

# Molecular Structure and Some Physicochemical Properties of Buckwheat Starches

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## ABSTRACT

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The molecular structure and pasting properties of starches from eight buckwheat cultivars were examined. Rapid viscosograms showed that buckwheat starches had similar pasting properties among cultivars. The actual amylose content was 16–18%, which was lower than the apparent amylose content (26–27%), due to the high iodine affinity (IA) of amylopectin (2.21–2.48 g/100 g). Amylopectins resembled each other in average chain-length (23–24) and chain-length distributions. The long-chains fraction (LC) was abundant (12–13% by weight) in all the amylopectins, which was consistent with high

IA values. The amyloses were also similar among the cultivars in number-average DP 1,020–1,380 with 3.1–4.3 chains per molecule. The molar-based distribution indicated that all the amyloses comprised two molecular species differing in molecular size, although the weight-based distribution showed a single species. A comparison of molecular structures of buckwheat starches to cereal starches indicated buckwheat amylopectins had a larger amount of LC, and their distributions of amylose and short chains of amylopectin on molar basis were similar to those of wheat and barley starches.

Buckwheat is cultivated worldwide and has some advantages in cultivation such as ability to grow in a cool climate and a short growing period (Lorenz and Dilsaver 1982). Recent studies revealed some functional properties of the buckwheat grains (Kusano et al 1992; Lu et al 1992; Song et al 1992), and scientific attention on the crop has been increasing. There are two major species, common (*Fagopyrum esculentum* Moench) and tartary (*F. tataricum* (L.) Gaertn.), and Japanese common-buckwheat is classified into two groups according to harvest season (summer and autumn). Both the common and tartary species are utilized in Japan in food production such as noodles and alcoholic beverages. Starch is a main component of buckwheat grains, and some physicochemical properties have been investigated (Li et al 1997; Noda et al 1998; Qian et al 1998; Zheng et al 1998). For example, almost no significant differences were observed in the analyses of the pasting and thermal characteristics between common and tartary buckwheat starches (Li et al 1997). Starches from common buckwheat showed higher peak viscosity and setback than did maize and rice starches (Zheng et al 1998), and had higher amylose content, water-binding capacity, and peak viscosity, but lower intrinsic viscosity than maize and wheat starches (Qian et al 1998). However, molecular structures of amylose and amylopectin have not been well characterized. Recent analytical methods (Hanashiro and Takeda 1998; Hanashiro et al 2002; Takeda et al 2003) elucidated molecular structures of starch components from various plants in more detail. We examined the molecular structures of amylose and amylopectin from buckwheat of eight cultivars, seven common cultivars and one tartary cultivar, together with pasting properties of the starches. Characteristics of buckwheat starches were compared with those of rice, maize, wheat and barley starches.

ethanol (Takeda et al 1986). Starch was fractionated into amylose and amylopectin by precipitation of amylose with 1-butanol and 3-methyl-1-butanol (Lansky et al 1949; Takeda et al 1986). The purity of amylose specimens was confirmed by gel-permeation chromatography (Toyopearl HW-75F, Tosoh, Tokyo, Japan) (Takeda et al 1984). Crystalline *Pseudomonas* isoamylase was a product of Hayashibara Biochemical Labs, Inc. (Okayama, Japan). Sweet potato  $\beta$ -amylase (Sigma Chemical Co., St. Louis, MO) was further purified by the method of Marshall and Whelan (1973).

## Physicochemical Analyses

Iodine affinity (IA, g/100 g) was determined by the amperometric titration method (Larson et al 1953) with modification (Takeda et al 1987a). Pasting properties and thermal behavior of starch were determined with a Rapid Visco Analyser (RVA-3D, Newport Scientific, Narrabeen, Australia) and differential scanning calorimetry (DSC-7, Perkin Elmer, Norwalk, CT), respectively, under conditions described previously (Yoshimoto et al 2000). X-ray diffraction was performed on an X-ray diffractometer (Rotaflex RV-20013, Rigaku Denki, Tokyo, Japan) on wet specimens under conditions described previously (Hizukuri et al 1988).

