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Effects of the sugar reformulation in cookies on healthy characteristics and aroma compounds

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Biscuits are among the highest consumed baking products in the developed countries and they are perceived by consumers as an essential part of human diet; unfortunately, they are usually high in sugar.

The aim of this work was to study the influence of different sugars under different baking conditions on healthy characteristics of cookies, in relation to Maillard reaction products and furanoic aroma compounds.

Model biscuits were prepared using different sugars, such as sucrose, fructose, and glucose. The biscuits were baked at three different temperatures, 150 °C, 170 °C and 190 °C, for 25, 20 and 15 min, respectively. Determination of the moisture content, pH, total titratable acidity, 1,2-dicarbonyl compounds, Maillard reactive compounds and volatile furanoic compound have been determined.

The results of this work have shown that the replacement of sucrose with other sugars in the processing of cookies, affects pH, titratable acidity, and the ability to retain water. Moreover, it influenced the production of HMF, dicarbonyl and furanoic compounds.

1. Introduction

Biscuits are one of the key foods consumed for breakfast in Western countries and its consumption is expected to increase in the coming years. Despite their high intake, these products contain a considerable amount of sugars, reason why they are often considered an unhealthy product especially for that people suffering from diseases such as obesity and diabetes. Moreover, in foods containing high quantity of reducing sugars subjected to the cooking process, a series of potentially toxic substances for consumer’s health can be generated. In this concern, many studies on baked goods have been undertaken with particularly attention to dicarbonyl compounds (DCs) advanced glycation end products (AGEs) and Maillard reaction products (Ahmed and Thornalley, 2007).

(DCs) as 3-deoxyglucosone (3DG), methylglyoxal (MGO), glyoxal (GO), 5-hydroxymethylfurfural (HMF) and furanoic volatile compounds are formed in food during processing, cooking and prolonged storage (Arena et al., 2011; Degen et al., 2012; Fallico et al., 2004; Hellwig et al., 2018; Condurso et al., 2018). These compounds are important promotors of caramelization, Maillard reaction and lipid oxidation. Their presence in processed foods is desirable as they are precursor of color and flavor compounds and undesirable due to safety concerns. A cancer-promoting effects have been attributed to DCs (Hellwig et al., 2018; Brighina et al., 2021) reported that DCs pass almost unaltered through the *in-vitro* gastrointestinal digestion phases and strongly depressed the microbial community. Moreover, DCs are also reactive precursors in the formation of the advanced glycation end products (AGEs) (Poulsen at al.,2013) and the accumulation of both DCs and AGEs in the body was related to various chronic-degenerative diseases (diabetes, cataract, cardiovascular disease, Alzheimer disease) (Šebeková and Somoza, 2007). Furanoic compounds has been found to exhibit carcinogenic and cytotoxic activity on animals and harmful effects on human health (Byrns et al., 2006) included in the Group 2B (possibly carcinogenic to humans).

High levels of DCs and HMF were reported in cookies (Degen et al., 2012; Maasen et al., 2021) and several approaches have been proposed with the aim to reduce their amount in baked goods. The role played by sugars and leavening agent on HMF production, the effect of different biscuits formulation and baking conditions on both DCs and HMF was investigated by different Authors (Ameur et al., 2007; Kocadağlı et al., 2016; Kocadağlı and Gökmen 2016; Navarro and Morales, 2017; Arribas-Lorenzo et al.2010; Gökmen et al., 2008).

The aim of this work was to study the influence of different sugars under different baking conditions on healthy characteristics of cookies, in relation to Maillard reaction products, (3DG, GO, MGO and HMF), and furanoic aroma compounds. For this purpose, model biscuits were prepared using different sugars, such as sucrose, fructose, and glucose and were baked at three different temperatures, 150 °C, 170 °C and 190 °C.

2. Data and Method

2.1. Preparation of cookies

Model biscuits were prepared by mixing 80 g of wheat flour, 34 g of sugar (sucrose, fructose, or glucose), 32 g of butter, 1 g of salt, 0.8 g of sodium bicarbonate, 0.4 g of ammonium bicarbonate and 18 mL of deionised water. After, the dough was rolled out three times (thickness, 0.2 cm) and was cut into discs with a diameter of 5 cm. The biscuits were baked in a laboratory oven (Thermo Scientific, Herathermoven, Italy) at three different temperatures: 150 °C up to 25 minutes, 170 °C up to 20 min and 190 °C up to 15 minutes, respectively. After cooling cookie samples were ground in a home grinder (La Moulinette, Moulinex, 2002) and immediately analysed.

