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The contribution of lysophospholipids to pasting and thermal properties of nonwaxy rice starch

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ABSTRACT

It is known that lysophospholipids (LPLs) may affect rice starch pasting and thermal properties possibly through the formation of an amylose–lipid complex. However, whether these effects of rice LPLs are independent of amylose are still not understood. Here, the diversity of rice flour pasting and thermal properties and their relationship with individual LPL components in native rice endosperm were studied. Several significant correlations between LPLs and pasting properties, such as cool paste viscosity (CPV), breakdown (BD) and consistency (CS) were clearly evident. Thermal properties generally had no relationship with LPLs except for gelatinization enthalpy. Using partial correlation analysis we found that, irrespective of apparent amylose content, CPV and individual LPLs were positively correlated, while BD, CS and other individual LPLs were negatively correlated. This study suggests naturally occurring individual LPLs can contribute to rice flour pasting and thermal properties, either independently or in combination with amylose.

1. Introduction

Rice (*Oryza Sativa* L.) is high in starch, providing a vital source of dietary carbohydrates and energy, which makes it a fundamental foodstuff for over half the world's population. With economic development and improvement in living standards, the enhancement of rice quality has become the major target for rice breeding programs. Evaluation of rice quality depends on the end-use application but generally includes milling, appearance, nutrition, cooking and eating quality (Bao, 2012; Fitzgerald, McCouch, & Hall, 2009).

Polished rice grains are primarily composed of starch (~90%), the physicochemical characters of which are considered as the main parameters that determine rice eating quality, whereas the amount and proportion of lipids could significantly affect rice sensory properties (Martin & Fitzgerald, 2002; Moazzami, Lampi, & Kamal-Eldin, 2011). Lysophospholipids (LPLs), which are also known as starch lipids, account for 24–56% of lipids complexed with the starch in polished rice (Juliano, 1983). The LPLs may significantly influence rice flour physicochemical properties and provide additional nutritional and human-health benefits (Liu, Waters, Rose, Bao, & King, 2013).

LPLs complex with amylose to modify pasting properties (Lopez, de Vries, & Marrink, 2012; Putseys, Lamberts, & Delcour, 2010), with significant linear correlations observed between amylose content, lipid content, gelatinization temprature (GT) and enthalpies of gelatinization (Morrison & Azudin, 1987). In contrast to saturated fatty acids, the double bond in unsaturated fatty acids may hinder complexation with amylose (Zhou, Robards, Helliwell, & Blanchard, 2007) while addition of lysophosphatidylcholine (LPC) and lysophosphatidylethanolamine (LPE) into rice starch increases cool paste viscosity (CPV), breakdown (BD), setback (SB) and pasting temperature (PT) (Liang, King, & Shih, 2002). Removal of lipids has a minor but measurable influence on starch gelatinization (Marshall, Normand, & Goynes, 1990) and thermal stability in cereals (Vasanthan & Hoover, 1992). Defatting starch reduced gel viscosity and GT (Maniñgat & Juliano, 1980) and reduced PV and HPV in cereal starches (Vasanthan & Hoover, 1992). However, there are few published data in the public domain which describe the relationship in rice grain between pasting and thermal properties of rice flour and native LPL levels in rice grain. It is also unclear

Abbreviations: AAC, apparent amylose content; BD, breakdown; CPV, cool paste viscosity; CS, consistency; DSC, differential scanning calorimetry; GT, gelatinization temperature; HPV, hot paste viscosity; LPC, lysophosphatidylcholine; LPE, lysophosphatidylethanolamine; LPL, lysophospholipids; PT, pasting temperature; PV, peak viscosity; SB, setback viscosity; TLPC, total lysophosphatidylcholine; TLPE, total lysophosphatidylethanolamine; TLPL, total lysophospholipids; T_o, onset temperature; T_p, peak temperature; T_c, conclusion temperature; ΔH_g, enthalpy of gelatinization ;.

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whether native LPLs have a role in determining rice flour physicochemical properties independently of amylose.

The aim of the present study was to quantify the contribution of native rice endosperm LPLs to rice flour pasting and thermal properties and determine if this contribution is dependent on amylose using partial correlation analysis. A better understanding of the influence of native LPLs on rice physicochemical properties may provide additional tools for selection of cultivars with improved cooking and eating quality.

2. Materials and methods

2.1. Materials

Two sets of nonwaxy rice (*Oryza sativa* L.) accessions were used in this study (Supplementary Table 1). The first set of accessions (Set 1) included 11 non-waxy rice accessions. Of these, three accessions belonged to *japonica* subspecies, and the remainder to the *indica* subspecies, for which the rice apparent amylose content (AAC) and endosperm lysophospholipid contents have previously been reported (Liu et al., 2014). The second set (Set 2) included 20 non-waxy rice accessions consisting of eight *japonica* subspecies, eight *indica* subspecies and four from the *aus* group (Xu et al., 2014), for which lysophospholipid contents, AAC and some physicochemical properties of the milled rice flour were previously reported (Tong, Chen, et al., 2014; Tong, Liu, et al., 2014).

