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Total antioxidant capacity and starch digestibility of muffins baked with rice, wheat, oat, corn and barley flour

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ABSTRACT

Muffins are a popular snack consumed in western and emerging countries. Increased glycemic load has been implicated in the aetiology of diabetes. This study examined the starch digestibility of muffins baked with rice, wheat, corn, oat and barley flour. Rapidly digested starch (RDS) was greatest in rice (445 mg/g) and wheat (444 mg/g) muffins, followed by oat (416 mg/g), corn (402 mg/g) and barley (387 mg/g). Total phenolic content was found to be positively correlated with total antioxidative capacity and inversely related to the RDS of muffins. The phenolic content was highest in muffin baked with barley flour (1687 μg/g), followed by corn (1454 μg/g), oat (945 μg/g), wheat (705 μg/g), and rice (675 μg/g) flour. Browning was shown not to correlate with free radical scavenging capacity and digestibility of muffins. The presence of high phenolic content and low RDS makes barley muffin an ideal snack to modulate glycemic response.

1. Introduction

Cereal grains are an important source of carbohydrates providing not just energy but also glycemic load to the consumers. Glycemic index (GI) is a system of classifying carbohydrate-containing foods according to the extent to which they raise blood glucose levels after ingestion. Glycemic load (GL) is a concept mathematically derived by combining GI and the amount of carbohydrate intake intended to represent the overall glycemic effect of a diet (Salmerón et al., 1997). In many countries, 60–80% of total daily energy is gained from carbohydrate consumption, where starch is the predominant source of carbohydrates. Starch is composed of amylose, a linear polymer of α-1,4 glycosidic linkages, and amylopectin, a branched polymer of α-D-glucose units linked by α-1,4 and α-1,6 glycosidic linkages. However, a diet rich in carbohydrates and with a high GI is associated with increased risk of type 2 diabetes (Villegas et al., 2007). Cereal grains, ranging from the dominant wheat, rice and corn to the minor oats, barley, rye, triticale, sorghum, and millet contain different particle size of starch granule, amylose and amylopectin ratio, dietary fibre, protein, lipid and phenolic content (Singh, Dartois, & Kaur, 2010). These divergences can greatly influence the starch digestibility and thereby resulting in different GI of the cereal grains and cereal products.

Owing to the change in lifestyle, busy consumers are increasingly purchasing convenient baked goods, such as muffins. Muffins are a popular baked product that enjoys wide consumption in both western and emerging countries. During baking, the simultaneous heat and mass transfer process leads to water evaporation, volume changes, dough/crumb transition attributed to protein denaturation, starch gelatinisation, and formation of crust and non-enzymatic browning (Mondal & Datta, 2008). Browning developed from advanced Maillard reaction, occurs between free amino group of lysine and/or other amino acids and carbonyl groups of reducing sugars such as glucose and maltose, could play a part in the nutritional quality of baked goods (Camire, Camire, & Krumbar, 1990). Besides, cereal grains are good source of antioxidants including vitamin E, folates, minerals (iron, zinc) and trace elements (copper, selenium and manganese), carotenoids and phytic acid (Fardet, Rock, & Rémésy, 2008).

Epidemiologic studies have unveiled the preventive role of consuming low GI foods against development of diabetes (Salmerón et al., 1997). Evidence-based dietary guideline can therefore be the cornerstone for improving glycemic control as the prevalence of diabetes has reached pandemic level worldwide. This study aimed to investigate the total antioxidant capacity and starch digestibility of muffins baked with rice, wheat, corn, oat and barley flour. A pre-validated *in vitro* starch digestion model was employed. *In vitro* digestibility studies have been shown to be a valid proxy to *in vivo* starch digestibility (Monro et al., 2010). The

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results presented provide indicative glycemic potential of muffins assayed and serve as a predictor for the *in vivo* glycemic response. Preliminary work was also carried out to investigate the effects of Maillard reaction products (MRPs) and phenolics on total antioxidant capacity and carbohydrate digestibility of muffins.

2. Materials and methods

2.1. Chemicals, reagents and muffin ingredients

Pronase E, Folin–Ciocalteu reagent, sodium hydroxide pellets and concentrated hydrochloric acid (5 M) were purchased from Merck chemicals (Darmstadt, Germany). 2,4,6-Tris(2-pyridyl)-S-triazine (TRIS) was purchased from Mallinckrodt Baker (Phillipsburg, USA). HPLC grade ethyl acetate, potassium persulphate, gallic acid, 2-thiobarbituric acid, 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,2′-azinobis3-etheylbenzothiazoline-6-sulfonic acid (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH), α-amylase (30 U/mg), pepsin (800–2500 U/mg), bile extract (porcine), amyloglucosidase (⩾300 U/ml), invertase (⩾30 U/mg) and pancreatin (P7545, 8X USP specifications) were purchased from Sigma–Aldrich Company Ltd (St Louis, USA). Amyloglucosidase (E-AMGDF; 3260 U/ml) used for the secondary digestion in reducing sugar assay was obtained from Megazyme International (Wicklow, Ireland). Analytical reagent grade diethyl ether and absolute ethanol were purchased from Fisher Scientific (Loughborough, UK). HPLC grade *n*-Hexane 95% and methyl alcohol were purchased from Tedia Company (Fairfield, USA). Sodium carbonate anhydrous was purchased from GCE Chemicals. Milli-Q ultrapure water was used throughout the experiments (Billerica, USA). The maleate (0.2 M/pH 6) and acetate (0.1 M/pH 5.2) buffers were prepared according to previously described methods (Monro et al., 2009). Baking powder, salt, sugar, milk, vegetable oil, egg, sifted Bob's Red Mill whole grain barley flour, whole grain oat flour, whole grain yellow corn flour and white rice flour (Milwaukie, USA), as well as Prima refined wheat flour (Singapore) were used in muffins baking.

