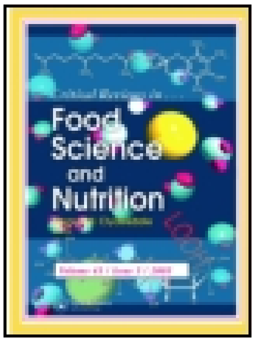

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REVIEW

Factors influencing the sensory perception of reformulated baked confectionary products

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ABSTRACT
Baked confectionary products such as cakes, biscuits, cookies, and muffins are consumed globally as they are coveted for their sensory attributes. However, due to their high sugar and fat content, baked confectionary products are also considered major contributors to the prevalence of obesity and the rise of type II diabetes in industrialized nations and in emerging economies. Both sugar and fat have multiple roles in baked confectionary products in terms of structure, texture, shelf-life, aroma, and taste. Considerable efforts have been undertaken to modify product formulations to decrease sugar and fat contents without compromising on product or sensory quality, and this review focuses on relevant research undertaken to date. Aspects addressed include the impact of decreasing sugar and fat content, the impact of sugar or fat substitutes in relation to sensory perception, with a focus on the role of key product constituents, processing parameters, flavor reactions, aromatic compounds, and flavor chemical and sensory techniques.

KEYWORDS
Aroma; baked confectionary; fat; sensory; sugar

Introduction

Baked confectionary is an umbrella term used to categorize a variety of cakes, muffins, biscuits, cookies etc. (O'Sullivan 2016). Globally, these products are highly appreciated by consumers across all populations. They are characterized by their aroma, flavor, texture, and esthetic appeal, having the ability to induce a feeling of satisfaction and happiness when consumed (Poonnakasem et al. 2016). As cakes and other confectionary products are associated with celebrations, they are considered as a "reward" or a "treat" and are anticipated to be of high quality. These products are predominantly comprised of sugar, flour, water, fat, eggs, and a leavening agent. Combined in different ratios, these ingredients produce various products such as cakes, muffins, cookies etc. It is the individual contribution of these raw materials that deliver the desired organoleptic properties and therefore drive consumer liking. Fat and sugar have been identified as the most important contributors to the overall acceptability of sweet bakery products with both contributing to texture, mouthfeel, volume, color, and flavor (Heenan et al. 2010; Manohar and Rao 1999; Zoulias, Oreopoulou, and Kounalaki 2002).

In 2016, 13% of the global adult population was reported obese with 39% of adults aged 18 years and over classified as overweight (WHO 2017). As a result, the food industry have become motivated to modify product formulations through sugar and fat reduction in order to aid consumer welfare, while simultaneously striving to retain the sensory appeal and maintain purchase intent. There is also a demand for "clean label" products that are both nutritious and low in calories, yet consumers still expect a product that is not compromised in sensory quality. However, there is a vast quantity of literature exploring sugar (sucrose)/fat replacement or reduction, with the majority of results correlating sugar and fat reduction with a decrease in consumer acceptability (Cavalcante and Silva 2015; Eslava-Zomeño, Quiles, and Hernando 2016; Giarnetti et al. 2015; Karp et al. 2016; Onacik-Gür et al. 2016; Serin and Sayar 2016; Zahn, Pepke, and Rohm 2010).

Taste and aroma are considered paramount to a consumer's acceptability of a food product. When a food is eaten, a complex mechanism occurs between the taste receptors in the mouth and aroma receptors in the nasal cavity that result in flavor perception (Naknean and Meenune 2010). Although nonvolatile compounds and structural components contribute significantly to the recognition of taste, volatile aroma compounds are considered the major influencer in the overall liking and acceptability of food (Taylor and Linforth 1996). The process of baking induces many changes; structural enhancement, development of the desired texture, and improved digestibility, but the major effect is the transformation of the sensory attributes, specifically aroma formation (Mohsen et al. 2009). Baking promotes thermal reactions and other interactions within the matrix which are thought to be the main precursors of the

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"characterizing" volatile aroma compounds associated with baked goods (Pozo-Bayón, Guichard, and Cayot 2006a). Identification of the most significant compounds responsible for the desired flavor (taste and aroma) of baked confectionary products could be a stepping stone for innovative development of healthier confectionary that possess an integral appeal to the consumer.