2.2. Determination of the moisture content, pH and the total titratable acidity

The moisture content, the pH, and the total titratable acidity (TTA) were determined according to Spina et al., 2015. The TTA results were expressed, for the dry matter as milliliters of 0.1 M NaOH consumed (Spina et al., 2015).

2.3. HMF and dicarbonyl compounds extraction

An aliquot of the ground sample (1 g) was transferred into a volumetric flask (10 mL) and added with 5 mL of deionised water. The solution was stirred for 10 min, then the sample was diluted up to 10 mL with deionised water and centrifuged at 10 °C for 15 min at 8500 rpm (ALC 4128, Italy) (Spina et al., 2015; Spina et al., 2019). An aliquot of the supernatant was filtered through a 0.45 µm filter (Albet) and injected into an HPLC system to determine HMF content, while dicarbonyl compounds were derivatised prior to HPLC analysis.

2.4 HMF analysis

The analysis was performed using an HPLC system (Shimadzu Class VP LC-10ADvp) equipped with a DAD (Shimadzu SPD-M10Avp). A Gemini NX C18 (150 mm × 4.6 mm, 5 µm, Phenomenex) column fitted with a guard cartridge packed with the same stationary phase was used. The HPLC conditions were as follows: 0.1 % (v/v) acetic acid in water (94 %) and methanol (6 %); flow rate, 0.7 mL/min; injection volume, 20 µL. The wavelength range was 220–660 nm and the chromatograms were monitored at 283 nm. All the solvents used were HPLC purity grade: water from J.T. Baker, and acetic acid and methanol from Merck. Quantification was carried out using external standard calibration of HMF (≥98 %, Sigma-Aldrich).

2.5 Determination of dicarbonyl compounds

An aliquot of the filtered supernatant was derivatised with a 0.6 % o-phenylenediamine (OPD) (Sigma-Aldrich) solution in water (Weigel et al., 2004). After 12 h the derivatised mixture was injected into an HPLC (Spectra System) equipped with a diode array detector (UV6000LP) and an autosampler (AS3000) (Thermo Electron, San Jose, Calif., USA). The HPLC column used was a Luna C18 (250 mm × 4.6 mm, 5 µm, Phenomenex) and the HPLC conditions were as follows: eluent A was 0.1 % (v/v) acetic acid in water and eluent B was methanol; the flow rate was 0.7 mL/min; the injection volume was 20 µL. The gradient program was: t0 85 % A and 15 % B; t10 65 % A and 35 % B; t15 35 % A and 65 % B; t25 100 % B; t30 85 % A and 15 % B. The detector wavelength was set to 312 nm. All compounds were identified by comparing retention times and UV spectra to those of standard solutions and by spiking each sample with standards (GO, 40 % in water, Sigma-Aldrich;

MGO, 40 % in water, Sigma Aldrich; 3-DG, P>95 %, Santa Cruz Biotechnology). All the solvents used were HPLC purity grade: water from J.T. Baker, and acetic acid and methanol from Merck.

2.6 Determination of furanoic volatile compounds

Furanoic volatile compounds were analyzed by headspace-solid-phase microextraction (HS-SPME). A SPME fiber coated with Divinilbenzene/Polydimethylsiloxane (DVB/PDMS) was used to sampling the headspace of cookies; for each analyzed sample, 1,5 g of homogenized cookie sample, with 2 mL of saturated aqueous NaCl solution was inserted into a 7 mL glass vial and allowed to equilibrate for 15 minutes at 35 °C. After the equilibration time, the fiber was exposed to the headspace for 15 minutes. Afterward, the fiber was withdrawn into the needle and transferred to the injection port of the GC at 260 °C for 3 minutes for thermal desorption of the analytes onto the capillary GC column.