2.2. Pasting viscosity

The pasting properties were measured using a Rapid Visco Analyzer (RVA) (Model 3-D, Newport Scientific, Warriewood, Australia). Rice flour was weighed (3.0 g, 12%, m.b.) and mixed with 25 mL double-distilled water in the aluminum RVA sample canister. A 12.5-min Rice Method 1 program was applied. Briefly, the rice flour slurry was held at 50 °C for 1 min, heated to 95 °C in 3.8 min (12 °C/min) and then held at 95 °C for 2.5 min, cooled to 50 °C in 3.8 min with constant rate and held at 50 °C for 1.4 min. The initial agitator speed was 960 rpm/min for 60 s which then reduced to 160 rpm/min which was maintained the remainder of the program. The major viscosity parameters, peak (PV), hot paste (HPV), cool paste (CPV) were directly recorded by the Thermo Cycle for Windows software (version 1.2), while the derivative parameters such as breakdown (BD; =PV-HPV), setback (SB; =CPV-PV) and consistency (CS; =CPV-HPV) were calculated. The pasting temperature (PT) was estimated based on the method of Bao (2008). Viscosity was reported as Rapid Visco Units (RVU).

2.3. Thermal properties

Differential Scanning Calorimetry Model Q20 (DSC, TA Instruments, Newcastle, DE) was used for determination of thermal properties. In brief, 2.0 mg rice flour samples (dry weight) was weighed and 6 μL distilled water added into an aluminum pan. The pans were sealed hermetically and maintained for 1 h at room temperature. An empty sealed aluminum pan was utilized as reference. Then, the sample was heated from 30 °C to 110 °C at a rate of 10 °C/min. Onset (T_o), peak (T_p), conclusion (T_c) and gelatinization enthalpy (ΔH_g) of gelatinization were determined by Universal Analysis 2000 (TA Instruments).

2.4. Rice endosperm lysophospholipids

The rice endosperm lysophospholipids were determined according to Liu et al. (2014) and all data from the two sets of rice accessions were previously reported (Liu et al., 2014; Tong, Liu, et al., 2014).

2.5. Statistical analysis

All pasting and thermal properties were determined in duplicate. Multiple comparisons analysis of data was conducted with SAS System Edition for Windows version 9.1 (SAS Institute Inc., Cary, NC, USA). The analysis of Pearson and partial correlations between flour physicochemical properties and lysophospholipids were performed with IBM SPSS version 19.0 (IBM, Chicago, IL, USA).

3. Results

This study focused on the characterization of physicochemical properties for two sets of rice, and included analysis of the relationship between physicochemical properties and LPLs in endosperm, taking into account the interaction with AAC. Thirty one accessions were analyzed, with profiling of LPLs as previously reported (Liu et al., 2014; Tong, Liu, et al., 2014). The first set of 11 rice accessions included mostly Chinese cultivars or breeding lines, while the second set of 20 accessions included cultivars and landraces derived from other geographical regions. The data derived from these two sets were analyzed independently and in combination.

3.1. Set 1: pasting and thermal properties

Extensive variation was observed in flour physicochemical properties within Set 1 (Table 1). AAC ranged from 13.1% to 26.4%, with five accessions classified as low amylose (13.1–18.0%), one intermediate amylose (22.8%) and five high amylose (24.8–26.4%) (Liu et al., 2014). The PV ranged from 147.8 to 282.1 RVU, with a mean of 224.8. HPV ranged from 74.9 RVU for R03, a low amylose rice accession, to 194.1 RVU in R12, a high amylose rice accession (Table 1). R03 also had the lowest CPV (129.6 RVU) while R12 had the highest CPV (341.6 RVU) (Table 1). BD, SB and CS ranged from 23.5 to 146.3 RVU, 60.6 to 93.9 RVU and 54.7 to 147.9 RVU, respectively (Table 1). PT ranged from 69.5 °C in a low amylose rice to 83.4 °C in another low amylose rice accession (Table 1).

The average values of T_o, T_p and T_c, were 68.0 °C, 73.0 °C and 78.4 °C, respectively. These accessions could be subdivided into three groups based on T_p. The low gelatinization temperature (GT) accessions included R04-R07, R13 with T_p ranging from 66.2 °C to 70.9 °C. The intermediate GT group included R08-R12 with T_p ranging from 75.2 °C to 76.6 °C while the high GT group only had one member, R03, which had T_p of 81.1 °C. ΔH_g ranged from 8.1 J/g (R13) to 11.8 J/g (R03) and the average was 9.6 J/g (Table 1).

3.2. Set 1: relationship between physicochemical properties and lysophospholipids

The correlation coefficients between rice flour physicochemical parameters and lysophospholipid content of the 11 rice accessions are shown in Table 2. Significant correlations between several individual LPL and physicochemical parameters were evident (Table 2). AAC, CPV and SB were significantly positively correlated to LPC16:0, TLPC, LPE16:0, LPE18:2, TLPE and TLPL, whereas the BD had negative correlation with these LPL components. CS was positively correlated with LPC16:0 and negatively with LPC18:1. Thermal properties were generally not correlated with LPL components apart from ΔHg which was negatively correlated with LPC18:3 and LPE18:3 (Table 2). Nevertheless, partial correlation analysis excluding the effect of AAC indicated a significant correlation ($P < 0.05$) between LPC16:0 vs HPV and CPV; LPC18:1 and LPE18:1 vs BD and CS; LPC18:3 and LPE18:3 vs ΔH_g (Table 3).