Pysicochemical properties of Tibetan hull-less barley starch

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A B S T R A C T

Objectives of this study were to (1) determine the starch physicochemical properties of two commercial Tibetan hull-less barley varieties, Beijing (BQ) and Kangqing (KQ); and (2) understand the relationship between unique properties of the starches, their structures, and impacts of growing conditions. The BQ barleys were grown at a location with lower temperature and less rainfall compared with the KQ barleys. The BQ starches showed significantly lower onset-gelatinization temperature (54.1–54.9 °C), larger gelatinization-temperature range (9.4–10.6 °C), and higher peak-viscosities (138.9–153.9 RVU) than the KQ starches (55.1–56.1 °C, 7.4–8.8 °C, and 63.4–64.7 RVU, respectively). After a treatment with 2% sodium-dodecyl-sulphate solution, the KQ starches showed substantially greater increases in peak viscosities than the BQ starches. Annealing of starch and enhanced amylose–lignoid complex formation, resulting from higher growing temperature during the development of the KQ starches, likely contributed to the differences in thermal and pasting properties between the BQ and KQ starches.

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1. Introduction

Barley is the fourth largest cereal crop produced worldwide, following maize, rice, and wheat (FAOSTAT, 2012). Barley grain is mainly used for the production of alcoholic beverage and livestock feed (Li, Vasanthan, Rossnagel, & Hoover, 2001a). Hull-less barley, also known as naked barley, is different from hulled barley because kernels of hull-less barley can easily detach from the hull during threshing. This is attributed to a recessive gene, nud, expressed in hull-less barley varieties, which inhibits the development of husks and caryopsis (Franczkowiack & Konishi, 1997). Compared with hulled barley, hull-less barley needs less space for storage and transportation and can avoid the loss of vitamins and minerals resulting from the peeling operation (Liu et al., 1996).

Hull-less barley usually has greater starch, protein, and β-glucan contents than the hulled barley because hull-less barley does not have the fibrous hull (Bhaty, 1999). Applications of hull-less barley have been studied, including for swine and poultry feeds (Darroch, Aherne, Helm, Sauer, & Jaikaran, 1996; Liu et al., 1996), production of bran and flour for food ingredients (Bhaty, 1995a), extraction of β-glucan for food applications (Bhaty, 1995b), and production of fuel ethanol (Ingleedew, Jones, Bhaty, & Rossnagel, 1995; Tomas, Dhax, Rossnagel, & Ingleedew, 1995). Different genotypes of hull-less barley, including normal (25–50% amylose), waxy (1–5% amylose), zero-amylose (0%), and high-amylose (35–45%) varieties, have been developed through traditional breeding practices (Bhaty & Rossnagel, 1997; Li et al., 2001a). Starches isolated from these hull-less barley varieties showed diverse physicochemical properties, such as pasting temperature and pasting viscosity, pastel clarity, and freeze–thaw stability (Li, Vasanthan, Rossnagel, & Hoover, 2001b; Song & Jane, 2000; Zheng, Han, & Bhaty, 1998), which extends the potential of using hull-less barley starch for various food and industrial applications.

As a traditional staple food for Tibetan people, hull-less barley is a major food crop grown on the Tibetan Plateau, representing 64% of the total crop production in Tibet (Zou et al., 2008). The recent growing interest in Tibetan hull-less barley (THLB) has been sparked by its high nutritional values and health benefits. The low incidence of hyperlipidemia and diabetes in Tibetan population has been associated with the consumption of hull-less barley (Gou, Li, & Guo, 2005). Studies have shown that, among 164 barley cultivars collected from China, Canada and Australia, THLB has the largest β-glucan content, up to 8.62% (average 5.25%) (Zhang, Wang, & Chen, 2002). The bran of THLB is a good source of linoleic acid and palmitic acid (Qian, Jiang, Su, & Gao, 2009). THLB is also a rich source of soluble phenolic compound, which displays an excellent

**Abbreviations:** THLB, Tibetan hull-less barley; BQ, Beijing; KQ, Kangqing; DSC, differential scanning calorimeter; FAME, fatty acid methyl ester; NMR, nuclear magnetic resonance; SDS, sodium dodecyl sulphate; RDS, rapidly-digestible starch; SDS, slowly-digestible starch; RS, resistant starch.