The GC–MS analyses were performed with A Shimadzu GC 2010 Plus gas chromatograph directly interfaced with a TQMS 8040 triple quadrupole mass spectrometer (Shimadzu, Milan, Italy) equipped with a CP-Wax- 52-CB capillary column (60 m. 0.25 mm i.d.; coating thickness 0.25 µm). The analysis conditions were as follows: injector temperature, 260°C; injection mode, splitless; oven temperature, 50 °C held for 5 minutes, then increased to 190 °C at a rate of 3 °C/minute, and to 240 °C at 6 °C/minute; carrier gas, helium used at a constant pressure of 10 psi; transfer line temperature, 250 °C; acquisition range 40–400 m/z; scan rate, 1 µscan/second. Each compound was identified using mass spectral data, NIST’14 library (NIST/EPA/NIH Mass Spectra Library, version 2.0g USA), linear retention indices (LRIs), literature data and the injection of standards where available. LRIs were determined based on a homologous n-alkane hydrocarbon mixture, analyzed under the same GC conditions; LRIs were calculated according to Van den Dool and Kratz Equation (Cincotta et al. 2020).

3. Results

3.1 moisture content, pH, and the total titratable acidity

Table 1 reports the trend of moisture, pH and TTA determined in cookie samples obtained with different sugars and cooked at different temperatures and time. Samples prepared with sucrose lost water faster than the other samples. This trend was particularly noticeable at 150 and 170°C. Differences were also observed for both pH and titratable acidity values (Table 1). Cookies prepared with sucrose had the highest pH (min 7.08, max 7.28) and the lowest TTA values (min 1.5, max 1.8), independently from baking parameters (temperature and time). Samples with fructose or glucose showed a similar trend, with a pH value ranging from 6.28 to 6.52 and 6.31 to 6.89, for biscuits with fructose and glucose, respectively.

The highest TTA values were found in cookie samples with fructose (min 3.7 max 4.8) mainly due to the degradation reactions of 1,2 and 2,3 enediol species (sugar degradation pathway) rather than via Maillard reaction (Brands et al., 2001).

Table 1: Chemical parameter of the cookie samples at different baking time and temperature.

		150 °C / 25 min			170°C / 20 min			190°C / 15 min		
		S	F	G	S	F	G	S	F	G
Moisture (g/100 g)	min	1.7	5.6	4.6	1.9	5.9	4.7	3.5	6	4.9
	max	2.3	6.6	5.8	2.7	6.5	5.1	4.9	6.6	6.1
pH	min	7.08	6.48	6.31	7.12	6.28	6.34	7.16	6.3	6.51
	max	7.12	6.52	6.89	7.28	6.52	6.66	7.24	6.4	6.69
TTAa (ml NaOH N/10)	min	1.6	4.0	3.5	1.6	4.0	3.6	1.5	3.7	3.6
	max	1.8	4.0	3.9	1.8	4.8	3.8	1.7	4.3	3.8

3.2 HMF and dicarbonyl compounds

Table 2 summarises the level of HMF and the dicarbonyls 3-DG, GO and MGO in cookie samples as function of sugar type, temperature, and baking time. Although values are highly variable, generally the use of sucrose limits both the HMF and dicarbonyl compounds formation due to a lower reactivity of sucrose to Maillard reaction than monosaccharides. The lowest HMF levels were found in biscuits with sucrose with a range from 3.7 to 12.6 mg/kg. The highest HMF levels were determined in cookies with fructose cooked at 170°C for 20 min with a range from 69.6 to 80.2 mg/kg, while in biscuits with glucose the HMF levels ranged from 12.3 to 26.7 mg/kg.

Substitution of sucrose with fructose or glucose in cookies recipe, drastically affected the production of the dicarbonyl compounds 3-DG, GO and MGO, particularly 3-DG (Table 2). At 150°C, samples with sucrose developed from 5 to 8.4 mg/kg of 3-DG, a while samples with fructose or glucose contains from 973.8 to 1350.8 mg/kg and from 3772.7 to 4110.7 mg/kg, respectively. In the glucose samples, 3-DG reached the highest level also at 170 and 190°C.

MGO levels seems to be more influenced respect to GO by the sugars used in the recipe. MGO levels in samples with fructose were approximately twice as high as glucose containing samples and four times as high as cookies with sucrose.

Table 2: Dicarbonyl compounds concentration (mg/kg dry matter) in the investigated cookies cooked at different baking time and temperature.

