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Identification of bitter compounds in extruded corn puffed products

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ABSTRACT

Differences in the taste profile of corn puffed products formulated with refined versus whole grain mix flour were characterized. The perceived bitter intensity was reported to be the main taste difference between the samples. Based on multidimensional sensory-guided fractionation techniques and subsequent identification by MS and NMR analysis, the primary bitter compounds identified in the whole grain sample were L-tryptophan, chaenorpine, N^1,N^5-Di-[*E*]-*p*-coumaroyl-spermidine, and terrestribisamide. All compounds were reported to contribute to bitterness perception at the concentrations reported in the saliva after mastication of the extruded products; chaenorphine had the highest contribution to the perceived bitterness. All bitter compounds were endogenous products of the corn.

1. Introduction

Whole grain cereals play an important role in our diet, providing convenient food choices and health benefits (Albertson, Franko, Thompson, Tuttle, & Holschuh, 2013). Of the main cultivated cereal crops grown worldwide, corn is the only one indigenous to the New World and one of the principal grains used for cereal based foods (Shukla & Cheryan, 2001). The intake of whole grain corn has been found to lower the risk of chronic diseases, such as cardiovascular disease, type II diabetes, and obesity (Liu, 2007). The Dietary Guidelines for Americans recommend that half of all cereal products consumed should contain whole grains. However, less than 20% of Americans consume the recommended intake (48 g/day) and up to 20% consume no whole grain products (U.S. Department of Health and Human Services and U.S. Department of Agriculture, 2015).

Food choices are mainly driven by acceptability, cost and convenience (Carrillo, Varela, Salvador, & Fiszman, 2011; Glanz, Basil, Maibach, Goldberg, & Snyder, 1998). Negative taste attributes associated with whole grains have been reported as one of the most influential factors limiting consumption (McMackin, Dean, Woodside, & McKinley, 2013). Higher perceived bitterness in whole grain products has been suggested to contribute to lower consumer acceptability, especially for children who are less tolerant to bitterness (Burgess-Champoux, Marquart, Vickers, & Reicks, 2006). Traditionally, food producers have incorporated flour mixing (51% whole grain and 49% refined flour) and bitterness masking ingredients (sugar and salt) to their formulation in order to improve the flavor profile. To accommodate the taste preferences of children or even adults, common industrial practice often involves coating the whole grain cereals with sugar or salt to mask negative flavor attributes, such as excessive bitterness (Fan & General Mills Inc., 1991; Van Hulle, Anker, Franssell, & General Mills Inc., 1983). Consequently, an important step to improve the palatability of whole grain cereals is to identify the origin of bitterness. A number of flavor studies on whole grain foods have focused on the aroma compounds generated during extrusion (Grosch and Schieberle, 1997; Nair, Shi, Karwe Mukund, Ho, & Daun, 1993; Zhou, Robards, Glennie-Holmes, & Helliwell, 1999) but less is known about the taste attributes (Zhang, 2016).

The main goal of this study was to characterize the changes in the taste profile of puffed corn cereal made with whole-grain and refined corn flour formulations, and quantitatively monitor the taste compounds from the flour to the finished products.

2. Materials and methods

2.1. Materials and chemicals

Trisodium phosphate, calcium carbonate, sodium chloride, d4-methanol, methylparaben, HPLC grade methanol were purchased from Millipore Sigma (St. Louis, MO). Innovasure refined corn flour and Maizewise 101 whole grain corn flour samples were received from Cargill, Inc. (Wayzata, MN).

2.2. Twin-screw corn extrusion

Extrusion conditions were designed to yield uniform cell structure

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throughout each puff. Briefly, extrusion processing was carried out using a Buhler DNDL-44 twin-screw extruder. Two formulations were designed: the refined corn flour formulation and the whole grain corn flour formulation. The refined grain flour (RGF) formulation consisted of 1000 g (97%) refined corn flour (Innovasure, Cargill, MN) with 10 g (1%) trisodium phosphate, 10 g (1%) calcium carbonate and 10 g (1%) sodium chloride. The whole grain flour mixture (WGFM) formulation consisted of 480 g (47%) refined corn flour (Innovasure, Cargill, MN) and 520 g (50%) whole grain corn flour (Maizewise 101, Cargill, MN), with 10 g (1%) trisodium phosphate, 10 g (1%) calcium carbonate and 10 g (1%) sodium chloride. The ingredients and the flour were added to a ribbon mixer and mixed for 10 min. The flour mixture was introduced to the extruder and processed using the following extrusion parameters: computer controlled shaft speed of 350 rpm, measured die pressure of 10.1 ± 0.5 bar, die temperature of 160 ± 1 °C, dry material throughput of 50.8 ± 0.1 kg/h, water addition of 7 kg/h water, and a cutter speed of 1200 rpm, resulting in 1/4 in. puffs. Due to differences in the physical and chemical characteristics of the refined and the whole grain flour mixes, the refined corn flour formulation showed an increased shaft torque of 224 NM over the whole grain corn flour formulation which had a shaft torque of 215 NM; the specific mechanical energy for the refined corn flour formulation was 164 kw/h while for the whole grain corn flour was 159 kw/h. All other parameters were consistent across both formulations. The resulting puffed products were dried on a liquid air bed, packaged in high-density polyethylene bags and stored at −40 °C prior to analysis.