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radical-scavenging capacity in plasma (Gong, Cheng, Wu, Wu, & Zhang, 2012). The THLB extracts inhibit lipid oxidation in rat tissues (Li, Yan, & Zhong, 2005) and increase the survival time of rats under hypoxia conditions (Zhang et al., 2007).

Beiqing (BQ) and Kangqing (KQ) hull-less barley are the most important commercial varieties grown in Tibet area (Feng, Yang, Liu, Guo, & Tang, 2005; Ma, 2011). The production yields of BQ (1518–1822 kg/ha) and KQ varieties (1570–1744 kg/ha) are 10–20% higher than other commercial varieties (Feng et al., 2005; Ma, 2011). The two THLB varieties, however, have quite different eating quality. Starch is the major component of hull-less barley grain (59–64%) (Li et al., 2001a), which affects the eating quality of the grain. In contrast to abundant literature on health-promoting values of THLB, there is a scarcity of information on its starch physicochemical properties and the impacts on the eating quality and value-added applications (Li et al., 2014).

Objectives of this study were to (1) determine the starch physicochemical properties of two commercial THLB varieties, Beiqing (BQ) and Kangqing (KQ); and (2) understand the relationship between unique properties of the starches, their structures, and impacts of growing conditions. Results obtained from this study will unveil the mechanism of the variations in starch properties of THLB and is important for development of value-added utilization of the THLB starch.

2. Materials and methods

2.1. Materials

Six Tibetan spring hull-less barley varieties (Hordeum vulgare L. var. nudum hook. f.) were used in this study. Three of the six barley varieties, Beiqing 4 (BQ4), Beiqing 6 (BQ6), and Beiqing 7 (BQ7), were grown in Tibetan autonomous prefecture of Haibei, Qinghai province (N36°5′, E100°52′, ~3110 m altitude). The other three varieties, Kangqing 3 (KQ3), Kangqing 6 (KQ6), and Kangqing 7 (KQ7), were grown in Tibetan autonomous prefecture of Ganze, Sichuan province (N30°04′, E101°95′, ~3500 m altitude). The growing season of the six THLB varieties was from May to September. The average temperature and accumulated rainfall of the growing season in the Beiqing location were 7.4℃ and 27.0 cm, respectively, whereas that in the Kangqing location were 13.3℃ and 58.9 cm, respectively (Public Weather Service Center of China Meteorological Administration (CMA), 2014). THLB kernels were coarsely crushed before shipping to Iowa State University.

Pseudomonas isoamylase (EC 3.2.1.68, 280 U/mg) was purchased from Megazyme International Ireland (Wicklow, Ireland). Porcine pancreatic α-amylase (EC 3.2.1.1, 21.6 U/mg) and Aspergillus niger amyloglucosidase (EC 3.2.1.3, ≥300 U/ml) were from Sigma-Aldrich Co. (St. Louis, MO). All other chemicals were reagent grade and were purchased from either Sigma-Aldrich Co. (St. Louis, MO) or Fisher Scientific (Pittsburgh, PA) and used without further purification.

2.2. Starch Isolation by wet-milling

Starches were isolated from the coarsely-crushed THLB kernels using a wet-milling method reported by Li, Jiang, Campbell, Blanco, and Jane (2008).

2.3. Scanning electron microscopy

Scanning electron micrographs of isolated starch granules were taken using a scanning electron microscope (JEOL JSM-35, Tokyo, Japan) following the methods previously reported (Song & Jane, 2000). The average starch granule size was determined by measuring 200 granules using an Infinity Analyze software (version 6.1.0, Lumenera Corp., Canada).

2.4. X-ray diffraction pattern

X-ray diffraction patterns of starch samples were obtained using a diffractometer (Siemens D-500, Madison, WI) following the methods previously reported (Song & Jane, 2000). The copper tube was operated at 30 mA and 45 kV, and the scanning region of the two-theta angle (2θ) was from 4 to 40°. The crystallinity of the starch was calculated using a MDI JADE software (version 6.5, Materials Data Inc., Livermore, CA, USA).