## Analytical Methods

The blue value,  $\lambda_{\text{max}}$ , and  $\beta$ -amylolysis limit were determined as described previously (Suzuki et al 1981; Takeda et al 1983). Total carbohydrate and reducing sugars were determined by the phenol-sulfuric acid method (Dubois et al 1956) and the Somogyi-Nelson method (Nelson 1944; Somogyi 1952) with a minor modification of heating time extended to 30 min (Hizukuri et al 1970). Phosphorus content was determined as inorganic phosphorus (Itaya and Ui 1966)

## MATERIALS AND METHODS

### Materials

Eight cultivars of buckwheat used are listed in Table I. Starch was isolated from buckwheat grains by an alkaline steeping method (Takeda et al 1988b). Defatted starch was prepared by three replicates of dissolution in dimethyl sulfoxide (DMSO) and precipitation with

TABLE I  
List of Buckwheat Grains

Species/Cultivar	Area Harvested (season)	Main Use in Japan
Common <sup>a</sup>		
Shinanonatsusoba	Nagano, Japan (summer)	Noodle
Kitawasesoba	Nagano, Japan (summer)	Noodle
Shinano No. 1	Nagano, Japan (autumn)	Noodle
Hitachiakisoba	Nagano, Japan (autumn)	Noodle
Dewakaori	Nagano, Japan (autumn)	Noodle
Mancan <sup>b</sup>	China	Shochu (liquor) brewing
Mongolia <sup>c</sup>	China	Shochu (liquor) brewing
Tartary <sup>d</sup>		
Hokuriku No.4	Nagano, Japan	Noodle

<sup>a</sup> *Fagopyrum esculentum* Moench.

<sup>b</sup> Originated in Manitoba, Canada.

<sup>c</sup> Originated in Mongolia.

<sup>d</sup> *F. tataricum* (L.) Gaertn.

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after treatment with perchloric acid (Allen 1940). The number-average degree of polymerization ( $DP_n$ ) of amylose was determined by the modified Park-Johnson method (Hizukuri et al 1981) and the fluorescent-labeling/HPSEC method (Hanashiro and Takeda 1998). The average chain-length (CL) was determined by the rapid Smith degradation (Hizukuri and Osaki 1978; Hizukuri et al 1981) and hydrolysis with isoamylase followed by determination of reducing residues (Suzuki et al 1981). The average number of chains per molecule (NC) was calculated as  $DP_n/CL$ . The molar- and weight-based distributions of amylose were determined by the fluorescent-labeling/HPSEC method (Hanashiro and Takeda 1998). The molar fraction of branched and linear amyloses was determined by fluorescent-labeling/HPSEC after  $\beta$ -amylolysis of labeled amylose with 2-aminopyridine. Labeled amylose (2 mg) was dissolved in 1M NaOH (50  $\mu$ L) followed by adding water (90  $\mu$ L), 1M acetate buffer (pH 4.8, 10  $\mu$ L) and 1M HCl to adjust to pH 4.8, and degraded with 100U of  $\beta$ -amylase at 37°C for 3 hr. After heating in a boiling water bath for 5 min, to the resulting  $\beta$ -amylolyzate were added water (600  $\mu$ L) and 0.5M phosphate buffer (pH 6.1, 200  $\mu$ L) and 500  $\mu$ L (1 mg) of the solution was used for the analysis after filtration through a 0.22- $\mu$ m membrane filter. The chain-length distribution of amylopectin was examined by high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Hanashiro et al 1996) and the fluorescent-labeling/HPSEC method (Hanashiro et al 2002).

## RESULTS AND DISCUSSION

### Pasting Properties

Starches from buckwheat of eight cultivars showed a similar pasting profile (profiles not shown). Increase in viscosity with increase of temperature was rapid and then slow before reaching the maximum viscosity. Similar behaviors were reported for other buckwheat cultivars (Li et al 1997). The pasting temperature was similar ( $\approx 70^\circ\text{C}$ ) among the cultivars, but slight differences were observed in maximum (226–261 RVU) and minimum viscosities (156–202 RVU), viscosity at 40°C (336–404 RVU), breakdown (37–98 RVU), and setback (181–226 RVU) (Table II). The differences among cultivars were much smaller than those for wheat (Shibanuma et al 1996), rice (Mizukami et al 1996), and barley (Yoshimoto et al 2001). Buckwheat starches had higher maximum viscosity, viscosity at 40°C, and

setback than maize (Jideani et al 1996), and barley (Yoshimoto et al 2001) starches. These results suggested that buckwheat starches had higher granule swelling and gelling tendency than the cereal starches.

