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# Gluten free rice cookies with resistant starch ingredients from modified waxy rice starches: Nutritional aspects and textural characteristics



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## ABSTRACT

Experimental gluten-free (GF) rice cookies were formulated with 100% rice flour (CTR) or by substituting 50% of rice flour with native waxy rice starch (WRS) or with three different resistant starch (RS) ingredients obtained from debranched, annealed or acid and heat-moisture treated WRS (RS<sub>a</sub>, RS<sub>b</sub> and RS<sub>c</sub>, respectively). Chemical composition, *in vitro* starch digestibility and physical and textural characteristics were carried out. Among cookies, RS<sub>a</sub>-cookies had the highest total dietary fibre content, the lowest rapidly digestible starch and the highest RS contents. All the three RS preparations have proved effective in increasing the proportion that tested as RS with respect to native WRS. However, the estimated RS loss for each applied RS ingredients caused by the baking process followed the order of RS<sub>a</sub> < RS<sub>c</sub> < RS<sub>b</sub>. Last, the lowest *in vitro* glycaemic index value was measured for RS<sub>a</sub>-cookies. Among cookies, differences in colour and hardness were reported. The partial replacement of commercial rice flour with RS<sub>a</sub> could contribute to formulate GF cookies with higher dietary fibre content and likely slowly digestible starch properties more than equivalent amounts of RS<sub>b</sub> and RS<sub>c</sub>.

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## 1. Introduction

Coeliac disease is considered one of the most common food induced enteropathy caused by the ingestion of gluten containing grains in genetically susceptible individuals and, till date, the only successful treatment for coeliac affected patients is a lifelong adherence to a gluten-free (GF) diet (Pellegrini and Agostoni, 2015). However, indications suggested that several GF-rendered foods exhibit lower nutritional quality than their gluten containing counterparts, relatively higher total digestible carbohydrates and saturated fats and lower dietary fibre, protein and resistant starch (RS) contents being often reported comparing GF products to their gluten containing equivalents (Pellegrini and Agostoni, 2015; Foschia et al., 2017). In particular, the RS fraction has attracted the interest of nutritionists and food processors because of its

potential physiological benefits. The RS fraction represents a particular form of starch able to reach the large intestine of human subject mainly undigested where can be fermented by gut microbiota favouring butyrate production (Raigond et al., 2015). There is ample justification through nutritional studies that RS consumption has the potential to promote hypoglycaemic effects, prevention of colorectal cancer, lower plasma cholesterol and triglyceride concentrations, inhibition of fat accumulation and an enhanced vitamin and mineral absorptions (Raigond et al., 2015). Accordingly, in order to bear aforementioned health claims, international dietary guidelines suggest that starch-baked foods should contain at least 14% of RS on total starch (EFSA, 2011).

Extensive research has been therefore conducted to investigate the preparation of a new generation of cereal-based GF foods formulated with high-RS sources as value-enriched ingredients (Foschia et al., 2017). One of the most common approaches is based on the partial replacement of digestible starch with RS ingredients derived from high amylose starch (HAS), either in the native form or after modification through hydrothermal, enzymatic and/or chemical treatments (Haralampu, 2000). Besides HAS, analogous processing schemes have been applied in different granular

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starches prior to food inclusion in an effort to enhance the proportion that tests as RS (Thompson, 2000). Accordingly, the interest in the preparation of value-added RS ingredients starting from waxy rice starch (WRS) is becoming more popular because of its wide-ranging food and industrial applications. Several studies revealed that higher amount of RS (from about +60% to about +90%) could be obtained from debranched WRS (Shi and Gao, 2011), from annealed WRS (Van Hung et al., 2016a) or from WRS subjected to a combination of acid and heat-moisture treatments when compared to native WRS (Van Hung et al., 2016b).

Even if promising results have been obtained, to the best of our knowledge no information is currently available concerning the utilization in baked GF products and the behaviour after cooking of high-RS ingredients obtained from WRS. A better understanding of their functionality issue would allow for the development of GF baked products with favourably improved nutritional value and starch digestion properties. Within this perspective, cookies, being one the largest categories of ready-to-eat foods worldwide consumed, could represent a potentially nutritious GF snack through the selection of ingredients (Sharma et al., 2016).

Therefore, the aim of this study was to evaluate if RS ingredients obtained from WRS could be advantageous to produce GF cookies with better nutritional qualities. Developed GF cookies were examined for nutritional composition, *in vitro* starch digestion properties and physical and textural characteristics that are considered important parameters in the formulation of related food products.

## 2. Materials & methods

### 2.1. Ingredients and resistant starch preparation

Commercial WRS (native waxy rice starch; 1.0–2.0% amylose) was obtained from Riso Scotti SpA (Pavia, Italy). All other components (food grade) were acquired in local supermarkets and stored depends on individual requirements. All the chemicals and reagents were all of analytical grade.

