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Molecular Structure and Gelatinization Properties of Turnip Starch (*Brassica rapa* L.)

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Abstract Starch was isolated from turnip (*Brassica rapa* L.), and to elucidate the structure-function relationship its structural and physical properties were characterized. Morphological structure of the starch was analyzed by SEM (Scanning Electron Microscopy). Most of the starch granules were spherical in shape with diameter ranging from 0.5-10mm. Apart from larger granules (<10 μm) which dominated the population size of turnip starch, significant amount of small (0.5-2 μm) and mid-size granules (~5 μm) were also detected. It was revealed that presumably, erosion damages occurred due to the attack of amylase-type enzymes on the surface of some granules. Branch chain-length distribution was analyzed by HPAEC (High-Performance Anion-Exchange Chromatography). The chain-length distribution of turnip starch revealed a peak at DP12 with obvious shoulder at DP18-21. The weight-average chain length (CL_{avg}) was 16.6, and a large proportion (11.8%) of very short chains (DP6-9) was also observed. The melting properties of starch were determined by DSC (Differential Scanning Calorimetry). The onset temperature (T_o) and the enthalpy change (ΔH) of starch gelatinization were 50.5°C and 12.5 J/g, respectively. The ΔH of the retrograded turnip starch was 3.5 J/g, which indicates 28.2% of recrystallization. Larger proportion of short chains as well as smaller average chain-length can very well explain relatively lower degree of retrogradation in turnip starch.

Keywords: turnip, starch, chain length, gelatinization, retrogradation

Introduction

Starch is one of the most abundant natural biopolymers on earth. It was found in every niche in plant kingdom, since it is used as storage for energy source in plant system. Amylose (AM) and amylopectin (AP) are two major components of starch. The AM content varies from 16 - 28% in normal starch materials (1). The food and non-food industrial applications of starch are enormously distributed. The physical properties of starch are greatly affected by the ratio of AP to AM, chain-length distribution, presence of minor components, etc (2). The structure-function relationship of starch materials has been scrutinized from the various plant sources (3-5). Recently, physical and chemical characteristics of the starches from unconventional sources have been reported to determine the structure-function relationship because of their potential industrial applications and role in food processing (6-10). Turnip is not a major plant source for starch production, because starch content in root tissue is less than 0.5% on fresh weight basis at 21 DAS (days after sowing), and then it rapidly declines during the sink-root development period (11). Thus, it is quite unrealistic to use turnip as a commercial starch source. However, the unique structure of turnip starch may help to understand the structure-function relationship, and to provide a right direction for starch modification by either chemical or biochemical method. Furthermore, genetically-modified, tailor-made starch can be designed by investigating starches from various sources, and by screening and expressing the relevant enzymes required for the synthesis of starch. In our present study, the molecular structure and gelatinization properties of turnip starch were characterized, and the effect of structure of starch on the physical properties has also been discussed.

Materials and Methods

Starch samples Turnip (*Brassica rapa* L.) was purchased from a local market in Philadelphia, USA, and a commercial corn starch was provided by Daesang Cor., Korea.

Starch isolation Starch was isolated from turnip by following the method of Badenhuizen (12) with some minor modifications (13). Isolated starch was washed three times with distilled water, rinsed twice with ethanol, and the final product was recovered by filteration through a Whatman No. 4 filter paper. Purified starch cake was dried in a convection oven at 35°C for 24 hr.

Starch granule morphology by scanning electron microscopy (SEM) Starch granules were spread on silver tape and mounted on a brass disk coated with gold/palladium (60/40). Sample images were observed under a scanning electron microscope (JEOL model 1850, Tokyo, Japan) by following the method of Jane *et al.* (14).

Apparent amylose contents and molecular weight distribution by gel permeation chromatography (GPC) Apparent amylose content of starches was determined by following the method of Yoo *et al.* (15). The starch solution (3 mL) was loaded into a GPC system consisting of a peristaltic pump (Masterflex, Cole-Parmer Inst. Co., USA), a Sepharose CL-2B column (16 × 700 mm), and a fraction collector (RediFrac, Amershamm Biosci., Sweden). A solution of sodium chloride (20 mM) containing 1 mM NaOH was used as an eluent, and the

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flow rate was 0.5 mL/min. The volume of each collected fraction was 2.5 mL.