### Thermal Properties of Starch

Table III summarizes thermal properties of buckwheat starches. Ranges for the first transition were 59.5–64.1°C for onset ( $T_o$ ), 63.7–68.4°C for peak ( $T_p$ ), and 81.7–85.8°C for complete ( $T_c$ ) temperatures, and  $\Delta H$  values were 14.5–15.0 J/g. These values were higher than those of barley starches ( $T_o$  53.6–57.0°C,  $T_p$  56.9–60.0°C,  $T_c$  72.1–77.7°C,  $\Delta H$  12.1–13.0 J/g) (Yoshimoto et al 2001) examined under the same experimental conditions, indicating that buckwheat starches had a larger crystalline region, to which size and perfection of crystallite contribute. Because the first transition corresponded to melting of crystallite of starch, which is mainly amylopectin (Morrison et al 1993), the number of long chains of amylopectin also is a factor affecting the thermal properties. The second transition, corresponding to melting of amylose-lipid complex (Kugimiya et al 1980), appeared to be present for all buckwheat starches, but thermal values could not be determined.

### Iodine Affinity and Amylose Content of Starch

The iodine affinity (IA, g/100 g) of buckwheat starches increased from 3.66–4.00 to 5.09–5.30 by defatting (Table IV) as for cereal starches. The increase of IA indicated the presence of amylose-lipid complex in buckwheat starches. The increased IA (1.09–1.59) was similar to those of wheat starches (1.02–1.59) (Shibanuma et al 1996) but lower than those of barley starches (1.68–2.35) (Yoshimoto et al 2001). The ratio of amount of amylose forming a complex with lipids against whole amylose was 0.21–0.30 for buckwheat starches, comparable to wheat starches (0.18–0.28) (Shibanuma et al 1996), but lower than barley starches (0.32–0.44) (Yoshimoto et al 2001).

The actual amylose content, calculated from IA of defatted starch, amylose, and amylopectin was 15.6–17.9%. The values were similar to those for rice (16–19%) (Takeda et al 1987a, 1989) but lower than those for maize (19–21%) (Takeda et al 1988a, Takeda and Preiss 1993), wheat (22–27%) (Shibanuma et al 1994, 1996), and barley (23–28%) (Takeda et al 1999; Yoshimoto et al 2000, 2001, 2002) starches. The apparent amylose content calculated without consideration of amylopectin IA was 25.5–26.5%, which was in the range

TABLE II  
Pasting Properties of Buckwheat Starches (conc. 9%)

Cultivar	Pasting Temp. (°C)	Viscosity (RVU)			Breakdown (RVU)	Setback (RVU)
		Maximum	Minimum	40°C		
Shinanonatsusoba	71.0	239	202	392	37	190
Kitawasesoba	70.2	226	174	390	52	216
Shinano No. 1	69.0	261	178	404	83	226
Hitachiakisoba	68.6	244	174	382	70	208
Dewakaori	69.0	254	156	336	98	180
Hokuriku No. 4	68.5	242	175	398	67	223
Mancan	69.6	228	188	369	40	181
Mongolia	70.5	230	192	397	38	205

