materials. The characteristics and harvest area of normal cultivars of barley are shown in Table 1. Starch was isolated from barley grains by an alkaline steeping method.²⁾ Defatted starch was prepared by three replications of dissolution in dimethyl sulfoxide and precipitation with ethanol.⁴⁾ Amylose and amylopectin were fractionated from

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Table 1. List of barley grains.

Cultivar	Row type	Hull	Harvest area
Schooner	2	+ ^a	Australia (South)
Grimmett	2	+	Australia (Q. land)
Starling	2	+	Australia (West)
Nishinochikara	2	+	Japan (Kagoshima)
Minorimugi	6	+	Japan (Toyama)
Hinodehadaka	6	— ^b	Japan (Ehime)
Aohadakamugi	6	—	Japan (Kagoshima)

^aHulled barley. ^bHull-less barley.

Table 2. Properties of barley starches.

Cultivar	Amylose content (%)			Crystalline type
	Actual ^a (A)	Apparent ^b (B)	B – A	
Schooner	27.9	28.5	0.6	A
Grimmett	26.8	28.2	1.4	A
Starling	26.4	27.9	1.5	A
Nishinochikara	25.5	26.7	1.2	A
Minorimugi	26.8	28.0	1.2	A
Hinodehadaka	24.6	26.6	2.0	A
Aohadakamugi	24.3	24.8	0.5	A

^aCalculated by $[(\text{IA}_{\text{defatted starch}} - \text{IA}_{\text{amylopectin}}) / (\text{IA}_{\text{amylose}} - \text{IA}_{\text{amylopectin}})] \times 100$. IA, iodine affinity. IA values of defatted starch, amylopectin and amylose are those in Tables 6, 7, and 9, respectively. ^bCalculated by $(\text{IA}_{\text{defatted starch}} / 20) \times 100$.

the defatted starch by the method of Lansky *et al.*¹⁹⁾ with modifications.^{4,5)} The purity of amylose was examined by gel chromatography (Toyopearl HW-75F, Tosoh, Tokyo, Japan).²⁰⁾ Crystalline *Pseudomonas* isoamylase was the product of Haya-shibara Biochemical Lab. Inc. (Okayama, Japan). β -Amylase was further purified from a commercial product (Sigma Chemical Co., St. Louis, MO) by the method of Marshall and Whelan.²¹⁾

Physicochemical analyses. Iodine affinity (IA, g/100 g) was determined by the amperometric titration method²²⁾ with modification.⁵⁾ Pasting properties and thermal behavior of starch were determined by using a Rapid Visco Analyzer (RVA-3D, Newport Scientific, Narrabeen, Australia) and Differential Scanning Calorimetry (DSC-7, Perkin-Elmer, Norwalk, CT), respectively, as described

elsewhere.⁹⁾ X-ray diffraction was performed on an X-ray diffractometer (Rotaflex RV-20013, Rigaku Denki Co., Tokyo, Japan) on wet specimens under the conditions described by Hizukuri *et al.*²³⁾ The degree of gelatinization of starch paste was determined by glucoamylase digestion and iodine titration methods.²⁴⁾

Analytical methods. The blue value, λ_{max} and β -amylolysis limit (β -AL) were determined as described previously.^{25,26)} The average chain-length (CL) was determined by the rapid Smith degradation^{27,28)} and by hydrolysis with isoamylase.²⁵⁾ The number-average degree of polymerization (DP_n) of amylose was determined by the modified Park-Johnson's method.²⁸⁾ The average number of chains per molecule was calculated as DP_n/CL. Phosphorus was determined as inorganic phosphate²⁹⁾ after treatment with hot perchloric acid.³⁰⁾ The chain-length distribution of amylopectin debranched with isoamylase was determined by gel-permeation HPLC with a low-angle laser-light scattering photometer and a differential refractometer,³¹⁾ and high performance anion-exchange chromatography with pulsed amperometric detection.³²⁾ The weight-average degree of polymerization (DP_w) and the DP distribution of amylose were determined by gel-permeation HPLC.³³⁾ Carbohydrate was determined by the phenol-sulfuric acid method.³⁴⁾

RESULTS AND DISCUSSION

General properties of starch.