2.5. Amylose content of starch

The amylose content of the THLB starch was determined using an iodine potentiometric-autotitrator (702 SM Titirno, Brinkmann Instrument, Westbury, NY) (Song & Jane, 2000). Starch was defatted using 85% methanol in a Soxhlet extractor for 16 h prior to the analysis. The iodine affinity of amylose used for the calculation was 0.2 (Takeda & Hizukuri, 1987). The amylose content was calculated using the equation: Amylose (%) = 100% IA0/0.2, where IA0 was the iodine affinity of the starch.

2.6. Lipid content of starch

Lipid contents of the starches were determined using a Gas Chromatography-Flame Ionization Detection system (HP 5890 Series II, Hewlett-Packard, Palo Alto, CA), equipped with a Supelco SP-2340 capillary column (Sigma-Aldrich Co., St. Louis, MO). The fatty acid methyl ester (FAME) was prepared directly using the native starch without prior lipid extraction. Starch (500 mg, dbw) was suspended in 4 ml of methanol chloride (1:1) containing 3% (v/v) sulfuric acid. Margaric acid (C17:0, 1 mg) was added as the internal reference. The mixture was incubated at 80℃ overnight to completely convert the lipids to FAME. The mixture was washed twice with deionized water, and the chloroform layer containing the FAME was collected. The chloroform was evaporated under nitrogen gas-flow, and the obtained FMAE was re-dissolved in 0.5 ml of analytical-grade hexanes for gas-chromatography analysis. The oven temperature was programmed with an initial hold of 1 min at 100℃, heating from 100 to 240℃ at 4℃/min, and a final hold of 5 min (the total analysis time was 41 min). The lipid content was calculated following the equation:

\[
\text{Lipid(\%)} = \left( \frac{\text{(100\% - PeakC_{17.0\%})}}{\text{PeakC_{17.0\%} \times 1 mg}} \times 500\ mg \right) \times 100\%
\]

2.7. Phosphorus analysis and characterization

Total phosphorus contents of the THLB starches were determined using a colorimetric method after an ashing process (Singh & Ali, 1987). The chemical structure of phosphorus of the starch was characterized using a 31P NMR spectrometer (Bruker Instruments, Billerica, MA) following the method reported by Kasemswan and Jane (1996).

2.8. Amylopectin branch-chain length distribution

Amylopectin of the THLB starch was separated from amylose and collected using a gel-permeation chromatographic column packed with Sepharose CL-2B gel. The isolated amylopectin was debranched using Pseudomonas isoamylase (Megazyme
International Irelands, Wicklow, Ireland). The branch chains of the debranched amylopectin were labeled with 8-amino-1,3,6-pyrenetrisulfonic acid (0.2 M in 15% acetic acid), and the branch-chain length distribution was analyzed using a fluorophore-assisted capillary electrophoresis (Beckman Coulter, Fullerton, CA) following the methods previously reported (Jiang, Campbell, Blanco, & Jane, 2010; Morell, Samuel, & O’Shea, 1998).

2.9. Starch thermal properties

Thermal properties of the isolated starch were analyzed using a differential scanning calorimeter (DSC, Diamond, Perkin-Elmer, Norwalk, CT). Starch gelatinization onset ($T_o$), peak ($T_p$), and conclusion temperatures ($T_c$), and enthalpy change ($\Delta H$) were obtained using a Pyris software (Perkin–Elmer). The gelatinized starch samples were stored at 4 °C for 7 days and then analyzed using the same parameters for their percentages retrogradation. The percentage retrogradation was calculated using the equation: Retrogradation (%) = 100 $\Delta H$ of dissociation of retrograded starch/$\Delta H$ of starch gelatinization.

2.10. Starch pasting properties

Pasting properties of both the native THLB starch and the starch treated with a sodium-dodecyl-sulphate (sds) solution were analyzed. Isolated starches were treated with a sds solution (2%, w/v) at room temperature for 30 min following the method previously reported (Debet & Gidley, 2006; Nierle, Baya, Kersting, & Meyer, 1990).

Starch pasting properties were analyzed using a Rapid Visco-Analyzer (Newport Scientific, Sydney, Australia) following the method of Jane et al. (1999). The pasting temperature, and the peak, breakdown, and final viscosities were determined using the Thermocline software (Newport Scientific).