TABLE III  
Thermal Properties of Buckwheat Starches at Peak 1<sup>ab</sup>

Cultivar	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)
Shinanonatsusoba	64.1 ± 3.2	68.4 ± 2.1	83.3 ± 2.1	14.9 ± 0.4
Kitawasesoba	61.2 ± 2.6	65.1 ± 1.3	85.8 ± 1.0	14.5 ± 0.2
Shinano No. 1	59.5 ± 1.8	63.9 ± 1.7	82.5 ± 3.0	15.0 ± 0.5
Hitachiakisoba	60.4 ± 1.2	63.7 ± 2.2	83.3 ± 2.7	14.7 ± 0.4
Dewakaori	61.0 ± 1.8	66.9 ± 1.3	82.5 ± 2.5	14.7 ± 0.1
Hokuriku No. 4	61.0 ± 2.4	64.1 ± 1.3	81.7 ± 2.0	14.7 ± 0.3
Mancan	62.0 ± 2.7	65.3 ± 0.7	82.5 ± 3.0	14.6 ± 0.2
Mongolia	62.3 ± 1.9	66.9 ± 2.7	83.3 ± 1.2	14.8 ± 0.2

<sup>a</sup> Onset temperature ( $T_o$ ); peak temperature ( $T_p$ ); completion temperature ( $T_c$ ); enthalpy change ( $\Delta H$ ).

<sup>b</sup> Results of duplicate measurements shown as average  $\pm$  standard deviation.

(21.1–27.4%) for other cultivars of buckwheat (Li et al 1997; Noda et al 1998; Qian et al 1998; Zheng et al 1998). The large difference between actual and apparent amylose contents (9–11%) was due to the high IA of buckwheat amylopectin. The high IA indicated that buckwheat amylopectins have a large amount of long chains (LC) that are capable of forming complexes with iodine.

### Amylopectin Structure

Buckwheat amylopectins resembled each other in iodine-binding properties (IA 2.21–2.48, blue value 0.25–0.28, and  $\lambda_{\max}$  582–584 nm) (Table V). The IA values were higher than those for maize (0.80–1.10) (Takeda et al 1988a; Takeda and Preiss 1993), wheat (0.40–1.12) (Shibanuma et al 1994, 1996), and barley (0.42–0.70) (Takeda et al 1999; Yoshimoto et al 2000, 2001, 2002) amylopectins but comparable to those of indica rice amylopectins (1.62–2.57) (Takeda et al 1987a). The CL was 23–24 determined by three independent methods of rapid Smith-degradation, isoamylolysis, and fluorescent labeling/ HPSEC. These values were higher than those of the cereal amylopectins (18–22) (Takeda et al 1987a, 1988a, 1989, 1999; Takeda and Preiss 1993; Shibanuma et al 1994, 1996; Yoshimoto et al 2000, 2001, 2002). The  $\beta$ -amylolysis limit of 52–56% for

buckwheat amylopectins were within the value ranges for the cereal amylopectins (52–59%). No organic phosphorus, or a slight amount, was found except for Mancan (95 ppm) and Mongolia (64 ppm) cultivars. The minor portion of phosphorus (<10%) was linked to C-6 of the glucosyl residue, and the remainder might bind to C-3 as in potato amylopectins (Hizukuri et al 1970; Lim and Seib 1993; Lim et al 1994).

The molar- and weight-based distributions of unit chains of buckwheat amylopectins were similar (Fig. 1). The distributions were fractionated into LC (long chains), B2+B3, B1 and A chain fractions in order of elution (Hanashiro et al 2002). B chain is a unit chain that carries other chains through  $\alpha$ -1,6 linkage; A chain carries no side chains (Peat et al 1956). B1 and B2 denote B chain involved in one cluster and two clusters, respectively (Hizukuri 1986). The amount of these fractions were similar both on weight and molar bases (Table VI). The amylopectins contained a larger amount of LC (12–13% by weight) than those of cereal amylopectins (Hanashiro et al 2002). The large amount of LC corresponded to the high amylopectin IA. B1 and A chains showed clear shoulder and peak, respectively, both on the weight- and molar-based distributions, similar to wheat amylopectin but different from rice and maize amylopectins. Molar ratio of