Three distinct RS preparations were conducted, by subjecting native WRS to hydrolysis by pullulanase debranching enzyme, annealing and a combination of acid and heat-moisture treatments, respectively. The debranched treatment was based on the protocol detailed by Shi and Gao (2011). A WRS slurry (10% w/w in diluted pH 4.5 buffer solution containing 0.2 M acetic acid and 0.2 M sodium acetate) was cooked at 95 °C for 30 min and then cooled to 58 °C. Then, 55 ASPU of heat-stable pullulanase (Diazyme® P10, 1000 ASPU/g, 1.15 g/ml; Danisco Company, USA) for each g of dry starch was added. The ASPU is defined as the amount of enzyme that liberates 1.0 mg of glucose from starch in 1 min at pH 4.4 and 60 °C. The slurry was re-incubated in a water bath at 58 °C for 12 h. After the reaction, the solution was heated at 100 °C for 30 min to stop the reaction and then cooled to room temperature for 24 h. The precipitated debranched starch residue was oven dried at 40 °C to a moisture content of about 9–10%. For the annealing treatment, native WRS was mixed with distilled water at a ratio of 1:2 (w/w) in a sealed container and heated in a water bath at 45 °C for 24 h (Van Hung et al., 2016a). After incubation, the starch sample was dried as previously described. For the third preparation, native WRS was dispersed in a measured volume of 0.2 M citric acid solution with moisture level adjusted to 30% in a sealed container (Van Hung et al., 2016b). After equilibration at room temperature for 24 h, the starch sample was heated at 110 °C for 8 h, neutralized with 1 M sodium hydroxide and then washed thoroughly with distilled water. The treated starch was recovered by centrifugation and then dried as previously reported. All resulting RS ingredients were finely ground (1-mm screen; Retsch ZM1; Brinkman Instruments,

Rexdale, ON, Canada) and stored at room temperature. Hereafter, RS<sub>a</sub>, RS<sub>b</sub> and RS<sub>c</sub> indicate the three different RS ingredients derived from debranched, annealed and acid-heat-moisture treated WRS, respectively.

### 2.2. Characterization of native and treated waxy rice starches

The thermal properties of native WRS and debranched, annealed and acid-heat-moisture treated WRS (RS<sub>a</sub>, RS<sub>b</sub> and RS<sub>c</sub>, respectively) were studied in duplicate by differential scanning calorimetry (DSC) (DSC8000, Perkin Elmer Inc., USA) as detailed by Shi and Gao (2011). Briefly, samples (suspension of 30% w/w solid:water) were heated from 30 °C to 150 °C at 10 °C/min. Parameters of interest were the onset ( $T_0$ ), peak ( $T_p$ ), the conclusion ( $T_c$ ) temperatures and the enthalpy of gelatinization ( $\Delta H$ ).

The pasting properties were determined using the Rapid Viscoanalyzer (RVA-4500, Perten, Sweden) according to the approved method AACC (76–21.01) (AACC, 2000). An aliquot of starch (3.0 g) was dispersed in distilled water (25 ml), scaling both sample and water weight on a 14% (w/w) sample moisture basis. The suspension was subjected to the following temperature profile: holding at 50 °C for 1 min; heating from 50 to 95 °C; holding at 95 °C for 7.5 min; cooling from 95 °C to 50 °C; holding at 50 °C for 2 min. A heating/cooling rate of 6 °C/min was applied. Measurements were performed in duplicate and the average curve was reported. The water absorption capacity (WAC, %) was determined in duplicate following the procedure as reported by Dundar and Gocmen (2013).

### 2.3. Experimental gluten free rice cookie formulation and preparation

Five different GF rice cookies were prepared. For GF control cookies (CTR-cookies), the recipe was based on commercial rice flour (120 g), whole egg (80 g), distilled water (30 g), unsalted butter (20 g), salt (1.0 g) and sodium bicarbonate (1.0 g). For experimental GF rice cookies, part of rice flour equivalent to 50% was replaced with the previously obtained RS ingredients to formulate RS<sub>a</sub>-, RS<sub>b</sub>- and RS<sub>c</sub>-cookies, respectively. In addition, WRS-cookies were prepared, by replacing 50% of rice flour with native WRS. For all formulations, no sugars were added to limit the amount of glycaemic carbohydrates. Briefly, butter was creamed, mixed with liquid ingredients and then added to dry ingredients. Materials were combined with a domestic blender (Kitchen Aid, Model K5SSWH, St. Joseph, Mich., U.S.A.) for 5 min to obtain homogeneous dough. The dough was laminated by a pasta roller attachment at 0.4 cm height, allowed to rest for 30 min at 4 °C, cut with a circular mould (4 cm diameter) and baked using a household oven (RKK 66130, Rex International, Italy) at a temperature of 180 ± 4 °C for 20 ± 2 min. Once baked, all GF cookies (i.e., CTR-, WRS-, RS<sub>a</sub>-, RS<sub>b</sub>- and RS<sub>c</sub>-cookies) were cooled and kept in separate airtight plastic bags at room temperature until analysis. For each recipe, three batch replicates were produced on the same day.

### 2.4. Chemical composition of gluten free rice cookies

Cookie samples were dried at 55 °C for 24 h in a forced-air oven and ground through a 1-mm screen using a laboratory mill (Retsch grinder model ZM1; Brinkman Instruments, Rexdale, ON, Canada). Analyses were performed according to AOAC (2000) for dry matter (DM; method 930.15), ash (method 942.05), crude protein (method 976.05) and crude lipid (method 954.02 without acid hydrolysis) contents. Enzymatic quantifications of total dietary fibre (Megazyme assay kit K-INTDF 02/15, which includes RS and non-digestible oligosaccharides as a component of total dietary fibre), total starch (Megazyme assay kit K-TSTA 07/11) and free sugars

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