		150°C / 25 min			170°C / 20 min			190°C / 15 min		
		S	F	G	S	F	G	S	F	G
HMF	min	4.2	8.8	12.3	3.7	69.6	13.0	4.2	15.6	20.3
	max	6.0	12.0	12.9	6.7	80.2	16.8	12.6	29.8	26.7
3-DG	min	5	905.8	3772.7	4.8	973.8	3311.9	4	841.5	3195.6
	max	8.4	1171.8	4110.7	7.4	1350.8	3723.9	6.6	1080.3	3305
GO	min	10.3	12.7	18.4	9.7	13.7	11.4	10.3	12.6	11.5
	max	11.1	16.3	44.9	10.9	18.3	19.4	11.1	15.6	19.7
MGO	min	8.1	32.6	16	7.9	37.7	16	8.1	35.4	17.9
	max	8.7	34.4	19.8	8.7	41.9	18.6	8.7	39.6	19.5

2.5 Furanoic volatile compounds

Table 3 reports the furanoic volatile compounds identified in the cookie samples. Different behaviour was observed in relation to the backing time and temperature.

Furfural and furfuryl alcohol were the two volatile compounds present at high concentration and their amount increased as the cooking temperature increased. Furfural content was higher in glucose biscuits compared with fructose and sucrose samples mainly when cooked at 170 °C and 190 °C, whereas the content of furfuryl alcohol resulted higher in sucrose and fructose biscuits. Differently, 2-Pentyl-furan content was higher in biscuits samples cooked at lower temperatures for longer time, whereas decreased as the temperature increased. Moreover, cookies prepared with glucose and fructose showed the highest content. In fact, 2-akylfurans mainly resulted from lipid degradation and not from Maillard reaction, being oxidation products of polyunsaturated fatty acids such as linoleic acid (Min et al., 2003).

Acetyl furan, 5-Methylfurfural and dihydro-2-methyl-3-furanone showed the lowest content in sucrose samples if cooked at 150 °C for 25 min increasing at the same rate for all type of sugars at higher cooking temperatures.

Table 3: Furanoic compounds average amount (peak area) in the cookie samples at different baking time and temperature.

		150 °C / 25 min			170 °C / 20 min			190 °C / 15 min		
	LRI	S	F	G	S	F	G	S	F	G
2-Pentyl-furan	1221	113	127	191	115	134	125	45	74	56
Dihydro-2-methyl-3-furanone	1264	14	38	38	18	58	53	19	61	71
Furfural	1468	318	580	557	334	1274	1229	1173	1298	1455
Acetyl furan	1509	1	10	15	50	67	40	83	92	63
5-Methylfurfural	1584	20	19	13	67	73	75	94	62	111
Furfuryl alcohol	1666	33	141	59	595	290	102	229	588	166

4. Conclusions

The results of this work have shown that the replacement of sucrose with other sugars in the processing of cookies, affects their ability to retain water, their titrable acidity and/or the pH of the products. Kinetic analysis could allow us to obtain the parameters needed for developing models that predict the formation of HMF, DC and furanoic volatile compounds. Control of cooking time is also important for some of them. The exclusive use of sucrose is required if one wants to control most of the volatile furanoic compound and maintain 3-DG levels to a few mg/kg. In the analysed systems and processing conditions, fructose appeared to contribute less than glucose to the development of 3-DG.

These data could be useful for kinetics studies and to implement a reduction and/or control strategy for limiting the formation of these chemicals during cookie production.

References

Ahmed, N., Thornalley, P. J., 2007, Advanced glycation endproducts: what is their relevance to diabetes complications? Diabetes, Obesity and Metabolism, 9, 233-245.

Ameur, L. A., Mathieu, O., Lalanne, V., Trystram, G., Birlouez-Aragon, I. 2007, Comparison of the effects of sucrose and hexose on furfural formation and browning in cookies baked at different temperatures. Food Chemistry, 101, 1407-1416.

Arena, E., Ballistreri, G., Tomaselli, F., Fallico, B. 2011, Survey of 1,2-dicarbonyl compounds in commercial honey of different floral origin. Journal of Food Science, 76, C1203-C1210.

Arribas-Lorenzo, G., Morales, F.J. 2010, Analysis, distribution, and dietary exposure of glyoxal and methylglyoxal in cookies and their relationship with other heat-induced contaminants. Journal of Agricultural and Food Chemistry, 58, 2966–2972.

Brands, C. M., & van Boekel, M. A. 2001, Reactions of monosaccharides during heating of sugar− casein systems: Building of a reaction network model. Journal of Agricultural and Food Chemistry, 49(10), 4667-4675.

Brighina, S., Poveda Turrado, C., Restuccia, C., Walton, G., Fallico, B., Oruna-Concha, M.J., Arena, E. 2021, Detrimental effect on the gut microbiota of 1,2-dicarbonyl compounds after in vitro gastro-intestinal and fermentative digestion. Food Chemistry, 341, 128237.