The consumption of food is an elaborate process which includes mastication, salivation, tongue movement and swallowing (Piggott 2000), and therefore these events have an impact on the rate and intensity at which an aroma is perceived (Linforth, Baek, and Taylor 1999; Wilson and Brown 1997). In addition, the food matrix can possess a number of factors that influence aroma release; for example, viscosity (Hollowood, Linforth, and Taylor 2002), fat content (van Ruth, King, and Giannouli 2002), and the presence of hydrocolloids and emulsifiers (Koliandris et al. 2008). Different sensory methods can be employed to gain an insight into the consumer's experience during food consumption and aftertaste. Combining instrumental data of volatile compounds with the application of an appropriate sensory methodology can yield important correlations between aroma and flavor perception and therefore, consumer acceptance (Heenan et al. 2009; Lee and Ahn 2009; Quílez, Ruiz, and Romero 2006). Gas chromatography coupled to mass spectrometry (GC-MS) is the separation technique usually applied for the identification and quantification of volatile aromatic compounds in foods (Kilcawley 2017). Although there may be a vast quantity of compounds present in a food product, only a fraction will impact on the flavor perception (Dunkel et al. 2014).

This review aims to provide information on the factors that impact the sensory acceptance of baked confectionary, especially in products where fat and/or sugar has been decreased or replaced.

Raw materials

Although baked confectionaries share many similar ingredients, it is the proportion and ratio of the ingredients that generally defines them on an individual basis. Cakes and muffins are of a similar classification, as the finished products are characterized by a light aerated structure with a moisture content of 20–30% (Fiszman, Sanz, and Salvador 2013). Whereas, biscuits and cookies possess a much lower moisture content (1–4%) and aeration is not as critical as the desired texture of the end product is favorably described as "crispy" or "chewy" (O'Sullivan 2016). Before trying to decipher the complex mechanism of volatile production in baked confectionary products, it is noteworthy to consider the raw materials involved in the process, which act as precursors for the development of the desired aroma and flavor.

Flour

Wheat flour is a predominant ingredient in the bakery industry. Flour is mainly composed of starch and protein and is essentially the "glue" that binds all ingredients of a bakery product together. The functional properties that flour provides are attributed to the quantity and quality of the proteins present. Gluten proteins makeup 80–85% of total wheat protein and are responsible for its unique ability to form a viscoelastic dough. Gluten also plays a role in gas retention and determination of the overall quality of a baked product (Goesaert et al. 2005; Majzoobi et al. 2016). Although these properties are more important in bread manufacture, protein interactions are necessary for an adequate structure in sweet bakery products (Wilderjans et al. 2008).

In terms of its contribution to aroma and flavor production, compounds such as vanillin, 3-hydroxy-4.5-dimethyl-2(5H)-furanone, 4,5-epoxy-(E)-2-decenal and (E)-2-nonenal have been identified as the most odor active compounds in white wheat flour, with odor qualities ranging from vanilla-like to fatty (Czerny and Schieberle 2002). Widely utilized in baked confectionary, white wheat flour yields a soft, somewhat bland taste that allows the other ingredients to command flavor perception. Bakery products produced utilizing grains and plants with nutritional benefits (high in fiber, antioxidant properties etc.) receive a lot more attention in literature due to the presence of celiac disease in populations, and also the increasing demand for low glycaemic products fit for diabetic patients. As flour is usually the most abundant ingredient in a bakery product, replacement with a suitable alternative can be an opportunity to significantly enhance the nutritional profile.