2.11. Starch digestibility

Starch digestibility was analyzed following the Englyst’s method (Englyst, Kingman, & Cummings, 1992) with modifications (Li et al., 2008). Starch was suspended (5%, w/v) in a sodium-acetate buffer solution (0.1 M, pH 5.2) and heated in a boiling-water bath for 20 min with stirring. After cooling and equilibrating at 37 °C in

![Fig. 1. Scanning electron micrographs (SEM) of hull-less barley starch granules. (A) BQ4; (B) BQ6; (C) BQ7; (D) KQ3; (E) KQ6; (F) KQ7.](image-url)
a shaker water bath, the starch sample was hydrolyzed in *vitro* using porcine pancreatin extract and *A. niger* amyloglucosidase (Sigma-Aldrich Co., St. Louis, MO) with continuous agitation. Starch that was hydrolyzed within 20 min incubation-time was defined as rapidly-digestible starch. Starch that was hydrolyzed between 20 and 120 min was defined as slowly-digestible starch, and the portion that was not hydrolyzed at the end of 120 min was defined as resistant starch.

### 2.12. Syneresis of starch gels after Freeze–Thaw cycles

Starch paste (5%, w/w, dbw) was prepared following the same procedures for starch pasting properties. The resulting starch paste (1 ± 0.1 g) was quantitatively transferred to a pre-weighed microcentrifuge tube, and allowed to cool down at room temperature for 4 h. Starch gels in the tubes were stored at −18 °C for 20 h followed by thawing at 30 °C for 4 h. The process was repeated up to five cycles. After the 1st, 3rd, and 5th freeze–thaw cycles, the tubes were centrifuged at 6,600 g for 10 min to remove the water released from the gel. Percentage syneresis was calculated as the weight percentage of the water released on the basis of the initial gel weight.

### 2.13. Statistical analysis

Data were subjected to analysis of variance and Tukey’s multiple comparison analysis using PROC ANOVA procedure of SAS 9.2 (SAS Institute, Inc., Cary, NC).

### 3. Results

#### 3.1. Starch granule morphology and crystalline structure

THLB starch granules isolated from the BQ and KQ barley displayed typical bimodal size-distributions (Fig. 1). Large granules (A granules) had a lenticular shape and granule diameters of 10–30 μm, and small granules (B granules) had a spherical shape and granule diameters of 1–5 μm. These results were in line with those reported in previous studies on hulled and hull-less barley starches (Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994; Li et al., 2001a; Song & Jane, 2000; Vasanthan & Bhaty, 1996). Average diameters of the BQ starch A- and B-granules were 12.0–13.1 μm and 2.0–2.1 μm, respectively, which were smaller than that of the KQ starch granules, 13.3–14.0 μm and 2.2–2.3 μm, respectively (Table 1).

X-ray diffraction studies of the THLB starch showed a typical A-type diffraction pattern with strong peaks at 2θ of 15.1°, 16.8°, 17.8°, and 23.0° (Fig. 2). The BQ starches showed slightly lower percentage crystallinity (20.8–21.3%) than the KQ starches (21.3–21.9%).

#### 3.2. Amylose, lipid, and phosphorus contents of starch

Results of the amylose contents showed that the BQ starches had less amylose contents (24.0–25.0%) than the KQ starches (26.2–26.9%). Correlation analysis showed that amylose contents of the starches positively correlated with the granule diameters of the A granules for both the BQ and KQ starches (R² = 0.99, p < 0.01 for the BQ starches and R² = 0.90, p < 0.05 for the KQ starches, respectively). These results agreed with previous reports that the amylose content increases with the increase in starch granule-size (Duffus & Murdoch, 1979; Li, Blanco, & Jane, 2007). Lipid contents of the BQ starches ranged 0.41–0.45% (w/w), which were similar to that of the KQ starches (0.42–0.45%, w/w) (Table 1).

Starch phosphorus-contents of the six varieties ranged 0.045–0.050% (w/w) (Table 1). 31P NMR spectra of all the THLB starches showed signals at the chemical shift between −1 and 0 ppm (Data not shown), corresponding to phospholipids, and no signals appeared between 4 and 6 ppm, corresponding to phosphate monoester derivatives (Kasemsuwan & Jane, 1996; Lim, Kasemsuwan, & Jane, 1994). The results showed that the phosphorus in THLB starches was present exclusively in the form of phospholipids.