2.2. Preparation of muffins

Mixture of sifted flour (128 g), baking powder (5 g), salt (2 g), sugar (50 g), milk (100 ml), vegetable oil (30 g) and one egg was blended at the speed of 80 rpm for 1 min 20 s using an electronic mixer (5K45SS, KichenAid Europa, Inc., Belgium). Muffin batters (65 g) were weighed into muffin cups and baked for 13 min at 170 °C in the baking oven (MS01T04-2, Euroflours Baking Oven, France). Whole muffin sample was prepared by cutting one muffin into quadrants, then combined the opposite quadrants. The crust and crumb samples were prepared by skimming the entire exterior region (greater brown colour hue) and interior region (less brown colour development) of two muffins using a knife. Muffin, crust and crumb samples were stored at −20 °C overnight and then freeze-dried (VirTis, USA). The freeze-dried samples were ground using a blender (MX-J210GN, Panasonic, Singapore) and passed through a sieve of mesh 60 (250 μm) for subsequent analysis of browning index, total antioxidant and phenolic content in triplicate.

2.3. Measurement of browning index

The characteristic yellow and brown pigments evolved from Maillard reaction were extracted from crumbs, crusts and muffins. Adapted from the method described by Borrelli et al. (2003), freeze-dried samples (250 mg) were enzymatically digested by mixing with 3 ml of 20 Mm Tris–HCl (pH 8.0) containing 0.1 mg/ml of Pronase E (7.5 U/mg). The mixtures were incubated at 37 °C for 70 h with continuous shaking at 100 rpm. After digestion, the samples were centrifuged at 10,000 rpm for 15 min. Supernatants were diluted six times with distilled water and then subjected to measurement at 420 nm on UV–visible spectrophotometer (UVmini – 1240, Shimadzu, Singapore) using a 1 cm path length cell.

2.4. Determination of total phenolic content

The free and bound phenolic compounds were extracted from crumbs, crusts and muffins in combination with a hydrolytic step (Challacombe, Abdel-Aal, Seetharaman, & Duizer, 2012; Ragaee, Guzar, Dhull, & Seetharaman, 2011). Mixture of muffin sample (0.5 g) and 80% methanol (5 ml) was shaken for 30 min using a platform shaker (IKA-VIBRAX-VXR, Janke & Kunkel, Germany), followed by 10,000 rpm centrifugation at 20 °C for 5 min. The extraction was repeated twice. Pooled supernatants were evaporated to 10 ml under pressure using a rotary evaporator (Laborota 4000 Rotary Vacuum Evaporator, Heidolph, England) for free phenolics analysis. The residue was then washed with 15 ml hexane, shaken and centrifuged for 5 min. Supernatant was discarded. Bound phenolics were extracted from the residue by shaking with 2 M NaOH (5 ml) under N_2 for 1 h at room temperature. The suspension was adjusted to pH 2 (±0.1) (744 pH meter, Metrohm, Singapore) with concentrated hydrochloric acid. Acidified residue was shaken with 10 ml diethyl ether: ethyl acetate (1:1) for 1 min, then centrifuged for 10 min at 10,000 rpm. The extraction was performed thrice and pooled supernatants were evaporated to dryness at 33 °C under pressure. Resulting residue was made up to 5 ml using 80% methanol for bound phenolic analysis.

The phenolics content of extracts was estimated by Folin–Ciocalteu procedure (FCR) (Yousif, Nhepera, & Johnson, 2012). An aliquot of 50 μl extract was mixed with 650 μl ultrapure water, followed by adding 50 μl Folin–Ciocalteu reagent, mixed and left to stand for 5 min. Five hundred microlitres of 7.5% sodium carbonate was then added, mixed and left for 90 min at room temperature. The absorbance of the solution was read at 750 nm. Standard solutions of gallic acid in 80% methanol (0–150 μg/ml gallic acid) were used to prepare the standard curve. Total phenolic contents (sum of free and bound phenolic) of muffin samples were calculated as gallic acid equivalents (GAE) (μg/g).

2.5. Determination of total antioxidative capacity

The total antioxidative activity of crumbs, crusts and muffins was determined by the use of ABTS and DPPH free radical scavenging assays. ABTS free radical was produced by reacting 7 mM ABTS with 2.45 mM potassium persulphate (final concentration) for 12–16 h at room temperature in the dark. The working solution was prepared daily by diluting ABTS stock solution with 50% ethanol to give an absorbance of 1.22 ± 0.03 at 734 nm (Re et al., 1999). The DPPH working solution was prepared daily at a concentration of 0.05 g/L in water/ethanol mixture (1:1, v/v) to give an absorbance of 0.735 ± 0.02 at 525 nm (Brand-Williams, Cuvelier, & Berset, 1995). Modified from the method of Serpen, Gökmen, and Mogol (2012), the reaction was started by adding 10 ml of ABTS or DPPH working solution to 10 mg freeze-dried muffin sample. The mixture was vortexed for 1 min then shaken at 400 rpm on a platform shaker in the dark at room temperature. After reacting for 60 min, the mixture was centrifuged at 9200*g* for 5 min. The supernatant was filtered through a 0.45 μm microfilter. Absorbance of the filtrate was measured at 525 nm and 734 nm to determine the DPPH and ABTS free radicals scavenging capacity, respectively. Standard calibration curves were constructed by plotting percentage inhibition against the concentration of Trolox (40–