Many flour replacement ingredients have been evaluated. Hedonic assessments by untrained panelists revealed increasing substitution of wheat flour for pea and broad bean derived flours lead to a decrease in organoleptic properties of sponge cakes (Belghith-Fendri et al. 2016). The aroma of "cake like" donuts made with 20% and 30% cowpea meal was described as "slightly beany"; however, untrained panelists did not necessarily rate this as an adverse attribute (McWatters 1982). Similarly, cookies enriched with cowpea flour at 33 and 50% were described by untrained panelists as having a "beany", "nutty" or "fishy" flavor (McWatters et al. 2003). Trained panelists have also described biscuits enriched with soya flour as "beany" (Shrestha and Noomhorm 2002). Addition of resistant starch in muffins led to a significant decrease in the "typical taste" and "typical odor" by descriptive analysis (Baixauli et al. 2008). On replacement of $\geq$20% of wheat flour with β-glucan-rich hydrocolloids from oats, a descriptive sensory panel experienced an increase in "cardboard flavor" and a decrease in "sweetness" (Lee and Ahn 2009).

Chocolate chip cookies containing a mix of barley and wheat flour (30–70% replacement) were perceived by a semi-trained panel, using descriptive sensory analysis, as having an increase in "baked barley" aroma but attributes such as "chocolaty aroma", "sweet flavor" and "chocolaty flavor" were not impacted (Frost, Adhikari, and Lewis 2011). On replacement of 70% wheat flour with almond flour in Chinese moon cakes, quantitative descriptive analysis (QDA) yielded favorable results with trained panelists having appreciated the "almond flavor" derived from methyl-butyraldehyde (Jia et al. 2008).

Although these substitutes demonstrate potential, it is apparent from the literature that none replicate the same sensory experience as traditional formulas made with white wheat flour.

Eggs

Eggs are widely utilized in baking due to their multifunctional composition. Egg white proteins are excellent foaming agents capable of forming a network of air bubbles which coagulate on heating to form a porous aerated stable structure desirable in cakes and muffins (Arunepanlop et al. 1996). However, egg yolk also provides emulsifying capabilities, aids color development, and contributes to the flavor and aroma of baked confectionary products (Yang and Baldwin 1995). Eggs are responsible for the Maillard compounds which produce "roasty", "sweet" and "malty" aromas desirable in cakes and cake-like products. Literature regarding egg replacement in baked confectionary appears to be motivated by a number of factors; the cholesterol content of eggs and its association with cardiovascular disease, utilization of cheaper plant-based alternatives or the growing interest in vegetarian and vegan diets.

Shao, Lin, and Chen (2015) examined creating eggless cakes with the use of hydrocolloids. Sensory evaluation by trained panelists revealed a significant decrease in the intensity of "egg taste" and "egg smell" in eggless cakes compared to the control. Similarly, on evaluation of eggless cakes by QDA, trained panelists allocated a higher rating for "egg flavor" in control cakes compared to the formula without egg (Kohrs et al. 2010). Angel cake and muffins reformulated with lentil protein as an egg/milk replacer were assessed by untrained panelists using a hedonic scale (Jarpa-Parra et al. 2017). The results demonstrated that the cocoa in the muffin formula appeared to mask the direct taste of the lentils (100% replacement of milk and egg), but a "beany" taste was apparent. In the case of the angel cakes, panelists favorably described the flavor as "nutty."

The implementation of soy sources as an egg substitute in baked confectionary has been frequently reported. Muffins produced with soy flour as an egg replacement (Geera et al. 2011) resulted in untrained panelists rating the product as having the highest "off-favor", lowest "overall favor", and the most "intense aftertaste", compared to that of other muffins formulated with egg substitutes. QDA of eggless cakes produced with soy protein isolate (SPI), assessed by trained panelists, yielded significantly different scores for the attributes "beany taste", "eggy taste" and "overall aroma" compared to that of the control (Lin et al. 2017). Corresponding with these results, cakes reformulated with soy alternatives, in place of egg, generally score significantly lower for overall acceptability on hedonic scales, compared to that of the control (Geera et al. 2011; Rahmati and Mazaheri Tehrani 2015).

