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Nutrient composition and starch characteristics of *Quercus glandulifera Bl.* seeds from China

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ABSTRACT

The chemical composition and starch characteristics of acorn (*Quercus glandulifera Bl.*) were studied. The moisture content of acorn seeds was 7.55%. The crude fat, crude protein, dietary fiber, total ash, and nitrogen-free extract contents of acorn seed were 4.20%, 10.16%, 2.95%, 0.03%, and 82.66%, respectively, on a dry weight basis. Linoleic, oleic, and palmitic were the most predominant fatty acids. UFA:SFA and SFA:MUFA:PUFA ratios were 2.6:1 and 1.25:1.34:1, respectively. The essential amino acid content from acorn seeds was low based on FAO reference values. Acorn seeds were a good source of Fe, Zn, and Mn. The contents of vitamins A and E were 1.40 mg RE/100 g and 10.78 mg/100 g, respectively. Starch extracted from acorn seeds had round, triangle, and elliptical morphology with granule size of 3.3–126.2 μm. The ratio between amylose and amylopectin contents was 25.39:72.94. Acorn starch had a typical A-type crystal pattern with 23.53% relative crystallinity. The gelatinization temperature was 66.53 °C and the transition enthalpy was 4.33 J/g.

1. Introduction

Acorn-producing plants belong to the genus *Quercus*, which includes more than 300 species. Most of the *Quercus* species consist of tall trees or shrubs. *Quercus glandulifera Bl.* is an acorn-producing shrub.

Q. glandulifera Bl. grows in the hills of Qinhuai, China, i.e., in the provinces of Anhui, Jiangxi, Hunan, and Guangdong. The plant is a deciduous shrub different to *Cyclobalanopsis blakei* (*Skan*) *Schott* but with seeds similar to those of oak. In certain regions of China, the yield of *Quercus* seeds is high and comparable to that of cereal grains (Xie & Xie, 2002). Bainbridge (1986), who evaluated the nutritional composition of 18 acorn species but not of *Q. glandulifera Bl.*, reported that acorns contain 8.7–44.6% water, 2.3–8.6% protein, 1.1–31.3% fat, and 32.7–89.7% carbohydrate. Acorns are rich in several nutrients and are used in a variety of traditional dishes (Bainbridge, 1986) including tofu and cold noodles. The phenolic compound and antioxidant activity of *Quercus robur* and *Quercus cerris* methanol extracts were investigated (Rakić et al., 2007). Additionally, Rakić, Povrenović, Tešević, Simić, and Maletić (2006) evaluated the effects of thermal treatment on the physical and nutritive characteristic of *Q. robur*. Charef, Yousfi, Saidi, and Stocker (2008) and Petrovic, Sobajic, Rakic, Tomic, and Kukic (2004) reported that *Quercus* seeds are good sources of unsaturated fatty acids. However, the chemical composition of acorns varies with species and origin (Galván et al., 2012). *Quercus* seeds are harvested mainly for human consumption and livestock feed. This study evaluated the nutritional composition and starch characteristics of *Q. glandulifera Bl.* seeds.

2. Materials and methods

2.1. Sample collection and preparation

Acorn seeds were harvested from 50 *Quercus* shrubs. The seeds were hand-peeled, oven-dried at 40 ± 5 °C for 24 h, and dry-milled. The resulting acorn flour was passed through a 0.3-mm mesh sieve and stored in sealed containers for analysis.

2.2. Starch preparation

Acorn flour was dispersed in 0.3% sodium hydroxide (1:5, w/w), mixed, and allowed to stand for 2 h. The dispersion was passed through a 0.18-mm mesh sieve. The starch milk was allowed to settle, and the supernatant was subsequently decanted and discarded. The precipitate (containing the starch) was rinsed several times with distilled water, air-dried, and stored in sealed containers (Nwokocha & Williams, 2011).

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2.3. Proximate composition analyses

Acorn moisture and ash content were determined according to AOAC Methods (2000). Crude protein content was determined by the Kjeldahl instrument (VELP UDK159, Milan, Italy) using a nitrogen–protein conversion factor of 6.25 (AOAC, 2000). Crude fat was obtained following petroleum ether and hexane extractions (Charef et al., 2008; Petrovic et al., 2004). Dietary fiber content of the defatted samples was determined by hydrolyzing starch molecules with acid, denaturing protein molecules with base, and filtering these compounds (James, 1995). Total carbohydrate content, as nitrogen-free extract (NFE), was calculated using the following equation (Pérez-Pacheco et al., 2014; Rakić, Janković, Marčetić, Živković, & Kuzevski, 2014):

$$\%\text{NFE} = 100 - \%\ (\text{crude protein} + \text{crude fat} + \text{ash} + \text{crude fiber})$$

2.4. Nutrient analyses

2.4.1. Fatty acids

Acorn oils were converted to methyl esters using a boron trifluoride methanol complex (14% w/v) at 100 °C for 1 h. The reaction was stopped with the addition of 0.5 ml distilled water. The extracted fatty acid methyl esters (FAMES) were dissolved in pure heptane for gas chromatography–mass spectrometry (GC–MS) analyses (Besbes, Blecker, Deroanne, Drira, & Attia, 2004).

GC–MS analyses were performed in an Agilent 6890–5975c mass selective detector (Agilent, Folsom, California, USA). The desorption time was 5 min, the injection port was maintained at 250 °C, and the column consisted of an HP-5 ms (30 m × 0.25 mm i.d., 0.25 μm thick; J&W Scientific, Agilent). The temperature was held at 140 °C for 5 min, increased to 250 °C at 4 °C/min, and finally increased to 280 °C at 3 °C/min. The interface temperature was 200 °C (Dong et al., 2013).