Table 2 summarizes the properties of seven normal barley starches. The actual amylose content, calculated from the iodine affinity (IA, g/100 g) of defatted starch, amylose and amylopectin, was 24.3–27.9%. The values were similar to those reported for other normal barley cultivars (23–28%),^{9–12)} but higher than those for maize (19–21%)^{2,3)} and rice (16–19%),^{5,6)} and were comparable to those of wheat (22–27%)^{7,8)} starches. The actual amylose content was slightly lower than the apparent amylose content, which was calculated without consideration of the IA of amylopectin. The difference between apparent and actual amylose content was 0.5–2.0%, which was smaller than those of maize (4–5%),^{2,3)} rice (2–10%)^{5,6)} and wheat (1–

5%)^{7,8)} starches. This is due to a lower IA of barley amylopectins compared with those of other cereal amylopectins as described later. The lower IA suggested that barley amylopectins had fewer long chains that formed a complex with iodine.

Barley starches had A crystalline type, being the same as those of other cereal starches.³⁵⁾ From the relationship between the crystalline type of starch and the average chain-length (CL) of amylopectin investigated by Hizukuri *et al.*,³⁵⁾ the CL of barley amylopectins was expected to be around or below 20.

Pasting properties of starches.

Figure 1 shows the viscograms of barley starches (9%, w/w) determined by a Rapid Visco Analyzer, and Table 3 the pasting properties. The pasting temperature of the barley starches was in the range of 64.4–80.5°C, where Hinodehadaka starch had the highest temperature and Minorimugi starch the lowest. Nishinochikara starch showed the highest values for maximum viscosity, minimum viscosity and viscosity at 40°C, and Grimmer starch showed the lowest values except for minimum viscosity. The starch having a lower maximum viscosity tended to reach the maximum viscosity at a longer time. The breakdown values were low for Grimmer, Starling and Schooner starches (12–45 RVU), but high for Hinodehadaka (102 RVU) and Aohadakamugi (133 RVU) starches. The set back values ranged from 95 to 191 RVU, and the value was highest for Minorimugi starch and lowest for Grimmer. These results showed that pasting properties of starch were

Fig. 1. Rapid viscograms of barley starches. Concentration was 9% (w/w).

different among the cultivars of normal barley. However, the difference was much less than that between waxy and high-amylose barley starches, of which amylose contents ranged largely in 0–45%.^{9,10,18,36–38)} Therefore, the difference observed among the normal barley cultivars seemed to be not due to amylose content but probably due to starch granule size³⁷⁾ and phospholipid content,³⁸⁾ although no determination was made for the specimens in this study. As compared with other cereal starches,^{8,39,40)} the barley starches had lower maxi-

Table 3. Pasting properties of barley starches (conc. 9%).

Cultivar	Pasting temperature (°C)	Maximum viscosity			Viscosity (RVU)		Breakdown (RVU)	Set back (RVU)
		(RVU)	Temperature (°C)	Time (min)	Minimum	40°C		
Schooner	76.8	177	92.5	20.7	132	297	45	165
Grimmett	72.6	105	92.5	21.2	93	188	12	95
Starling	75.0	125	92.5	21.0	107	258	18	151
Nishinochikara	79.9	254	92.5	20.4	178	339	76	161
Minorimugi	64.4	201	92.5	19.7	120	311	81	191
Hinodehadaka	80.5	235	92.5	19.8	133	292	102	159
Aohadakamugi	66.7	221	92.5	18.9	88	234	133	146

Table 4. The changes of degree of gelatinization of barley starch pastes.

Cultivar	DG-g ^a (%)				DG-i ^b (%)			
	Time of storage (h)				Time of storage (h)			
	0	1	15	24	0	1	15	24
Schooner	100	90	88	89	93	49	45	46
Grimmett	99	86	85	87	89	50	53	45
Starling	98	90	85	84	89	45	39	40
Nishinochikara	99	93	91	90	99	58	41	41
Minorimugi	100	92	88	89	99	67	48	47
Hinodehadaka	98	91	89	89	95	43	44	45
Aohadakamugi	98	91	90	91	97	60	55	49

^aDegree of gelatinization determined by glucoamylase method. ^bDegree of gelatinization determined by iodine titration method.

Table 5. Thermal properties of barley starches.

Cultivar	Peak 1				Peak 2			
	<i>T</i> _o ^a (°C)	<i>T</i> _p ^b (°C)	<i>T</i> _c ^c (°C)	ΔH ^d (J/g)	<i>T</i> _o (°C)	<i>T</i> _p (°C)	<i>T</i> _c (°C)	ΔH (J/g)
Schooner	55.1	58.5	77.3	12.4	85.4	97.3	106.1	2.0
Grimmett	54.6	58.5	77.1	12.6	86.2	99.3	106.8	3.1
Starling	53.6	56.9	73.5	12.2	86.4	98.7	106.5	1.7
Nishinochikara	57.0	60.0	77.7	13.0	84.7	97.3	105.8	2.4
Minorimugi	55.4	58.1	75.8	12.5	86.2	97.2	106.1	2.6
Hinodehadaka	56.0	58.8	73.8	12.8	85.4	96.4	105.7	2.4
Aohadakamugi	56.5	59.1	72.1	12.1	86.6	96.6	104.4	1.0

^aOnset temperature. ^bPeak temperature. ^cComplete temperature. ^dEnthalpy change.

num viscosity and breakdown but higher set back values, suggesting that barley starches had less swelling and fragility and higher gelling tendency.