On replacement of egg with baking powder in sponge cake, Pozo-Bayón et al. (2007) demonstrated that characterizing "malty", "chocolate" (3-methylbutanal), "roasty", "nutty" (2-ethyl-6-methylpyrazine, 2-ethyl-5-methylpyrazine, trimethylpyrazine), "caramel-like" (5-methylfurfural), and "cherry", "almond" (benzaldehyde) compounds where absent in the formulas made without egg. Similarly, Maire et al. (2013) identified that sponge cakes made without egg yolk were lacking methional ("musty"/"potato"). In addition, the authors noted less lipid oxidation (LO) compounds in the sponge cake made with egg, suggesting that egg phospholipids may as act an antioxidant (Haeyoung and Eunok 2008).

Sensory evaluation of sponge cake, by hedonic scales, found that replacement of egg white with 12.5% and 25% whey protein isolate (WPI) did not significantly impact the odor, flavor or appearance of the cake (Díaz-Ramírez et al. 2016). Although WPI may seem promising as an egg replacer, the incentive for egg replacement is also motivated by cost, which limits the application of WPI. It is evident that eggs contribute to overall flavor acceptability in addition to structural properties in baked confectionary products.

Fat

Fat has a major influence on the overall acceptability of baked confectionary products and is usually present in the form of hydrogenated shortenings or butterfat. In terms of functionality, fat plays a critical role in the incorporation of air bubbles; enabling an increase in volume and the development of a porous structure. Additionally, fat aids in the entrapment of moisture leading to a moist and tender crumb (Conforti 2006; Eslava-Zomeño et al. 2016). Through the interaction with starch in the baked product matrix, fat forms lipid-amylose complexes, which hinder retrogradation; helping to maintain a desirable texture and hence extend shelf-life (Mert and Demirkesen 2016). However, due to the adverse health effects associated with saturated and trans fats, suitable alternatives are desirable.

Fat is a principle contributor to aroma and flavor perception. Fat has the ability to enhance palatability by imparting lubricity and a specific mouthfeel, whilst many aroma volatile compounds are fat soluble and bound within the lipid component of a product (O'Sullivan 2016; Zoulias, Oreopoulou, and Tzia 2002). Due to its unique fatty acid composition, butter is difficult to replace in recipes without having an adverse effect on the organoleptic qualities of the finished product. Compounds such as 2,3-butanedione, acetoin, δ-decalactone, δ-octalactone, and butyric acid are important contributors for the typical flavor/aroma of butter (Mallia, Escher, and Schlichtherle-Cerny 2008; Schieberle et al. 1993). Pastries produced with butter have been characterized by a "sweet" and "coconut" aroma originating from δ-decalactones (Gassenmeier and Schieberle 1994). Giarnetti et al. (2015) explored replacing butter in cookies with a combination of inulin and extra virgin olive oil at different percentages. Descriptive sensory analysis revealed that the reformulated cookies scored much lower in "caramel odor", "buttery odor", "buttery flavor", and lacked a sweet perception, compared to the control. Similarly, 50% butter replacement with prune puree in cookies resulted in a decrease in "butter flavor" intensity and a less desired product (Swanson and Perry 2007). It appears the amount of butter incorporated into a recipe strongly reflects the intensity of "butter flavor" and "butter aroma" perceived on consumption.

