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Note

Structures and amounts of branched molecules in rice amyloses

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Rice starches with low (japonica varieties) and high (indica varieties) affinities for iodine have similar contents of amylose but different affinities of their amylopectins for iodine[1]. Their amyloses have the same affinity for iodine and show no significant differences in molecular size, average chain-length, and number of chains[2]. However, the structures and amounts of their branched molecules have not been examined except for the amylose from a japonica, Sasanishiki variety[3]. We now report on five rice amyloses from starches with low [japonica: Hokkaido (unknown variety, produced in Hokkaido), and Sasanishiki] and high (indica: IR32, IR36, and IR42) affinities for iodine.

No method is available at present for the isolation of branched amyloses. Therefore, the beta-limit dextrins (β-LD) were isolated[3] after treatment of the amylose fraction with beta-amylase in order to remove all the linear molecules, and their properties are recorded in Table I. The iodine staining and binding properties of each β-LD were similar to those of the parent amylose, and their number- ($\overline{\text{d.p.}}_n$) and weight-average ($\overline{\text{d.p.}}_w$) degrees of polymerization were similar to each other except for IR32 β-LD, for which the values were slightly lower. These values were higher than those of amylomaize β-LD ($\overline{\text{d.p.}}_n$ 690–710, $\overline{\text{d.p.}}_w$ 1910–1990)[4], similar to those of corn β-LD ($\overline{\text{d.p.}}_n$ 790–850, $\overline{\text{d.p.}}_w$ 2700–3000)[5], and lower than those of water chestnut ($\overline{\text{d.p.}}_n$ 1200, $\overline{\text{d.p.}}_w$ 4150)[6] and sago ($\overline{\text{d.p.}}_n$ 1830–4090, $\overline{\text{d.p.}}_w$ 4150–12,500)[7] β-LDs. The rice β-LDs had similar molecular sizes, close to those ($\overline{\text{d.p.}}_n$ 920–1110, $\overline{\text{d.p.}}_w$ 2480–3500) of their respective parent amyloses and to those of corn[5], amylomaize[4], and sago amyloses[7]. The average chain-lengths ($\overline{\text{c.l.}}$) of the rice β-LDs were in the range 90–155, but the IR36 β-LD had a slightly higher $\overline{\text{c.l.}}$ This range resembles that for amyloses from other plants[3–6] and suggests that the branched molecules from rice have a similar inner chain-length. The average

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TABLE I

PROPERTIES OF BETA-LIMIT DEXTRINS FROM RICE AMYLOSES

Property	*Japonica*		*Indica*		
	Hokkaido	*Sasanishiki*	*IR32*	*IR36*	*IR42*
Iodine affinity (g/100 g)	18.8	19.5[a]	19.4	19.9	18.5
Blue value	1.35	1.35[a]	1.37	1.40	1.35
λ_{max} (nm)	653	659[a]	650	660	653
$\overline{D.p.}_n$[b]	890	1030[a]	790	890	840
$\overline{D.p.}_w$[c]	3080	3500	2480	3460	2760
$\overline{D.p.}_n/\overline{d.p.}_w$	3.46	3.40	3.10	3.89	3.39
Apparent d.p. distribution[d]	440–10,200	420–11,500	460–7400	410–11,300	370–9200
Average chain-length ($\overline{c.l.}$)	105	115[a]	105	155	90
Number of chains	8.5	9.0[a]	7.5	5.7	9.7

[a]From ref. 3. [b,c]Number- and weight-average degrees of polymerization, respectively. [d]$\overline{D.p.}$ values of the sub-fractions (10% by weight) having the lowest and highest molecular weights.

number of chains of the β-LDs indicate that the branched molecule from IR36 had 5.7 chains on average, whereas the others had 7.5–9.7 chains. These numbers were similar to those of branched molecules from most other plants except those from tapioca (17.1) and sago (17.3 and 19.4)[3–6].

Fig. 1 shows h.p.l.c. gel-permeation chromatograms of the β-LDs. Each β-LD gave a single peak with a maximum in the range d.p. 2240–3120. The elution profile resembled that of the parent amylose[2]. The linear plots of d.p. against retention time imply that both large and small β-LDs have similar hydrodynamic properties, due to their similar shapes. The β-LDs from water chestnut[6] and sago[7] have been suggested to be large and more spherical in shape, with more extensive branching, because of their concave curves of d.p. *versus* retention time in gel-permeation chromatography. The apparent distributions of d.p. of most rice β-LDs were in the range of 400–12,000, and the IR32 β-LD had a narrower distribution (460–7400). A similar range (200–13,000) was reported[2] for their parent amyloses. The high $\overline{d.p.}_w/\overline{d.p.}_n$ values (3.1–3.9) of the β-LDs suggest that the branched molecules from rice have a little broader distribution of molecular weights than their parent amyloses[2] (2.6–3.4). These resemblances between the β-LDs and their parent amyloses may imply that the branched molecules from rice are a little larger than the unbranched molecules and are degraded to small extents with beta-amylase, but have distributions of d.p. similar to those of the unbranched molecules.

Thus, the β-LDs have similar structures and, on the assumption that the branched molecules have a similar beta-amylolysis limit, there seem to be no significant differences.