Gelatinization and retrogradation of starch paste.

The 5% barley starch suspensions were heated at 100°C for 20 min, and the degree of gelatinization was determined by glucoamylase digestion (DG-g) and iodine titration (DG-i) methods (Table 4). The DG-g value reflects gelatinization of whole starch and the DG-i value is specific for amylose.²⁴⁾ Judging from the DG-g values (98–100%), all the barley starches were almost completely gelatinized. On the other hand, DG-i values were 89–99%, showing that gelatinization of the barley amyloses differed among the cultivars. Grimmett and Starling amyloses were less gelati-

Fig. 2. Relationship between maximum viscosity and gelatinization degree of amylose (DG-i).

nized than the others, and their relatively low DG-i values were similar to those of maize and wheat starches.²⁴⁾ The DG-i values showed a good correlation ($r=0.89$) with the maximum viscosity as shown in Fig. 2. The starches with a lower DG-i

value showed a lower maximum viscosity. The correlation suggested that the low degree of gelatinization of amylose resulted in restraint of the swelling of starch granules, and supported the results obtained for various kinds of plant starches reported by Takeda and Hizukuri.²⁴⁾

The retrogradation tendency of barley starch pastes during storage at 0°C was examined by monitoring the DG-g and DG-i values (Table 4). Both DG-g and DG-i values decreased rapidly within an hour and then slowly. This retrogradation tendency of barley starches was similar to those of the other cereal starches.⁴¹⁾ The DG-i values during storage at 0°C for 1 h, however, varied from 43 to 67%, indicating that retrogradation tendency of amylose also differed with the cultivars.

Differential scanning calorimetry of starch.

The DSC thermogram of the barley starches gave two prominent transitions in a similar temperature range (Fig. 3 and Table 5). The first (peak 1) and second (peak 2) transitions correspond to melting of starch crystallites⁴²⁾ and amylose-lipid complex,⁴³⁾ respectively. In the first transition, the onset (T_o), peak (T_p) and complete (T_c) temperatures were 53.6–57.0°C, 56.9–60.0°C and 72.1–77.7°C, respectively. Nishinochikara had slightly higher T_o , T_p and T_c , while Starling had slightly lower values than the other starches. The starches had a similar enthalpy (ΔH , 12.1–13.0 J/g) and the values were lower than those for maize³⁷⁾ and wheat⁴⁴⁾ starches. In the second transition, T_o (84.7–86.6°C), T_p (96.4–99.3°C) and T_c (104.4–106.8°C) seemed to be similar. The ΔH values ranged from 1.0 J/g (Aohadakamugi) to 3.1 J/g (Grimmett), implying a difference in the amount of amylose-lipid complex of the starches. The amount of the complex was estimated from the increase of IA (1.68–2.35) by defatting of starches (Table 6). However, no correlation was found ($r=0.42$) between the ΔH values and the increase of IA. Thus, it was considered that the difference in the ΔH value for the second transition among the normal barley cultivars might be caused by other factors, such as different growth conditions⁴⁵⁾ and starch granule size³⁷⁾ together with the amount of amylose-lipid complex.

Fig. 3. DSC thermograms of barley starches.

T_o , T_p and T_c are onset, peak and complete temperatures, respectively.

Table 6. Iodine affinities of barley starches.

Cultivar	Iodine affinity, IA (g/100 g)		
	Defatted starch (A)	Starch (B)	A - B
Schooner	5.69	3.34	2.35
Grimmett	5.64	3.77	1.87
Starling	5.57	3.40	2.17
Nishinochikara	5.33	3.65	1.68
Minorimugi	5.59	3.44	2.15
Hinodehadaka	5.31	3.03	2.28
Aohadakamugi	4.96	2.79	2.17

Table 7. Properties of barley amylopectins.

Cultivar	IA (g/100 g)	Blue value	$\lambda_{\max}$ (nm)	Average chain-length, CL		β -AL ^c (%)	Organic phosphorus (ppm)
				Smith ^a	Iso-A ^b		
Schooner	0.54	0.07	548	19	20	54	19
Grimmett	0.70	0.08	550	20	20	53	12
Starling	0.47	0.06	547	18	18	53	25
Nishinochikara	0.42	0.06	542	18	19	54	11
Minorimugi	0.64	0.07	549	18	18	52	37
Hinodehadaka	0.69	0.07	549	18	18	52	17
Aohadakamugi	0.61	0.06	547	18	18	53	13

^aDetermined by the rapid Smith degradation method. ^bDetermined by the isoamylolysis method. ^c β -Amylolysis limit.