#### 3.3. Amylopectin branch-chain length distribution

Amylopectin branch-chain length distributions of the THLB starches are shown in Table 2. Average branch-chain lengths of the BQ amylopectin molecules (DP 20.5–20.7) were similar to that of the KQ amylopectin (DP 20.2–20.6). The results were in line with the previous findings (DP 17.6–22.6) (Vasanthan & Hoover, 2009).

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**Table 1**

Amylose, lipid, and phosphorus contents, and average granule diameters of the hull-less barley starch.

<table>
<thead>
<tr>
<th>Amylose (w/w, %)</th>
<th>Lipid (w/w, %)</th>
<th>Total phosphorus (w/w, %)</th>
<th>Average granule diameter (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A granules</td>
</tr>
<tr>
<td>BQ4</td>
<td>24.0 ± 0.1</td>
<td>0.42 ± 0.01</td>
<td>0.049 ± 0.000</td>
</tr>
<tr>
<td>BQ6</td>
<td>25.0 ± 0.7</td>
<td>0.42 ± 0.02</td>
<td>0.048 ± 0.000</td>
</tr>
<tr>
<td>BQ7</td>
<td>24.3 ± 0.0</td>
<td>0.45 ± 0.02</td>
<td>0.048 ± 0.000</td>
</tr>
<tr>
<td>KQ3</td>
<td>26.5 ± 0.8</td>
<td>0.42 ± 0.01</td>
<td>0.047 ± 0.000</td>
</tr>
<tr>
<td>KQ6</td>
<td>26.5 ± 0.3</td>
<td>0.45 ± 0.00</td>
<td>0.050 ± 0.000</td>
</tr>
<tr>
<td>KQ7</td>
<td>26.2 ± 0.1</td>
<td>0.41 ± 0.02</td>
<td>0.045 ± 0.000</td>
</tr>
</tbody>
</table>

* Values are means ± standard deviations of two replicates. Different letters following the mean values within the same column indicate statistically different mean values (p < 0.05).
Table 2
Amylopectin branch-chain length distributions\(^a\) of hull-less barley starches\(^b\).

<table>
<thead>
<tr>
<th></th>
<th>DP&lt;12</th>
<th>DP 13–24</th>
<th>DP 25–37</th>
<th>DP&gt;37</th>
<th>Ave. CL(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BQ4</td>
<td>30.4 ± 0.3</td>
<td>47.0 ± 0.2</td>
<td>10.7 ± 0.6</td>
<td>11.9 ± 0.1</td>
<td>20.7 ± 0.1</td>
</tr>
<tr>
<td>BQ6</td>
<td>30.3 ± 0.6</td>
<td>46.2 ± 0.7</td>
<td>12.0 ± 2.1</td>
<td>11.5 ± 0.8</td>
<td>20.5 ± 0.4</td>
</tr>
<tr>
<td>BQ7</td>
<td>30.9 ± 0.3</td>
<td>47.3 ± 0.4</td>
<td>10.1 ± 0.1</td>
<td>11.7 ± 0.1</td>
<td>20.5 ± 0.1</td>
</tr>
<tr>
<td>KQ3</td>
<td>31.8 ± 0.6</td>
<td>47.5 ± 0.1</td>
<td>9.4 ± 0.4</td>
<td>11.3 ± 0.1</td>
<td>20.2 ± 0.1</td>
</tr>
<tr>
<td>KQ6</td>
<td>30.7 ± 0.1</td>
<td>46.9 ± 0.3</td>
<td>10.6 ± 0.1</td>
<td>11.8 ± 0.3</td>
<td>20.5 ± 0.2</td>
</tr>
<tr>
<td>KQ7</td>
<td>30.7 ± 0.5</td>
<td>47.2 ± 0.2</td>
<td>10.3 ± 0.4</td>
<td>11.8 ± 0.1</td>
<td>20.5 ± 0.0</td>
</tr>
</tbody>
</table>

\(^a\) Molar basis.
\(^b\) Values are means ± standard deviations of two replicates. Different letters following the mean values within the same columns indicate statistically different mean values (p<0.05).
\(^c\) Average branch-chain length of amylopectin.