**TABLE IV**  
Iodine Affinity and Amylose Content of Buckwheat Starches

Cultivar	Iodine Affinity (IA) (g/100 g)				Amylose Content (%)		
	Defatted Starch (A)	Starch (B)	A – B	(A – B)/A	Actual <sup>a</sup>	Apparent <sup>b</sup>	Difference <sup>c</sup>
Shinanonatsusoba	5.19	3.87	1.32	0.25	16.4	26.0	9.6
Kitawasesoba	5.25	3.73	1.52	0.29	15.8	26.3	10.5
Shinano No. 1	5.30	3.86	1.44	0.27	16.9	26.5	9.6
Hitachiakisoba	5.16	3.66	1.50	0.29	15.6	25.8	10.2
Dewakaori	5.30	3.71	1.59	0.30	17.9	26.5	8.6
Hokuriku No. 4	5.09	4.00	1.09	0.21	15.6	25.5	9.9
Mancan	5.13	3.70	1.43	0.28	16.8	25.7	8.9
Mongolia	5.17	3.83	1.34	0.26	16.9	25.9	9.0

<sup>a</sup> Calculated as  $(IA_{\text{defatted starch}} - IA_{\text{amylopectin}}) / (IA_{\text{amylose}} - IA_{\text{amylopectin}}) \times 100$ . IA values of amylose and amylopectin shown in Tables V and VII, respectively.

<sup>b</sup> Calculated as  $(IA_{\text{defatted starch}}/20) \times 100$ .

<sup>c</sup> Difference between apparent and actual amylose contents.

**TABLE V**  
Properties of Buckwheat Amylopectins

Cultivar	IA (g/100 g)	Blue Value	$\lambda_{\max}$ (nm)	Average Chain Length (CL)		$\beta$ -AL <sup>c</sup> (%)	Organic Phosphorus (ppm)
				Smith <sup>a</sup>	Iso-A <sup>b</sup>		
Shinanonatsusoba	2.43	0.28	582	24	24	54	3
Kitawasesoba	2.48	0.25	583	24	24	52	2
Shinano No. 1	2.39	0.26	583	24	23	56	1
Hitachiakisoba	2.37	0.26	583	24	23	55	0
Dewakaori	2.21	0.26	583	24	23	56	0
Hokuriku No. 4	2.42	0.26	584	24	23	55	0
Mancan	2.23	0.26	582	24	24	53	95
Mongolia	2.26	0.25	582	23	24	53	64

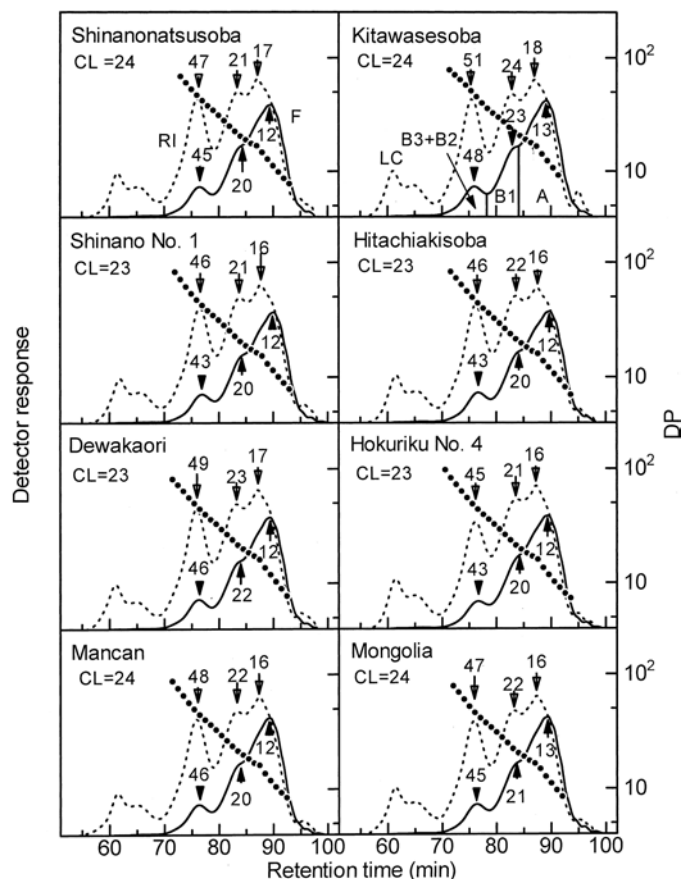
<sup>a</sup> Determined by rapid Smith degradation method.