Branch chain-length of amylopectin by high-performance anion exchange chromatography (HPAEC) Debranched amylopectin was analyzed by HPAEC (Bio-LC system, Dionex, USA) with a pulsed amperometric detector (PAD), according to the procedure described by Jane *et al.* (16) with some modifications.

Melting properties by differential scanning calorimetry (DSC) Thermal properties of starches were determined by Perkin-Elmer differential scanning calorimeter (DSC-7, Norwalk, CT), by following the procedure of Yoo *et al.* (15).

Results and Discussion

Morphology of turnip starch Morphological structure of turnip starch was analyzed by SEM. Most of the starch granules were spherical in shape with diameter ranging from 0.5-10 μm (Figure 1). Apart from larger granules (<10 μm) which dominated the population size of turnip starch, significant amounts of small (0.5-2 μm) and mid-size granules (~5 μm) were also detected. The average granular size of turnip starch was relatively smaller than that of other starches. It was presumed that the observed erosion damages were due to the attack of amylase-type enzymes on the surface of some granules. Since starch is not a major reserve of carbohydrates in turnips, it accumulates only 0.3 mg/g of tissue (fresh weight basis) in the mature turnip roots (11). The damaged surface detected from the large proportion of starch granules indicated that starch was still actively mobilized into the different types of carbohydrates in the sink tissue during the growth.

Molecular size distribution and apparent AM content Molecular size distribution and apparent AM content were determined by GPC analysis. The sharp AP peaks were followed by the broad AM peaks, as shown in the chromatograms of turnip and corn starches (Figure 2). The identity of each peak was also confirmed by the blue value (BV), which represents iodine binding capacity of starch components. When the ratio of total CHO content to BV was calculated, the value of turnip starch was substantially larger than corn starch. This result suggests that the turnip starch may contain extra-long chains in AP structure. The apparent AM content of turnip and corn starch was 36 and 30%, respectively.

Branch chain-length distribution by HPAEC analysis The chain-length distributions of both turnip and corn amylopectins (APs) represented peaks at DP12 after isoamylase-debranching treatment (Figure 3). The proportions of very short chains (DP6-9) of turnip and corn starches were 11.8 and 7.1%; 31.6 and 27.1% of DP6-12, respectively (Table 1). When compared with corn starch, the presence of relatively larger proportion of short chains in turnip AP explains the lower degree of retrogradation in turnip starch, as discussed below. It has been previously proposed that retrogradation rates of starches are inversely correlated with the proportion of short chains of DP6-9 (17). The weight-average chain length (CL_{avg}) of turnip and corn APs was 16.6 and 17.5, respectively. There was a presence of obvious shoulder at DP18-21 of turnip AP chain-length distribution, which