3.4. Starch thermal properties

Thermal properties of the THLB starches are shown in Table 3. The BQ starches showed significantly lower (p<0.05) onset-gelatinization temperatures (\(T_\text{onset}\)) (54.1–54.9 °C) than the KQ starches (55.1–56.1 °C). Gelatinization-temperature ranges (\(T_c–T_s\)) of the BQ starches (9.4–10.6 °C) were significantly (p<0.05) larger than that of the KQ starches (7.4–8.8 °C). Percentages retrogradation of the gelatinized KQ starches after storage at 4 °C for seven days (24.6–27.8%) were greater than that of the BQ starches (21.1–25.0%).

3.5. Starch pasting properties

Starch pasting properties are shown in Fig. 3. Remarkable differences in starch pasting properties were observed between the BQ and KQ barley. The BQ starches showed significantly greater peak viscosities (138.9–153.9 RVU) but lower pasting temperatures (90.6–91.3 °C) than the KQ starches (63.4–64.7 RVU and 92.5–93.2 °C, respectively) (Fig. 3(A)). The peak viscosities of the BQ starches were more than double of that of the KQ starches.

To investigate the effect of amylose–lipid complex on starch pasting properties, we analyzed the pasting properties of the THLB starches after being treated with a SDS solution (2%, w/v). It is known that SDS, as a surfactant, removes lipids from the starch, and SDS-treatment is unlikely to cause damage to the starch granules (Debet & Gidley, 2006; Nierle et al., 1990). The SDS-treated THLB starches showed significant reductions in the pasting temperature (70.3–72.5 °C) compared with that of the native starch (90.6–93.2 °C) (Fig. 3). The peak viscosities of the SDS-treated BQ starches (232.7–238.4 RVU) increased to ~1.6 times of that of the native BQ starches (138.9–153.9 RVU), whereas that of the SDS-treated KQ starches (191.6–214.8 RVU) increased to more than 3 times of that of the native KQ starches (63.4–64.7 RVU) (Fig. 3). The KQ starches showed substantially greater increases in peak viscosities than the BQ starches after the SDS treatment. Consequently, the differences in peak viscosities between the BQ and KQ starches were substantially reduced (from >2.1 times to <1.2 times) after the SDS treatment.

3.6. Starch digestibility

Digestibility of the THLB starch after cooking is shown in Table 4. The BQ starches contained more RDS (76.8–78.6%) but less SDS (11.7–14.2%) and RS (8.6–9.8%) than the KQ starches (74.6–75.6%, 14.1–16.0%, and 9.4–10.3%, respectively).

3.7. Freeze–thaw stability of starch gel

Freeze–thaw stability of the starch gel, determined after the 1st, 3rd, and 5th freeze–thaw cycles (FTC), is shown in Table 5. In general, the syneresis increased with increasing numbers of FTC. After the 1st FTC, corn, BQ4, and BQ7 starch gels showed good stability (<15% syneresis), whereas KQ starch gels had a syneresis ranging 46.3–49.8%. After the 3rd and 5th FTC, however, corn, BQ4, and BQ7 starch gels lost stability and reached ~50% of syneresis. The KQ

Table 3
Thermal properties of the hull-less barley starches\(^a\).

<table>
<thead>
<tr>
<th></th>
<th>(T_\text{onset}) (°C)</th>
<th>(T_c) (°C)</th>
<th>(\Delta H) (J/g)</th>
<th>(T_s–T_c) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BQ4</td>
<td>54.9 ± 0.0</td>
<td>64.3 ± 0.0</td>
<td>10.6 ± 0.1</td>
<td>9.4 ± 0.0</td>
</tr>
<tr>
<td>BQ6</td>
<td>54.1 ± 0.1</td>
<td>63.6 ± 0.0</td>
<td>10.5 ± 0.1</td>
<td>9.5 ± 0.1</td>
</tr>
<tr>
<td>BQ7</td>
<td>54.8 ± 0.1</td>
<td>65.4 ± 0.0</td>
<td>10.9 ± 0.1</td>
<td>10.6 ± 0.2</td>
</tr>
<tr>
<td>KQ3</td>
<td>55.4 ± 0.0</td>
<td>63.1 ± 0.0</td>
<td>10.1 ± 0.1</td>
<td>7.7 ± 0.0</td>
</tr>
<tr>
<td>KQ6</td>
<td>56.1 ± 0.0</td>
<td>63.5 ± 0.0</td>
<td>10.3 ± 0.0</td>
<td>7.4 ± 0.0</td>
</tr>
<tr>
<td>KQ7</td>
<td>55.1 ± 0.0</td>
<td>63.0 ± 0.2</td>
<td>10.5 ± 0.2</td>
<td>8.6 ± 0.2</td>
</tr>
</tbody>
</table>