<sup>b</sup> Determined by isoamylolysis method.

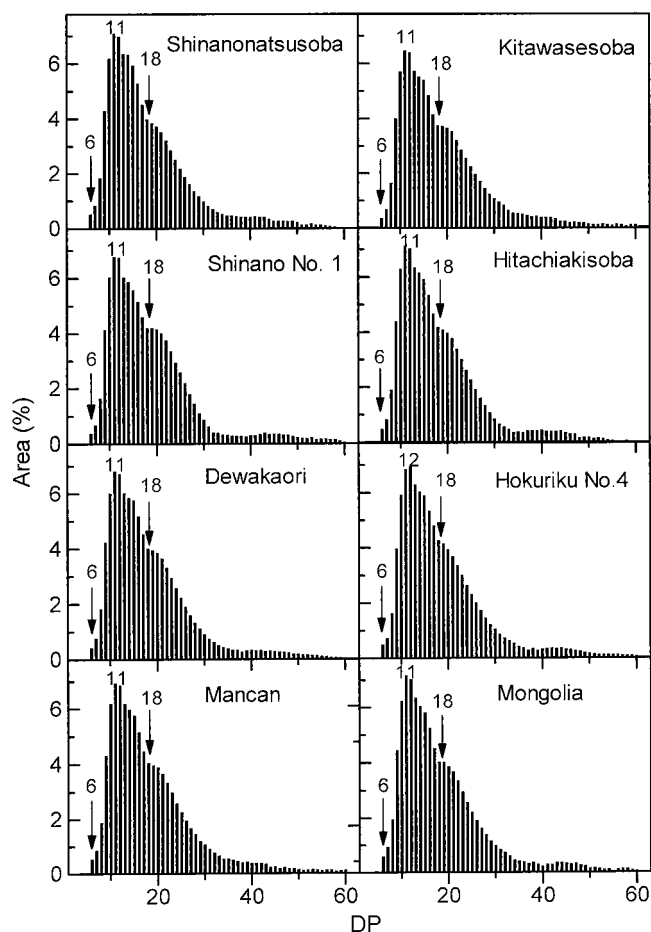
<sup>c</sup>  $\beta$ -Amylolysis limit.

**TABLE VI**  
Weight and Molar Ratios of Fractions of Amylopectin Unit Chains

Cultivar	Weight (%)				Mole (%)				(A + B1)/(B2 + B3)
	LC	B3 + B2	B1	A	LC	B3 + B2	B1	A	
Shinanonatsusoba	12	26	25	37	1	12	24	63	7.3
Kitawasesoba	12	26	24	38	1	12	24	63	7.3
Shinano No. 1	12	26	25	37	1	12	23	64	7.3
Hitachiakisoba	13	26	25	36	1	12	24	63	7.3
Dewakaori	12	26	24	38	1	12	23	64	7.3
Hokuriku No. 4	13	24	26	37	1	11	25	63	8.0
Mancan	12	26	25	37	1	12	23	64	7.3
Mongolia	13	26	24	37	1	12	23	64	7.3



**Fig. 1.** Molar- and weight-based distributions of unit chains of buckwheat amylopectins by the fluorescent labeling/HPSEC: —, fluorescence response; - - -, RI response; ●●●, DP (arrows indicate DP values).



**Fig. 2.** Chain-length distributions of buckwheat amylopectins by HPAEC-PAD.

**TABLE VII**  
Properties of Buckwheat Amyloses

Cultivar	IA (g/100 g)	Blue Value	$\lambda_{\text{Max}}$ (nm)	Number-Average DP		CL	Avg. No. of Chains	$\beta$ -AL (%)	Molar Fraction (%)	
				Colorimetric <sup>a</sup>	Labeling				Branched	Linear
Shinanonatsusoba	19.3	1.43	653	1,210	1,160	280	4.3	80	30	70
Kitawasesoba	20.0	1.38	653	1,020	1,070	330	3.1	77	33	67
Shinano No. 1	19.6	1.48	649	1,240	1,310	310	4.0	82	26	74
Hitachiakisoba	20.2	1.46	657	1,330	1,350	380	3.5	82	37	63
Dewakaori	19.5	1.41	652	1,380	1,360	370	3.7	80	26	74
Hokuriku No. 4	19.5	1.36	657	1,120	1,230	340	3.3	78	25	75
Mancan	19.5	1.40	647	1,160	1,090	340	3.4	78	23	77
Mongolia	19.5	1.37	645	1,210	1,310	360	3.4	76	31	69

<sup>a</sup> Modified Park-Johnson method.

