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# Chlorogenic acid induced colored reactions and their effect on carbonyls, phenolic content, and antioxidant capacity in sunflower butter cookies

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ABSTRACT

The high chlorogenic acid (CGA) content of sunflower seeds causes a greening reaction in sunflower butter baked products which can deter application of sunflower butter as an allergen-free alternative to other plant and dairy based butters. This study focused on how greening intensity of sunflower butter cookies made with different sweeteners (maple, agave, corn syrups, honey and xylitol) affected greening, protein oxidation products, Folin and $ABTS^{\bullet+}$ radical scavenging ability. Cookies made with maple syrup and xylitol had higher pH and resulted in more greening. The dough made with agave syrup had highest total carbonyls caused by its highest reducing sugar content resulting in more Maillard reaction during dough preparation, while after baking cookies with highest greening (maple syrup) and highest reducing sugar (agave syrup) had higher carbonyls than other sweetener treatments. Cookies made with maple syrup and xylitol also had lower folin-ciocalteau reagent reducing capacity and tryptophan fluorescence. The greening reaction did not affect Schiff bases from oxidation and antioxidant capacity in cookies made with different sweeteners. Higher pH sweeteners thus enhanced greening intensity, tryptophan loss and lowered the total phenolic content after baking and storage, but did not influence the $ABTS^{\bullet+}$ capacity of sunflower butter cookies.



## 1. Introduction

Sunflower butter offers an alternative nut butter for people allergic to legume and tree nut butters. Compared to peanut and almond butter, sunflower seed butter offers additional nutritional benefits. It is an excellent source (≥20% of Daily Value) of minerals, such as phosphorus, magnesium, copper and selenium (FDA, 2013; Thomas & Gebhardt, 2010), which are essential for building up bones and muscles, and are essential in formation of metabolic enzymes (NIH, 2017). Sunflower seed's lipids are 90 g unsaturated fatty acids/100 g total fatty acids with kernels containing 270–289 mg phyto-sterols/100 g (Phillips, Ruggio, & Ashraf-Khorassani, 2005; USDA, 2016).

In addition, sunflower butter is rich in phenolic compounds that have antioxidant health benefits (Olthof, Hollman, & Katan, 2001). In particular, sunflower seeds have approximately 3.0 g/100 g chlorogenic acid (CGA) of the 4.2 g/100 g total phenolic content (dry matter) in kernels (Weisz, Kammerer, & Carle, 2009). This high total phenolic content in sunflower seeds is almost 84 times higher than that in peanut butter, which has about 0.05 g/100 g (Ma et al., 2013). Chlorogenic acid prevents lipid oxidation reactions (Budryn, Nebesny, Zyzelewicz, & Oracz, 2014) by reducing free radical formation (Liang & Kitts, 2016), inhibiting low-density lipoprotein (LDL) oxidation and DNA damage in vitro (Budryn et al., 2017; Olthof et al., 2001). However, the high free CGA content induces a greening reaction in sunflower seed products which can hinder the application of sunflower butter in the bakery industry (Wildermuth, Young, & Were, 2016). The greening reaction also consumes free CGA, protein and primary amino acids, and thus may affect the nutritional properties of sunflower butter bakery products.

Different sweeteners have different sugar composition, pH and moisture (St-Pierre et al., 2014), which can influence the extent of Maillard and greening reactions (Devi & Khatkar, 2016; Yabuta, Koizumi, Namiki, Hida, & Namiki, 2001). Lower moisture, higher pH and reducing sugar cause more browning products (Pereyra Gonzales, Naranjo, Leiva, & Malec, 2010). Besides color, the Maillard reaction can produce unhealthy products, for instance

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acrylamide, α-dicarbonyls, and advanced glycation end products (AGEs) or healthy compounds such as antioxidant reductones (de Oliveira, dos Reis Coimbra, de Oliveira, Giraldo Zuniga, & Garcia Rojas, 2016). The effect of the greening reaction on formation of compounds with nutritional effects warrants investigation. The higher moisture ingredients and higher pH in baked products using baking soda promote formation of green and blue pigments when free CGA and primary amino acids and/or proteins interact (Yabuta et al., 2001). This study focused on whether the greening reaction as a function of different sweeteners affected appearance in sunflower butter cookies in addition to antioxidant capacity, total phenolic content, and protein oxidation products (total carbonyl, tryptophan fluorescence and Schiff bases) before and after baking. Correlation between greening and changes in total phenols, antioxidant capacity and loss of tryptophan in cookies made with sunflower butter were determined.

## 2. Materials and methods

### 2.1. Materials

Sucrose (≥99.5%), fructose (≥99.0%), glucose (≥99.5%), sodium carbonate (≥99.0%), (+)-6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (≥98.0%), monosodium phosphate (≥99.0%), 2,4-dinitrophenylhydrazine (97.0%), and disodium phosphate (≥98.0%) were purchased from Sigma-Aldrich (St. Louis, MO. USA). HPLC-grade water and ethanol were obtained from Thermo Fisher Scientific (Huntington Beach, CA. USA). Folin-Ciocalteu reagent was obtained from MP Biochemicals (Santa Ana, CA. USA).