2.4.2. Free amino acids

The extraction and purification of free amino acids were performed according to the method reported by Moore and Stein (1951) with slight modifications. Acorn flour (0.3 g) was weighed into a 50-ml volumetric flask and adjusted to 50 ml with 6 M HCl, containing 1 ml of 1 g/L reagent-grade phenol and 5000 nmol of norleucine (internal standard). Subsequently, the acid was removed in a rotary evaporator at 50 °C. The resulting hydrolysate was transferred to a 50-ml volumetric flask and the volume was adjusted to 50 ml with distilled water. Subsequently, 2 ml of this solution was centrifuged in Allegra 64R Centrifuge (Beckman coulter, California, USA) at 2,295 g for 2 min. The pellet was dissolved in 5 ml sodium citrate buffer (pH 2.2), passed through a 0.22-μm syringe filter, and stored at −80 °C. Aliquots were subsequently analyzed by ion-exchange chromatography (HITACHI L-8900 automatic amino acid analyzer, Tokyo, Japan), using the standard protein hydrolysate program with sodium citrate buffer and ninhydrin detection. The amino acids were detected at 440 and 570 nm. Amino acid identification and quantification were performed by comparisons to standard calibration curves using Ezchrom TM Chromatography Data System, version 6.7.

2.4.3. Vitamins

Vitamins were determined by HPLC (High Performance Liquid Chromatography) using the method reported by Chung, Shin, Hwang, and Choi (2013). Acorn flour (5 g) was saponified at room temperature with 10 ml of KOH (1 kg/L), 10 ml distilled water, 30 ml ethanol, and 0.5 g ascorbic acid. The reaction mixture was mixed under liquid nitrogen for 10 h, centrifuged at 825*g* for 15 min, and extracted with ethyl ether (3× 200 ml). The organic phase was rinsed twice with phosphate buffer (pH 7.4, 2× 100 ml), concentrated under vacuum, and diluted to 5 ml with the eluent phase. A 25-μl aliquot was injected into the chromatographic system. The chromatographic system consisted of an autosampler (Waters 2707, Milford, Massachusetts, USA) equipped with a binary HPLC pump (Waters 1525), a column heater, and a UV/visible detector (Waters 2489). Each chromatogram was analyzed with Breeze 2 (Waters 2008). Chromatography was performed at 1 ml/min on a Discovery C_{18} ODS reverse phase column (250 mm × 4.6 mm i.d., 5 μm film thickness; Hypersil, Dalian, China).

Tocopherol analysis was performed in isocratic mode using 65:26:9 (v/v/v) acetonitrile/dichloromethane/methanol as the solvent. Carotenoid analysis was performed in gradient mode using 45:10:9 (v/v/v) acetonitrile/dichloromethane/methanol (solvent A) and 65:26:9 (v/v/v) acetonitrile/dichloromethane/methanol (solvent B). The 25-min program was the following, 0–5 min, 100% solvent A; 10–11 min, increase from 0% to 100% solvent B; 11–19 min, 100% solvent B; 19–20 min, increase from 0% to 100% solvent A; and 20–25 min, 100% solvent A. Carotenoid and tocopherol contents were determined by diode array detection at 445 and 298 nm, respectively.

2.4.4. Minerals

Samples were ashed in the presence of nitric acid/perchloric acid (9:1, v/v) on a hot plate at 200 °C (James, 1995). Mineral content was determined by inductively coupled plasma-optical emission spectrometry (ICP-OES); K was analyzed by atomic absorbance spectroscopy (ZEEnit 700P, Jena, Germany). Standard curves of Cu (324.754 nm), Zn (202.548 nm), Fe (259.94 nm), Mn (257.610 nm), Ca (422.673 nm), Ni (231.604 nm), Pb (220.353 nm), Se (196.090 nm), Al (309.271 nm), As (189.042 nm), Cd (226.502 nm), and Mg (280.270 nm) were generated with different concentrations of each element (0–10 mg/L). The standard curve of K (766.5 nm) was generated with 0–40 mg K/L. The correlation coefficients were 0.999.

2.5. Starch analyses

2.5.1. Microstructure and granule size

Starch granule surface and shape were examined under a scanning electron microscope (SEMXL-20, Philips, Amsterdam, Netherlands). The starch sample was mounted onto circular aluminum stubs with double sticky tape, coated with 20 nm gold, and photographed in a Philips Hitachi S-4800 (Hitachi, Tokyo, Japan) at an accelerating potential of 30 kV. Granule size analysis was performed with a laser light scattering-based particle size analyzer (Mastersizer 2000, Malvern, Solihull, UK).

2.5.2. X-ray diffraction

The starch samples were oven-dried at 50 °C overnight and pulverized to a particle size < 63 μm. X-ray diffraction analysis was performed in an X-ray diffractometer (X'Pert PRO, Panalytical, Netherlands) operated at 40 kV and 200 mA. Diffractograms were obtained from 3° 2θ to 60° 2θ with a scanning speed of 8°/min and scanning step of 0.02°. Relative crystallinity was calculated based on the method reported by Hayakawa, Tanaka, Nakamura, Endo, and Hoshino (1997):

$$\text{Relative crystallinity}\ (\%) = \text{Ac}/(\text{Ac} + \text{Aa}) \times 100$$

where Ac is the crystalline area on the X-ray diffractogram and Aa is the amorphous area on the X-ray diffractogram.

2.5.3. Amylose content

Starch samples were first defatted with hot *n*-propanol–water (3:1 v/v) for 7 h and subsequently dissolved (20 mg) in 90%