$(A+B1)/(B2+B3)$  is regarded as a measure of the number of chains per cluster because A and B1 chains participate in formation of single cluster, while B2 and B3 chains span and connect multiple clusters. This molar ratio was 7.3–8.0, which was lower than wheat, rice, and maize amylopectins (10.0–12.9) (Hanashiro et al 2002).

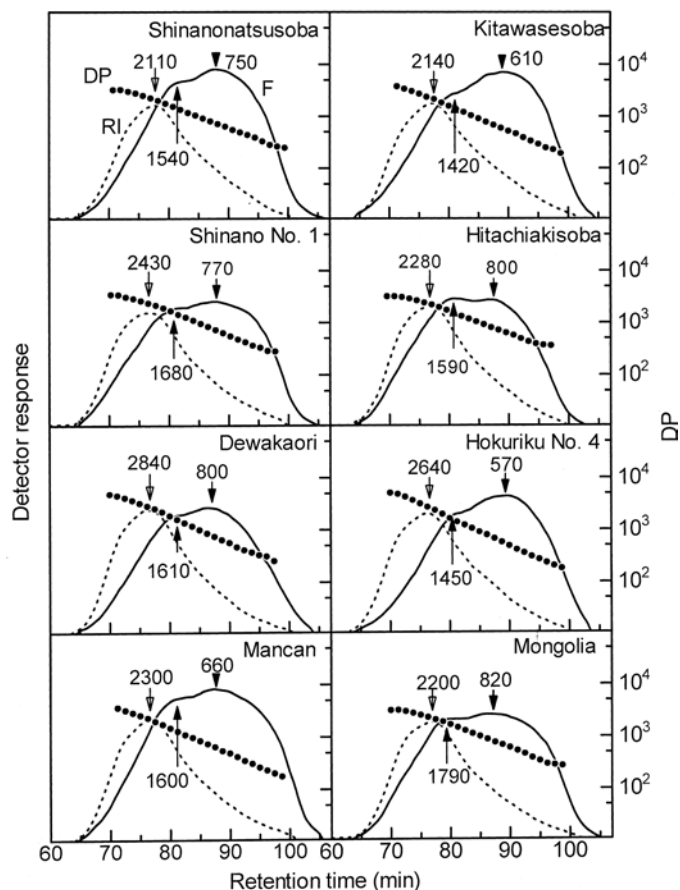
The distribution of short chains with DP < 60 was examined in detail by HPAEC and was expressed by relative peak areas (Fig. 2). Buckwheat amylopectins showed a similar chain-length distribution among the cultivars with a peak at DP 11–12 and a shoulder at DP 18. These distributions were similar to those for wheat (Shibanuma et al 1996) and barley (Takeda et al 1999; Yoshimoto et al 2001, 2002).

### Structure of Amylose

Table VII summarizes the properties of buckwheat amyloses. The amyloses were similar in IA (19.3–20.2 g/100 g), blue value (1.36–1.48), and  $\lambda_{\text{max}}$  (645–657 nm), and had DP<sub>n</sub> of 1,020–1,380. Buckwheat amyloses were slightly larger than maize (830–990) (Takeda et