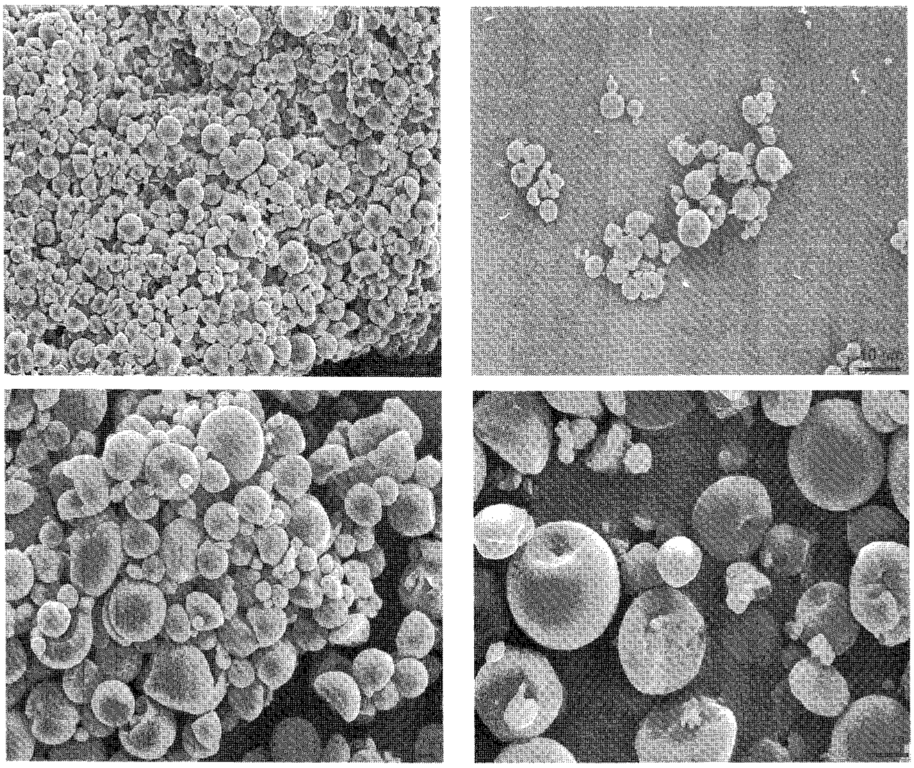

Fig. 1. SEM images of turnip starch.

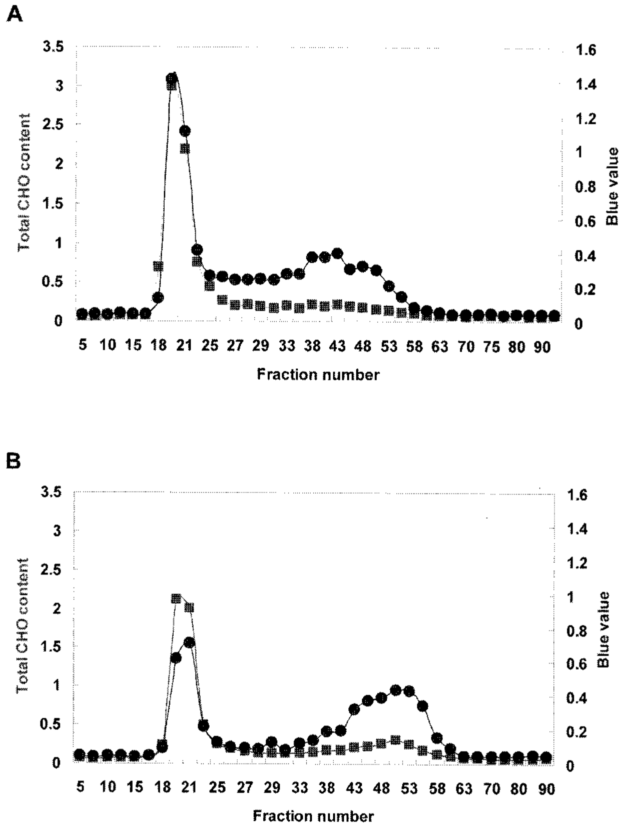

Fig. 2. GPC analysis of (A) turnip and (B) corn starches. – ■ – CHO content, – ● – blue value

was not observed in the chain-length distribution of debranched corn AP. Because chain length of DP18-21 represented the full length of crystalline region in AP structure, the shortage of these chains resulted in crystalline defects. (18, 19)

Gelatinization and retrogradation properties The thermal transition properties of starch were determined by DSC. The ΔH_{gel} reflected primarily the loss of molecular (double-helical) order (20). High thermal transition temperatures have been reported to arise from a high degree of crystallinity, which provides structural stability and makes the granule more resistant to gelatinization (21). The onset temperature (T_o) and the enthalpy change (ΔH_{gel}) of turnip starch gelatinization was shown to be 50.5°C and 12.5 J/g, respectively. Compared to 64.9°C (T_o) and 12.2 J/g (ΔH_{gel}) of corn starch, turnip starch displayed much lower T_o and almost identical ΔH. Although absolute amount of crystalline region was very similar, the defects in crystallinity of turnip AP as judged by the presence of obvious shoulder at DP18-21 in chain-length distribution could have been due to very low gelatinization temperature of turnip starch. It is known that T_os of