### 2.2. Cookie formulation and experimental design

Sunflower butter cookie dough treatments containing one of four sweeteners (maple syrup/UPC 096619955886, xylitol granules/UPC 875002000033 diluted xylitol: water = 8:2 (w:w), light corn syrup/UPC: 761720051108, organic blue agave syrup/UPC 012511204419 and honey/UPC 073299000075) were prepared using the formulation presented in Fig. 1. The doughs were formed into disks of 4.5 cm diameter and 0.5 ± 0.2 cm thickness and baked at 149 °C (300 °F) using a convection oven (JA12SL, Doyon, Inc. Saint-Côme-Linière, Canada) for 7 min. The baking temperature was monitored using a thermocouple thermometer (Nicety® K-type DT 1312). After baking, the cookies were stored uncovered at room temperature (20 ± 5 °C) for 24 h.

### 2.3. Sugar composition

Dough and cookie samples (0.9 ± 0.01 g) with 30 mL HPLC water were homogenized (Multi-prep Homogenizer, PRO Scientific Inc., Oxford, CT. USA) at 1.3 × $10^3$*g for 1 min. After centrifugation for 15 min at 0.3 × $10^3$*g and filtration using 0.45 μm nylon membrane filters, the filtrates were stored at 4 °C for later use. Sucrose, glucose and fructose standards (0.3–2.8 mg/mL) were used to create a standard curve. The sugar content was quantified using a Shodex® Sugar SP0810 column (300 mm × 8 mm i.d., 8.0 mm, Shodex, Colorado Springs, CO. USA) with a Shodex® Sugar SP-G 6B (50 mm × 6 mm i.d 6.0 mm) guard column. An Agilent HPLC 1100 series with a refractive index detector was used. The flow rate was 0.6 mL/min with an isocratic elution with HPLC water at a run time of 25 min (Wang, Yagiz, Buran, Nunes, & Gu, 2011).

### 2.4. pH and Hunter L*a*b*

pH of sample mixtures prepared by dissolving 0.5 g of dough and cookies in 5 mL nano filtered water was measured according to AACCI method 02–52.01 (1999). After 1 min homogenization (Multi-prep Homogenizer, PRO Scientific Inc., Oxford, CT. USA) at speed of 1.3 × $10^3$*g, mixtures were incubated for 1 h, centrifuged (AccuSpin 1R-75003449, Thermo Fisher Scientific, Inc. CA. USA) at 9 × $10^3$*g at 4 °C for 30 min, before pH testing using a pH meter (Vernier Software & Technology, OR. USA).

Internal greening intensity of cookies (lateral cut) was measured using a Hunter L*a*b* spectrophotometer (CM-2500d, Konica Minolta, Inc. Japan) where negative and positive a* value represents greeness and redness respectively (Zhang, Chen, & Wang, 2014).

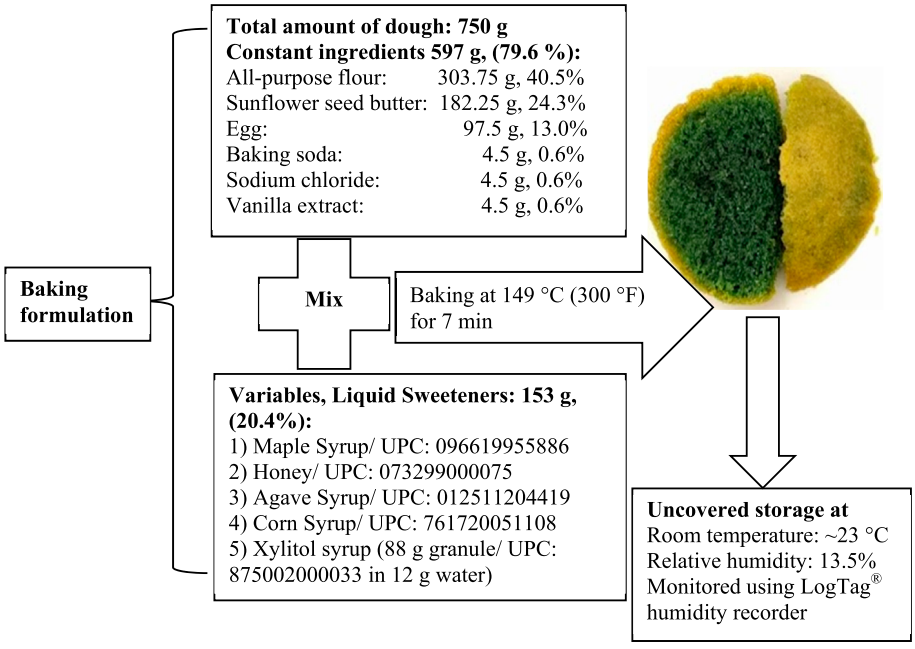


**Fig. 1.** Sunflower butter cookie formulation.