al 1988a; Takeda and Preiss 1993) and rice (920–1,110) (Takeda et al 1986, 1989) amyloses, and in the range of wheat (830–1,570) (Shibanuma et al 1994, 1996), and barley (810–1,570) (Takeda et al 1999; Yoshimoto et al 2000, 2001, 2002) amyloses. The DP<sub>n</sub> values were in agreement with those determined by the fluorescent labeling/HPSEC method. The molar-based distribution revealed that buckwheat amyloses were composed of large and small molecular species, although the weight-based distributions gave a single peak (Fig. 3). These profiles were similar to those of wheat and barley amyloses (Hanashiro et al 1998; Yoshimoto et al 2002). One of the buckwheat cultivars (Hitachiakisoba) had slightly more large species. The average number of chains was 3.1–4.3, which is in the range for cereal amyloses (1.8–6.5). Buckwheat amyloses had a  $\beta$ -amylolysis limit (76–82%) similar to those of cereal amyloses (74–86%) (Takeda et al 1986, 1988a, 1989, 1999; Takeda and Preiss 1993; Shibanuma et al 1994, 1996; Yoshimoto et al 2000, 2001, 2002).

Amylose comprises linear and branched molecules. Although no



**Fig. 3.** HPSEC chromatograms of fluorescently labeled amyloses: —, fluorescence response; - - -, RI response; ●●●, DP (arrows indicate DP values).

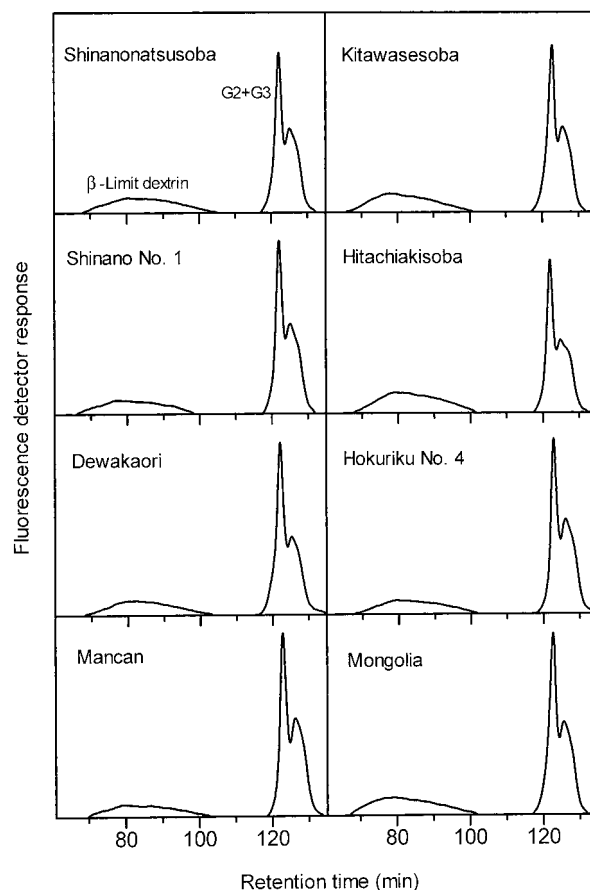
method is available for fractionation of the two components, the molar fraction of linear and branched amyloses was determined by HPSEC after  $\beta$ -amylolysis of fluorescently labeled amylose, where branched amylose produced labeled  $\beta$ -limit dextrin while linear amylose produced labeled maltotriose and maltose. The first (retention time 70–100 min) and second (120–130 min) elution peaks correspond to  $\beta$ -limit dextrin, and maltotriose and maltose, respectively (Fig. 4). Molar fraction of branched amylose was obtained as a percentage of fluorescent peak area of  $\beta$ -limit dextrin (Table VII). Molar fractions (23–27%) were in the range of cereal amyloses (15–45%) (Takeda et al 1987b, 1999; Shibamura et al 1994, 1996; Yoshimoto et al 2000, 2002), indicating that branched molecules of buckwheat amylose were minor species.

## CONCLUSIONS

Starches from seven common cultivars and one tartary cultivar of buckwheat were similar in pasting and thermal properties, amylose content, and molecular structures of amylose and amylopectin. The buckwheat starches had a lower amylose content and slightly larger amylose than maize and rice starches. The buckwheat amylopectins had chain-length distribution of short unit chains (CL < 60) similar to those of wheat and barley amylopectins and had a larger amount of long chains (LC) than cereal amylopectins.

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**Fig. 4.** HPSEC chromatograms of  $\beta$ -amylolyzate from fluorescently labeled amyloses from eight buckwheat cultivars.

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