Margarine and shortening blends are more commonly used in bakery products due to their plasticity and lower cost compared to butter. The make-up of margarine is relatively simplistic, consisting of a water in oil emulsion, whereas shortening is comprised solely of an oil blend. Although the characterizing compounds of butter are not as abundant in margarines and shortenings, they are still capable of imparting positive attributes such as "buttery", "fruity" and "sweet" derived from 2,3-butanedione, ethyl butanoate, and δ-decalactone, and δ-octalactone, respectively (Shiota et al. 2011). Shortening replaced with different fat replacers in cookies resulted in significantly lower intensity scores for "vanilla" and "sweet" on a descriptive scale compared to a control (Armbrister and Setser 1994), indicating that the source of these aromatic compounds was bound within the fat matrix. Similarly, biscuits formulated with vegetable shortening were identified by Free Choice Profiling to have stronger intensity in "buttery", "vanilla", "coconut", and "cinnamon" attributes than biscuits with the same percentage of dairy based shortening and liquid oils (Tarancón et al. 2013). Hedonic scales usually reveal lower aroma and flavor acceptability when sensory panelists evaluate sweet bakery products where the fat has been removed or replaced (Psimouli and Oreopoulou 2013; Rodríguez-García, Salvador, and Hernando 2014; Singh and Kumar 2018). However, when hydroxypropyl methylcellulose was used as a fat replacer for margarine in biscuits, it did not appear to adversely affect the sensory properties of biscuits at a substitution rate of 15%, but at 30%, "buttery" flavor was significantly reduced (Laguna et al. 2013).

Carbohydrate fat replacers have been extolled for their ability to replicate the texture of fat in the mouth as their globular structure can somewhat mimic the impression of creaminess (Meyer et al. 2011). However, maltodextrin and polydextrose were found unable to imitate the lubricity, taste, and flavor of fat in short dough biscuits (Sudha et al. 2007). Trained panelists associated an increase in "floury" and a decrease in "buttery" flavors with reduced fat biscuits formulated with N-DULGE® (a mixture of tapioca dextrin and tapioca starch) and resistant starch, by descriptive analysis (Laguna et al. 2012). Partial replacement of oil in chocolate muffins, with soluble cocoa-fiber, has been associated with an increase in "bitterness" by descriptive analysis (Martínez-Cervera et al. 2011). On the contrary, the addition of apricot kernel fiber to replace shortening in cookies, did not adversely impact sensory perception (Seker et al. 2010). Fat reduction can also coincide with a decreased in sweetness perception, which has been reported in biscuits (Biguzzi, Schlich, and Lange 2014; Forker, Zahn, and Rohm 2012).

Butter replacement in cookies corresponded with a significant decrease in the levels of methyl ketones (2-butanone, 2-heptanone, 2-nonanone, and 2-undecanone) (Giarnetti et al. 2015), which are known to impact on "buttery" and sweetness perception. As stated, the unique fatty acid profile of butter is comprised mostly of short and medium length fatty acids, having the capability to generate short chain methyl ketones via oxidation. These compounds contribute to the aroma of cookies and other sweet bakery products. On replacement of margarine with extra virgin olive oil in Madeira cakes, Matsakidou, Blekas, and Paraskevopoulou (2010) found that the alcohols ((Z)-2-pentenol, (Z)-3-hexenol, (E)-2-hexenol and (Z)-2-hexenol) were created from oxidation of the virgin olive oil. Although untrained panelists did not negatively rate the re-formulated sponge cake, the presence of these LO alcohols may have implications for product shelf-life as they can contribute to off-flavors over time.

Overall, there appears a lot more information is required to further understand the role of fat in consumer acceptability of confectionary products.

Sugar

Dominating a large proportion of the ingredient declaration for the majority of commercial cakes, muffins, biscuits etc., sugar or sucrose, is considered the most important raw material incorporated in baked confectionary products. Not only providing the characteristic sweetness, sugar also plays a vital role in creating and maintaining the structure, and texture of baked confectionary products. Sugar also restricts water activity, thus inhibiting microbial growth and contributing to the preservation of the product (Rodríguez, Magan, and Medina 2016). Sucrose is highly recognized in food manufacturing for its ability to impart a clean, sweet taste. However, providing 4 kcals of energy per gram, and usually present in large quantities in baked confectionary, excess sucrose consumption is identified as a major contributor to the prevalence of obesity and type II diabetes worldwide (Hashem, He, and MacGregor 2016).