Fig. 4. Gel-permeation HPLC chromatograms of barley amylopectins after isoamylolysis.

—, differential refractometry; ●, DP.

Structure of amylopectin.

Table 7 summarizes the properties of the barley amylopectins. The amylopectins from all the cultivars were similar in IA (0.42–0.70 g/100 g), blue value (0.06–0.08) and $\lambda_{\max}$ (542–550 nm). The IA values were lower than those for maize amylopectins (0.80–1.10 g/100 g)^{2,3)} and similar or lower than those for rice (0.39–2.57 g/100 g)^{5,6)} and wheat (0.40–1.12 g/100 g)^{7,8)} amylopectins. The CL was 18–20 and Schooner and Grimmatt amylopectins had a slightly larger CL than the others. These values were comparable to those of japonica rice (19–20)⁵⁾ and wheat (19–21)^{7,8)} amylopectins, but slightly lower than those of maize (21–22)^{2,3)} and indica rice (21–22)^{5,6)} amylopectins. The barley amylopectins had a lower β -amylolysis limit (52–54%) than maize (59%)^{2,3)} rice (56–59%)^{5,6)} and wheat (56–59%)^{7,8)} amylopectins. The amount of phosphorus (11–37 ppm) of the barley amylopectins was similar to those of maize (15 ppm),²⁾ rice (5–29 ppm)^{5,6)} and wheat (4–20 ppm)^{7,8)} amylopectins.

Table 8. Carbohydrate amounts and weight-average chain length (CLw) of the fractions of isoamylase-debranched amylopectins.

Cultivar	Amount (% of total)					CLw				
	LC	B3	B2	B1	A	B3	B2	B1	A	Σ (B3–A)
Schooner	1	5	17	36	41	118	37	20	11	24
Grimmett	1	5	16	37	41	110	39	21	12	25
Starling	1	6	16	36	41	115	42	20	12	26
Nishinochikara	0	6	16	36	42	99	46	24	13	27
Minorimugi	1	5	17	35	42	96	44	21	11	24
Hinodehadaka	1	5	17	35	42	118	40	21	12	24
Aohadakamugi	1	5	17	35	42	102	40	21	10	24

Figure 4 shows the chain-length distribution of barley amylopectins after debranching with iso-amylase. The chains were fractionated into LC, B 3, B2, B1 and A, in the order of elution.³¹⁾ All the amylopectins resembled each other in chain-length distribution and carbohydrate amount of each fraction, although the weight-average chain length of each fraction was somewhat different (Table 8). The LC fraction was absent in Nishinochikara amylopectin but present in the other amylopectins in a very small amount (1%). The relationship between the amount of LC fraction and the IA of amylopectins was consistent with the results for rice amylopectins.⁵⁾ The amount of long chains (LC+B3) was 6–7% for the barley amylopectins, being lower than those for maize (10%)²⁾ and rice (7–20%)^{5,6)} amylopectins but similar to those for wheat amylopectins (5–10%).^{7,8)} B1 and A-chains fractions of all the amylopectins showed individual peaks. This elution profile, together with the results for other normal barley cultivars,^{9–12)} was considered to be characteristic in barley amylopectins. This profile was also similar to those of wheat amylopectins,^{7,8)} and differed from those of maize and rice amylopectins^{2,5,6)} since these amylopectins showed B1 and A-chains fractions as a peak. The distribution of short chains was clarified by HPAEC (Fig. 5). The barley amylopectins showed a similar chain-length distribution among the cultivars with a peak at DP 11–12 and an apparent shoulder at DP 18. This result was in agreement with those obtained by gel-permeation HPLC

although the peak and shoulder DP was somewhat different. These distributions were also similar to those of other normal barley^{9,10,12,32)} and wheat^{8,32)} amylopectins, but slightly different from maize and rice amylopectins.³²⁾

Structure of amylose.

Table 9 summarizes the properties of the barley amyloses. The IA was in the range of 18.5–19.7 g/100 g. These values were slightly lower than those of maize (20.1–21.3 g/100 g)^{2,3)} and rice (20.1–21.1 g/100 g)^{4,6)} amyloses. The blue value and $\lambda_{\max}$ were 1.43–1.51 and 644–655 nm, re-

Fig. 5. Chain-length distribution of barley amylopectins by HPAEC.