2.3. Solvent extraction of corn puffed products

Corn puffs (300 g) were ground in a blender for 2 min, and then extracted using a 75% ethanol-25% water solution (500 ml). Extraction was performed at room temperature for 3 h and was repeated three times. The extracts were pooled and centrifuged at 4000*g* for 15 min at 4 °C. The resulting precipitate (Fig. 1, FI) was collected and the solvent-removed for sensory evaluation. The supernatants were combined, and the ethanol was removed using rotary evaporation and the aqueous mixture was then frozen and freeze-dried twice to yield fraction II (Fig. 1, FII).

2.4. Ultrafiltration

Fraction II was dissolved in 20% ethanol aqueous solution and subsequently underwent ultrafiltration using Millipore Amicon 8200 ultrafiltration cells (Bedford, MA) with cutoff membrane at 3 kDa, under a nitrogen pressure of 200 kPa. Upon completion, the membrane was rinsed by passing through deionized water. The resulting permeate and retentate underwent rotary evaporation separately for the removal of ethanol and were then frozen and freeze-dried. The bitter intensity of each fraction was determined by sensory evaluation and the most bitter fraction FII-UF1 was then selected for additional purification by LC fractionation.

2.5. First dimensional liquid chromatography fractionation

The dried bitter fraction FII-UF1 was dissolved in 95% water-5% ethanol solution (40 ml). Aliquots were filtered through a 4.5 µm hydrophilic syringe filter and then separated by HPLC using a preparative RP C-18 column (21.2 × 250 mm, pursuit 5, Varian, USA). Chromatography was performed with flow rate of 10 ml/min and a gradient starting with a 95% of aqueous formic acid (0.1%, pH 3) and ethanol with formic acid (0.1%, pH 3). Initial conditions were held for 5 min, then linearly increased the ethanol content to 50% within 20 min, and then to 100% within 1 min, finally maintained the ethanol content for another 10 min. The eluent was collected in 18 fractions from 3.5 to 21.5 min in 1 min intervals (Fig. 2). Each fraction was evaporated and freeze-dried twice to remove the solvent. Subsequently each fraction was rehydrated in 2 ml of water (dosage level was 30 g puffed cereal) and a trained sensory panel evaluated the bitterness intensity of each fraction.

2.6. Second dimensional liquid chromatography fractionation

The HPLC fractions from the first dimension (Fig. 2) with the high bitterness intensity (FII-UF1-10, 11, 13 and 16) were subsequently further fractionated using a Zorbax Bonus-RP column (21.2 × 100 mm, 5 µm), and a mobile phase consisting of methanol and water at a flow rate of 10 ml/min (shown in Fig. 3). Chromatography was performed using a gradient starting with 95% water and 5% methanol. Initial conditions were held for 3 min, then linearly increased the methanol

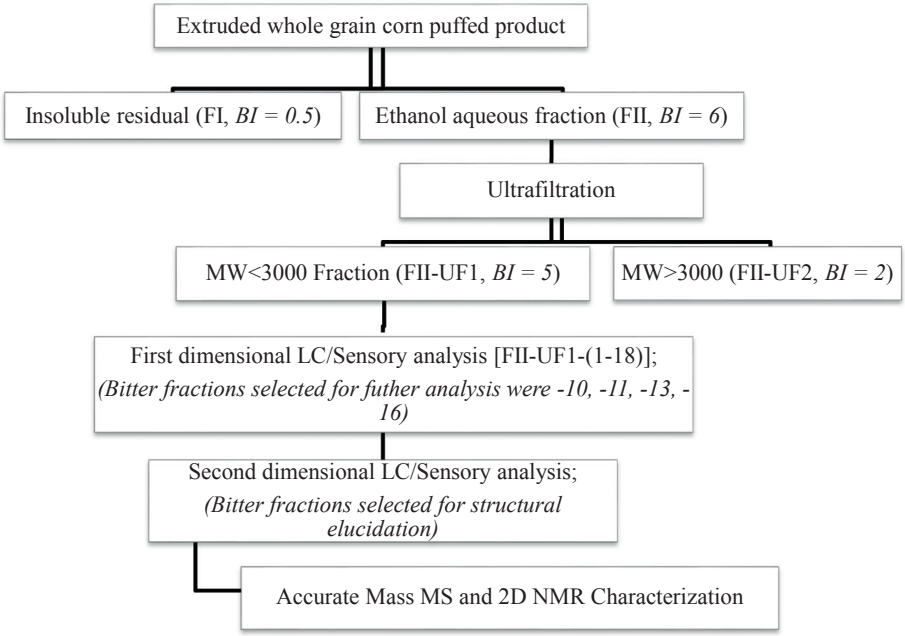

Fig. 1. Sensory-guided fractionation methodology (BI = bitterness intensity rating of fraction; bitter scale 0–10).