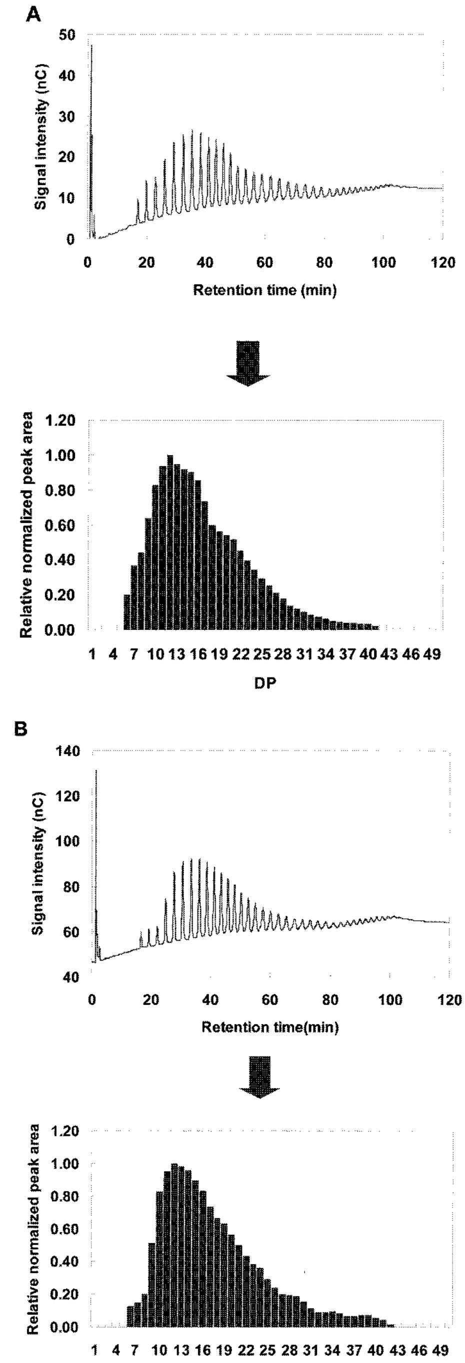

Fig. 3. HPAEC profiles of (A) turnip and (B) corn amylopectins.

Table 1. Branch chain-length distribution of amylopectins

starch source	% distribution					
	avg c.l.	dp 6-9	dp 6-12	dp 13-24	dp 25-36	dp 37+
turnip	16.6 (0.2)*	11.8 (0.2)	31.6 (0.2)	55.6 (0.1)	11.5 (0.0)	1.3 (0.3)
commercial corn	17.5 (0.4)	7.1 (0.2)	27.1 (0.0)	57.3 (0.0)	13.2 (0.0)	2.4 (0.0)

* ( ) Standard deviation

Table 2. Thermal properties of native turnip and corn starches

A

starch source	T_o	T_p	T_c	H_{gel} (J/g)
turnip	50.5 (0.0)	54.4 (0.2)	61.3 (0.6)	12.5 (0.0)
commercial corn	64.9 (0.0)	69.7 (0.1)	78.5 (1.4)	12.2 (0.2)

* This analysis was done after equilibrating sample pans at room temperature for 2 hr.

B

starch source	T_o	T_p	T_c	ΔH (J/g)	Retro (%)
turnip	39.3 (0.1)	50.4 (0.5)	64.2 (0.2)	3.5 (0.3)	28.2
commercial corn	41.7 (0.1)	50.7 (0.4)	62.7 (0.3)	5.6 (0.5)	46.2

* This analysis was done after storage of starch at 4°C for 10 days.

retrograded starch is lower than that of gelatinized native starch. The T_os of recrystallized turnip and corn starches was determined to be 39.3 and 41.7°C, respectively. The ΔH of the retrograded turnip starch was 3.5 J/g, indicating 28.2% of recrystallization, which was a much lower value when compared with 46.2% recrystallization of corn starch. Relatively larger proportion of short chains as well as smaller average chain-length explains lower degree of retrogradation. In general, cereal starches retrograde more rapidly than the tuber and root starches (19), which could be due to the presence of phosphate monoesters in the latter starches (22). It is possible that turnip starch obtained from the root tissue may contain phosphate monoesters in the AP structure and this may partly explain the lower degree of recrystallization.