The molar fractions (Table II) of the branched molecules from rice except that (0.49) of the IR32 molecule were ~0.3–0.4, similar to those of cereal[3], nut[3,6],

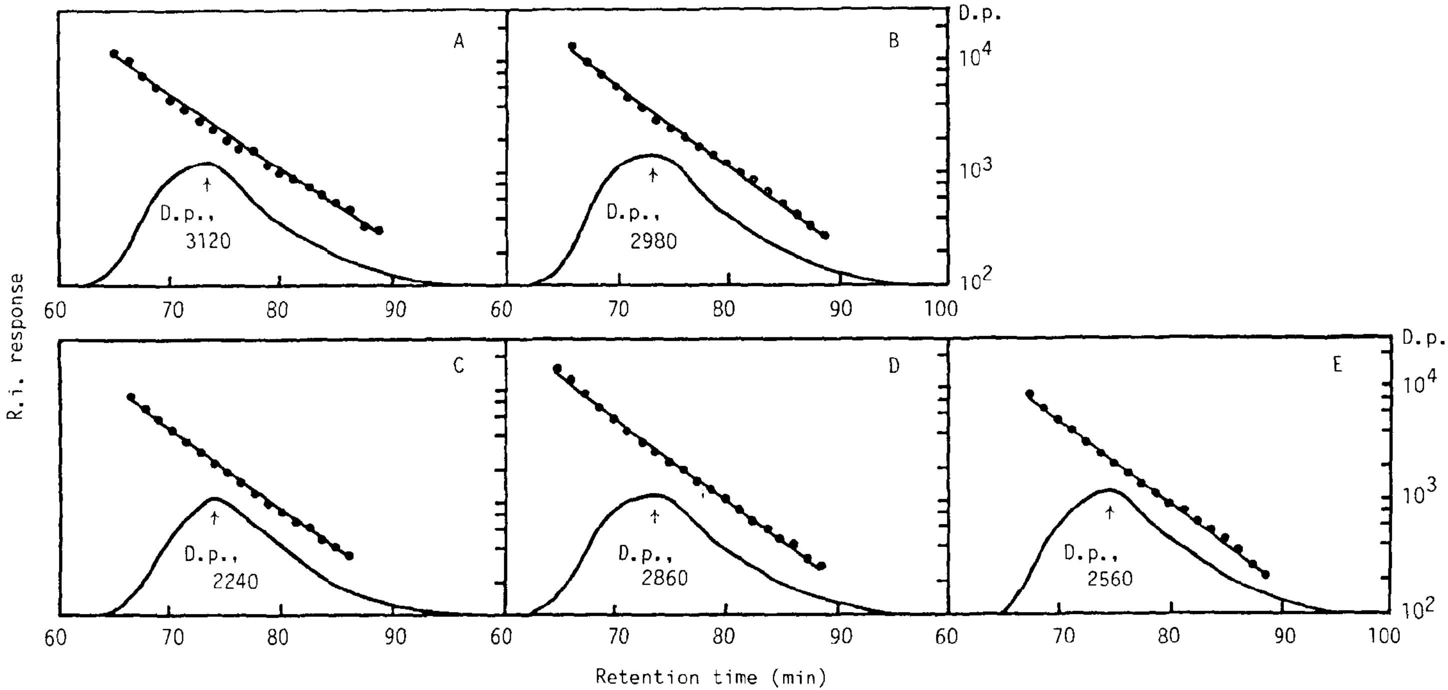

Fig. 1. H.p.l.c. elution curves for beta-limit dextrins from rice amyloses (A, B, C, D, and E: Hokkaido, Sasanishiki, IR32, IR36, and IR42 varieties, respectively). The conditions were as reported[11]. —, Response of the differential refractometer (R.i.). ●, D.p.

TABLE II

MOLAR FRACTIONS[a] OF BRANCHED AND UNBRANCHED MOLECULES IN RICE AMYLOSES

	Japonica		*Indica*		
	Hokkaido	*Sasanishiki*	*IR32*	*IR36*	*IR42*
Branched molecule	0.43	0.31	0.49	0.32	0.38
Unbranched molecule	0.57	0.69	0.51	0.68	0.62

[a]Molar fractions (Mf) were calculated from the average numbers of chains (Nc) of amylose and its beta-limit dextrin by the following equations: Mf of branched molecule = $(Nc_{amylose} - 1)/(Nc_{limit\ dextrin} - 1)$, Mf of unbranched molecule = $1 - Mf_{branched\ molecule}$.

root, tuber[3], and trunk[7] amyloses but different from that (0.70) of sweet-potato amylose[3], suggesting that the branched molecules are the minor component in most rice amyloses.

EXPERIMENTAL

Materials. — Pure rice amyloses from japonica and indica varieties were those used previously[2]. β-LDs from the amyloses were prepared as described[3].

Analytical methods. — Iodine affinity was determined at 25° by a modified[1] amperometric titration[8]. Blue values were determined as described[9]. The $\overline{d.p.}_n$ and $\overline{c.l.}$ were determined by the modified Park–Johnson method and the rapid Smith-degradation method[10] with minor modifications[2], respectively. The number of chains per molecule was calculated as $\overline{d.p.}_n/\overline{c.l.}$ The $\overline{d.p.}_w$ and apparent distribution of d.p. were determined by gel-permeation h.p.l.c., using connected columns (Tosoh TSKgel G6000PW, G4000PW, and G3000PW) with a differential refractometer (Tosoh RI-8000) and a low-angle laser-light-scattering photometer (Tosoh LS-8) as detectors[11].

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