Table 9. Properties of barley amyloses.

Cultivar	IA (g/100 g)	Blue value	$\lambda_{\max}$ (nm)	Number- average DP, DPn	Weight- average DP, DPw	DPw/DPn	Apparent DP distribution ^a	CL	β -AL (%)	Average number of chains
Schooner	19.0	1.45	649	1000	4240	4.2	350–18000	270	79	3.7
Grimmett	19.1	1.51	648	1090	5020	4.6	410–22000	240	74	4.5
Starling	19.8	1.47	644	810	2450	3.0	260–11000	220	79	3.7
Nishinochikara	19.7	1.47	646	870	2990	3.4	340–14000	240	80	3.6
Minorimugi	19.1	1.51	652	1180	6440	5.5	540–22000	310	80	3.8
Hinodehadaka	19.5	1.47	653	1320	5140	3.9	360–18000	360	78	3.7
Aohadakamugi	18.5	1.43	655	1410	6030	4.3	690–22000	270	80	5.2

^aDP values of the subfractions (10% by weight) having the lowest and highest molecular weights.

Fig. 6. Gel-permeation HPLC chromatograms of barley amyloses.

— and ●, differential refractometry and DP, respectively.

spectively. The number- (DPn) and weight- (DPw) average degree of polymerization were 810–1410 and 2450–6440, respectively, and Minorimugi amylose was largest in molecular size and Starling amylose was smallest. Other normal barley amyloses had DPn of 1110–1570 and DPw of 3440–5580.^{9–12)} Thus, barley amyloses were different in molecular size with the cultivar. These molecular sizes were similar to wheat amyloses (DPn=830–1570, DPw=2360–5450),^{7,8)} but, in general, larger than those for maize (DPn=830–990, DPw=2500–2680)^{2,3)} and rice (DPn=920–1110, DPw=2750–3230)^{4,6)} amyloses. HPLC gel-permeation chromatography (Fig. 6) of the barley amyloses gave a different elution profile with the cultivars. It was evident that Schooner, Grimmlett, Minorimugi, Hinodehadaka and Aohadakamugi amyloses were composed of two components because the elution profiles showed a flat top peak or a shoulder. Starling and Nishinochikara amyloses seemed to have a single component. The higher DPw/DPn value indicates higher polydispersity of an amylose population and in fact the apparent DP distribution for Minorimugi (DPw/DPn=5.5) was wider than

that for Starling amylose (3.0). The values suggested that barley amyloses had generally wider DP distribution than maize (2.5)²⁾ and rice (2.6–3.9)^{4,6)} amyloses, and similar to wheat amyloses (2.8–5.0).^{7,8)} The average number of chains per molecule (NC) was 3.6–5.2, which was higher or similar to those of other normal barley amyloses (NC=1.8, 3.7, 5.0 and 5.4),^{9–12)} while the NC values were 2.4–2.9 for maize,^{2,3)} 4.4–6.5 for wheat^{7,8)} and 2.5–4.3 for rice^{4,6)} amyloses. The barley amyloses had β -amylolysis limit of 74–80%, which were slightly lower than those for maize (81–84%)^{2,3)} and wheat (79–86%)^{7,8)} amyloses, and similar to those of some cultivars of rice amyloses (73–87%).^{4,6)}

In conclusion, barley starches were similar to wheat starches in amylose content and molecular structure, such as molecular size of amylose and chain-length distribution of amylopectin, among the cereal starches. As compared with maize and rice starches, barley starches had a higher amylose content, and their amyloses were generally larger molecules. Barley amylopectins differed from maize and rice amylopectins in some structural properties, especially in the distribution of short chains.

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普通種大麦澱粉の分子構造と糊化特性

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7品種の普通種大麦澱粉の分子構造と糊化特性を調べ、トウモロコシ、米、小麦澱粉と比較した。大麦澱粉は真のアミロース含量が²24.3–27.9%であった。糊化特性では、品種間で最高粘度やブレイクダウン、アミロースの糊化度などに相違が認められた。最高粘度とアミロースの糊化度の間に正の相関が認められ、アミロースの糊化が低いほど澱粉粒の膨潤が抑制されることが示唆された。アミロペクチンはヨウ素親和力が低く(0.42–0.70 g/100 g)、鎖長分布は互いに類似し、A鎖とB1鎖が明確に分かれた。アミロースは数平均重合度が²810–1410、平均鎖数は3.6–5.2で、品種間で分子構造が異なっていた。穀類澱粉の中で、大麦澱粉は小麦澱粉とアミロース含量や分子構造、とくにアミロース分子の大きさとアミロペクチンの鎖長分布が²類似していた。