\(^a\) Values are means and (standard deviations) of two replicates. Different letters following the mean values within the same columns indicate statistically different mean values (p<0.05).
\(^b\) \(T_\text{onset}\) = onset gelatinization temperature, \(T_c\) = conclusion temperature, \(\Delta H\) = enthalpy change.
\(^c\) Retrogradation (%) = 100% \(\Delta H\) of dissociation of retrograded starch/\(\Delta H\) of starch gelatinization.

Fig. 3. Pasting profiles of native (A) and sodium-dodecyl-sulphate-treated (B) hull-less barley starches.
starches were unlikely a convincing explanation of the significant differences in starch pasting properties. It has also been reported that starch granule swelling is significantly affected by the growing temperature of the plant during starch development (Tester, 1997). Elevated growing temperatures enhanced the development of double-helical crystalline structure as shown in Fig. 2, which reduced the rate of starch hydration and restricted granule swelling (Tester, 1997; Tester et al., 2000). After removing lipids by SDS-treatment, the KQ starches showed substantially greater increases in peak viscosities than the BQ starches. These results indicated that starch-lipid interactions in the KQ starches could be enhanced by the high growing temperature and moisture during the development of starch granules, which in turn further restricted granule swelling of the KQ starches. The higher pasting temperatures and lower viscosities of the KQ starches were likely results of starch annealing and the enhanced amylose–lipid complex formation during the development of starch granules. The KQ starch granules had restricted swelling after cooking, which were less susceptible to enzyme hydrolysis (Singh, Dartiis, & Kaur, 2010) and displayed less RDS contents but greater SDS and RS contents than the BQ starches.

5. Conclusions

The Tibetan hull-less barley starches contained 24.0–26.9% amylose, 0.41–0.45% lipids, and 0.045–0.050% (w/w) phosphorus, in the form of phospholipids. The BQ starches showed significantly lower onset-gelatinization temperature but larger gelatinization-temperature range than the KQ starches. The BQ starches showed significantly greater peak viscosities than the KQ starches. After a treatment with 2% sodium-dodecyl-sulphate solution, the starches showed significant decreases in pasting temperatures and increases in peak viscosities, and the KQ starches showed substantially greater increases in peak viscosities than the BQ starches. Annealing of starch and enhanced amylose–lipid complex formation, resulting from higher growing temperatures and more rainfall during the growth and development of the KQ starches, likely contributed to the differences in thermal and pasting properties between the BQ and KQ starches. The cooked KQ starches displayed less RDS content but more SDS and RS contents than the BQ starches, resulting from restricted swelling of the KQ starch granules compared with the BQ starch granules after cooking.

Acknowledgments

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References


### Table 4

<table>
<thead>
<tr>
<th>RDS (%)</th>
<th>SDS (%)</th>
<th>RS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BQ4</td>
<td>78.6 ± 0.0</td>
<td>12.6 ± 0.3</td>
</tr>
<tr>
<td>BQ6</td>
<td>76.8 ± 1.2</td>
<td>14.2 ± 0.3</td>
</tr>
<tr>
<td>BQ7</td>
<td>78.5 ± 0.1</td>
<td>11.7 ± 0.1</td>
</tr>
<tr>
<td>KQ3</td>
<td>74.7 ± 0.1</td>
<td>15.5 ± 0.6</td>
</tr>
<tr>
<td>KQ6</td>
<td>75.6 ± 0.9</td>
<td>14.1 ± 0.7</td>
</tr>
<tr>
<td>KQ7</td>
<td>74.5 ± 1.1</td>
<td>16.0 ± 0.8</td>
</tr>
</tbody>
</table>

* Values are means ± standard deviations of two replicates. Different letters following the mean values in the same column indicate statistically different mean values (p < 0.05).