Acknowledgments

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References

1. Hizukuri S. Starch: analytical aspects. In: Carbohydrates in food. Marcel Dekker, Inc., pp. 347-439 (1996)
2. Eliasson A-C, Gudmunsson M. Starch: Physicochemical and functional aspects. In: Carbohydrates in food. Marcel Dekker, Inc., pp. 431-503 (1996)
3. Hoover R. Composition, molecular structure, and physicochemical properties of tubers and root starches: a review. Carbohyd. Polym. 45: 253-267 (2001)
4. Singh N, Singh J, Kaur L, Sodhi NS, Gill BS. Morphological, thermal and rheological properties of starches from different botanical sources. Food Chem. 81: 219-231 (2003)
5. Tester RF, Karkalas J, Qi X. Starch-composition, fine structure and architecture. J. Cereal Sci. 39: 151-165 (2004)
6. Zhang P, Whistler RL, BeMiller JN, Hamaker BR. Banana starch: production, physicochemical properties, and digestibility-a review. Carbohyd. Polym. 59: 443-458 (2005)
7. Stevenson DG, Yoo SH, Hurst PL, Jane J. Structural and physicochemical characteristics of winter squash (*Cucurbita maxima* D.) fruit starches at harvest. Carbohyd. Polym. 59: 153-163 (2005)
8. Attanasio G, Cinquanta L, Albanese D, Di Matteo M. Effects of drying temperatures on physico-chemical properties of dried and rehydrated chestnuts (*Castanea sativa*). Food Chem. 88: 583-590 (2004)
9. Pérez E, Schultz FS, de Delahaye EP. Characterization of some properties of starches isolated from *Xanthosoma sagittifolium* (tannia) and *Colocassia esculenta* (taro). Carbohyd. Polym. 60: 139-145 (2005)
10. Carrín ME, Ceci LN, Lozano JE. Characterization of starch in apple juice and its degradation by amylases. Food Chem. 87: 173-178 (2004)
11. Gupta AK, Singh J, Kaur N. Sink development, sucrose metabolizing enzymes and carbohydrate status in turnip (*Brassica rapa* L.). Acta Physiol. Plant. 23: 31-36 (2001)
12. Badenhuizen NP. General method for starch isolation. Methods Carbohyd. Chem. 4: 14-15 (1964)
13. Kasemsuwan T, Jane J, Schnable P, Stinar P, Robertson D. Characterization of the dominant mutant amylose-extender (Ae1-5180) maize starch. Cereal Chem. 71: 457-464 (1995)
14. Jane J, Kasemsuwan T, Leas S, Zobel H, Robyt JF. Anthology of starch granule morphology by scanning electron microscopy. Starch/Staerke. 46: 121-129 (1994)
15. Yoo SH, Jane J. Structural and physical characteristics of waxy and other wheat starches Carbohyd. Polym. 49: 297-305 (2002)
16. Jane J, Wong K, McPherson AE. Branch-structure difference in starches of A- and B-type X-ray patterns revealed by their Naegeli dextrins. Carbohyd. Res. 300: 219-227 (1997)
17. Shi YC, Seib PA. The structure of four waxy starches related to gelatinization and retrogradation Dedicated to Professor David Manners. Carbohyd. Res. 227: 131-145 (1992)
18. Hanashiro I, Abe J, Hizukuri S. A periodic distribution of the chain length of amylopectin as revealed by high-performance anion-exchange chromatography. Carbohyd. Res. 283: 151- 159 (1996)
19. Jane J, Chen YY, Lee LF, McPherson AE, Wong KS, Radosavljevic M, Kasemsuwan T. Effects of amylopectin branch chain length and amylose content on the gelatinization and pasting properties of starch. Cereal Chem. 75: 629-637 (1999)
20. Cooke D, Gidley MJ. Loss of crystalline and molecular order during starch gelatinization: Origin of the enthalpic transition. Carbohyd. Res. 227: 103-112 (1992)
21. Barichello V, Yada RY, Coffin RH, Stanley DW. Low temperature sweetening in susceptible and resistant potatoes: Starch structure and composition. J. Food Sci. 54: 1054-1059 (1990)
22. Lim ST, Kasemsuwan T. Jane J. Characterization of phosphorus in starches using ^{31}P-NMR spectroscopy. Cereal Chem. 7: 488-493 (1994)