Byrns, M. C., Vu, C. C., Neidigh, J. W., Abad, J. L., Jones, R. A., & Peterson, L. A., 2006, Detection of DNA adducts derived from the reactive metabolite of furan, cis-2-butene-1, 4-dial. Chemical research in toxicology, 19(3), 414-420.

Cincotta, F., Tripodi, G., Merlino, M., Verzera, A., & Condurso, C., 2020, Variety and shelf-life of coffee packaged in capsules. LWT, 118, 108718.

Condurso, C., Cincotta, F., & Verzera, A., 2018, Determination of furan and furan derivatives in baby food. Food chemistry, 250, 155-161.

Degen, J., Hellwig, M., Henle, T., 2012, 1,2-Dicarbonyl compounds in commonly consumed foods. Journal of Agricultural and Food Chemistry, 60, 7071− 7079.

Fallico, B., Zappalà, M., Arena, E., Verzera A., 2004, Effect of conditioning on HMF content in unifloral honeys. Food Chemistry, 85, 305-313.

Gökmen, V., Açar, Ö. Ç., Serpen, A., & Morales, F. J., 2008, Effect of leavening agents and sugars on the formation of hydroxymethylfurfural in cookies during baking. European Food Research and Technology, 226, 1031-1037.

Hellwig, M., Gensberger-Reigl, S., Henle, T., Pischetsrieder, M., 2018, Food-derived 1,2-dicarbonyl compounds and their role in diseases. Seminars in Cancer Biology, 49,1-8.

Kocada• l1T. and Gökmen V., 2016, Effects of Sodium Chloride, Potassium Chloride, and Calcium Chloride on the Formation of ±-Dicarbonyl Compounds and Furfurals and the Development of Browning in Cookies during Baking. Journal of Agricultural and Food Chemistry, 64, 7838–7848

Kocada• l1, T., } ili• , S., Göncüo• lu Tas, N., Van• etovic, J., Dodig, D., Gökmen, V., 2016, Formation of ±-dicarbonyl compounds in cookies made from wheat, hull-less barley and colored corn and its relation with phenolic compounds, free amino acids and sugars. European Food Research and Technology, 242, 51–60.

Maasen, K., Scheijen, J.L.J.M., Opperhuizen, A., Stehouwer, C.D.A., Van Greevenbroek, M.M., Schalkwijk, C.G., 2021, Quantification of dicarbonyl compounds in commonly consumed foods and drinks; presentation of a food composition database for dicarbonyls. Food Chemistry,339,128063.

Min, D. B., Callison, A. L., & Lee, H. O., 2003, Singlet oxygen oxidation for 2-pentylfuran and 2-pentenyfuran formation in soybean oil. Journal of food science, 68(4), 1175-1178.

Navarro, M., Morales, F.J., 2017, Effect of hydroxytyrosol and olive leaf extract on 1,2-dicarbonyl compounds, hydroxymethylfurfural and advanced glycation endproducts in a biscuit model. Food Chemistry, 217, 602–609.

Poulsen, M.W., Hedegaard, R.V., Andersen, J.M., de Courten, B., Bügel, S., Nielsen, J., Dragsted, L.O., 2013, Advanced glycation endproducts in food and their effects on health. Food and Chemical Toxicology, 60, 10–37.

Šebeková, K., Somoza, V., 2007, Dietary advanced glycation endproducts (AGEs) and their health effects – PRO. Molecolar Nutrition & Food Research, 51, 1079–1084.

Spina, A., Brighina, S., Muccilli, S., Mazzaglia, A., Rapisarda, P., Fallico, B., & Arena, E., 2015, Partial replacement of NaCl in bread from durum wheat (Triticum turgidum L subsp. Durum Desf.) with KCl and yeast extract: evaluation of quality parameters during long storage. Food and Bioprocess Technology, 8(5), 1089-1101.

Spina, A., Brighina, S., Muccilli, S., Mazzaglia, A., Fabroni, S., Fallico, B., Rapisarda, P., Arena, E., 2019, Wholegrain Durum Wheat Bread Fortified with Citrus Fibers: Evaluation of Quality Parameters During Long Storage. Frontiers in nutrition, 6, 13.

Weigel, K. U., Opitz, T., & Henle, T., 2004, Studies on the occurrence and formation of 1, 2-dicarbonyls in honey. European Food Research and Technology, 218(2), 147-151.