### Table 5

| Syneresis (%) of maize, wheat, and hull-less barley starch gels (5%, w/w) |
|-------------------|----|----|----|
|                    | 0 FTC | 1 FTC | 3 FTC | 5 FTC |
| Maize              | 0.1 ± 0.0 | 10.9 ± 1.0 | 46.6 ± 1.5 | 53.6 ± 1.2 |
| Wheat              | 0.5 ± 0.1 | 21.6 ± 0.2 | 57.7 ± 1.2 | 62.8 ± 1.5 |
| BQ4                | 0.1 ± 0.0 | 14.4 ± 0.2 | 49.3 ± 0.6 | 50.3 ± 0.2 |
| BQ6                | 0.1 ± 0.0 | 39.1 ± 0.3 | 50.2 ± 2.5 | 50.7 ± 1.7 |
| BQ7                | 0.1 ± 0.1 | 12.1 ± 0.6 | 51.8 ± 0.1 | 51.2 ± 0.7 |
| KQ3                | 1.3 ± 0.1 | 40.6 ± 1.5 | 53.8 ± 1.5 | 56.4 ± 0.0 |
| KQ6                | 0.2 ± 0.0 | 47.7 ± 2.2 | 54.5 ± 4.3 | 54.7 ± 2.0 |
| KQ7                | 0.2 ± 0.0 | 46.3 ± 1.0 | 47.6 ± 2.9 | 54.0 ± 2.1 |

* Values are means ± standard deviations of two replicates.  
* FTC = Freeze–thaw cycle.

The physicochemical properties of the starch isolated from two commercial THLB varieties, BQ and KQ, were compared in this study. The results showed significant differences in starch physicochemical properties between the BQ and KQ varieties, especially in starch thermal and pasting properties.

The BQ starches showed significantly lower onset-amylose gelatinization temperature and larger gelatinization-temperature range than the KQ starches. The branch-chain lengths of amylopectin, however, were similar between the BQ and KQ starches, which unlikely contributed to the differences in the starch thermal properties between the BQ and KQ varieties. It is known that gelatinization temperatures can also be affected by the growing conditions, including temperature and moisture during the development of starch granules (Lu, Jane, Keeling, & Singletary, 1996; Tester, 1997), which resembles the annealing process of starch in vitro. The average temperature and accumulated rainfall during the growing season of the KQ varieties (13.3 °C and 58.9 cm, respectively) were substantially higher than that of the BQ varieties (7.4 °C and 27.0 cm, respectively). The higher growing temperature and abundant moisture during the development of starch granules could cause annealing of starch and resulted in the higher onset-gelatination temperatures and narrower gelatinization-temperature ranges of the KQ starches (Tester, Debon, & Sommerville, 2000).

The BQ starches showed significantly higher peak viscosities but lower pasting temperatures than the KQ starches. It is known that amylopectin is primarily responsible for granule swelling and viscosity (Tester & Morrison, 1990) and starch pasting properties are affected by amylose and lipid contents (Jane et al., 1999; Morrison, Tester, Snape, Law, & Gidley, 1993; Sunswung, Sunarti, Mishima, Isono, & Hisamatsu, 2005). The insignificant difference in amylopectin branch-chain length and lipid contents and small differences in the amylose contents between the BQ and KQ starches showed lower syneresis than the BQ starch gel (Table 5), and the results were consistent with the greater retrogradation rate of the KQ starches (Table 3), both resulting from the restricted swelling of the starch granules.

4. Discussion

The Tibetan hull-less barley starches contained 24.0–26.9% amylose, 0.41–0.45% lipids, and 0.045–0.050% (w/w) phosphorus, in the form of phospholipids. The BQ starches showed significantly lower onset-gelatinization temperature but larger gelatinization-temperature range than the KQ starches. The BQ starches showed significantly greater peak viscosities than the KQ starches. After a treatment with 2% sodium-dodecyl-sulphate solution, the starches showed significant decreases in pasting temperatures and increases in peak viscosities, and the KQ starches showed substantially greater increases in peak viscosities than the BQ starches. Annealing of starch and enhanced amylose–lipid complex formation, resulting from higher growing temperatures and more rainfall during the growth and development of the KQ starches, likely contributed to the differences in thermal and pasting properties between the BQ and KQ starches. The cooked KQ starches displayed less RDS content but more SDS and RS contents than the BQ starches, resulting from restricted swelling of the KQ starch granules compared with the BQ starch granules after cooking.