Sweeteners, both artificial and natural, are widely utilized for their ability to impart a conventional "sweet flavor" with only a fraction of the calorific value to that of sucrose. Although these sweeteners influence the perception of sweetness, they cannot fully imitate the role sucrose plays in structural development, functionality, or color formation (Struck et al. 2014). The sugar alcohol xylitol conjoined with bulking agents, such as oligofructose, has shown potential for reduced sugar cake formulation (Nourmohammadi and Peighambardoust 2016; Ronda et al. 2005), due to the synergistic effect of these substances. Xylitol imparts a high level of sweetness but is unable to partake in the Maillard reaction (MR), whereas bulking agents are less sweet by nature but are capable of aiding in structural and color development, thus resulting in an acceptable product.

Steviol glycosides are widely used as a sucrose replacement with their popularity due to their "clean label" status. Although these sweeteners deliver a high intensity of sweetness, 100–300 times sweeter than sucrose (Cardello, Da Silva, and Damasio 1999), they are unable to meet all the requirements of a sucrose substitute. Steviol glycosides have been shown to perform well with other bulking agents in confectionary systems (Periche et al. 2016; Shah, Jones, and

Vasiljevic 2010). Sucrose reduction of 30% was achieved in muffins with the use of a steviol glycoside (*rebaudioside A*) in addition to inulin and polydextrose (Zahn et al. 2013). Flash sensory profiling revealed these formulas were associated with attributes such as "buttery flavor", "sweet", and "aromatic". However, on evaluation of muffins where sucrose was partially replaced with Stevia (25%), trained panelists identified the control (sucrose), on a hedonic scale, as having the highest acceptability (Karp et al. 2016). Complete replacement of sucrose with stevia does not seem to be well received by consumers in baked confectioneries, but partial replacement shows potential (Wardy et al. 2018).

Although sucrose contributes hugely to the sweet flavor of baked confectionary, it can also play a role in the development of flavor and aroma that is not necessary related to sweetness. Reduced sucrose cookies have shown to have a significantly reduced perception of "buttery" flavor (Laguna et al. 2013). Similarly, on replacement of sucrose with isomaltose, cakes were perceived as having a significantly less "buttery" and "caramel" flavor (Heenan et al. 2010). This may be explained by the interaction sugar has in thermal processes that occur during baking. When sucrose is removed from the equation, volatile compounds may be lost or suppressed due to the lack of monosaccharaides available to partake in the MR and caramelization. Despite the desire for sugar to be eradicated in food formulations, it is evident sucrose directly impacts on the appreciated flavor and aroma of baked confectionaries, as well as playing an important role in functional properties.

Other ingredients

Introduction of non-conventional materials can also favor the production of desired aroma compounds in baked confectionary matrices and offers scope to improve the nutritional quality of a product. Wheat cookies supplemented with SPI at 10% scored significantly higher on a hedonic scale for "aroma" and "taste" compared to the control cookie (Mohsen et al. 2009). The addition of SPI, an additional source of amino acids, favored the generation of 2-ethyl-5-methylpyrazine ("biscuit-like") and maltol ("cotton-candy") with concentrations of these compounds higher than that of the control. Cookies re-formulated with an emulsion gel containing inulin (Giarnetti et al. 2015), showed increased levels of 3-methylbutanal ("malty/chocolate"), methylpyrazine and trimethylpyrazine ("roasty/nutty"). The formation of these compounds can be explained by the degradation of inulin that occurs during baking, producing mono- and di-saccharides that are then available to accelerate the MR. Similar results were found when inulin was added to wheat bread (Poinot et al. 2010). On replacement of whole meal flour with purple wheat flour in biscuits, Pasqualone et al. (2015) saw significantly higher amounts of potent aroma compounds 3-methylbutanal, 2-methylbutanal, benzaldehyde, and the furan compounds furfural, 5-methylfuran, and hydroxymethylfurfural (HMF).

Bi-products of wine fermentation, such as grape marc extract has been shown to increase the level of benzaldehyde ("cherry"/"almond"), phenylacetaldehyde ("floral"/"honey"), and furans 2-methylfuran, 2-acetylfuran, 5-methylfurfural and 2-furanmethanol ("sweet"/"caramel") in biscuits, resulting in enhanced consumer acceptability and purchase intention (Pasqualone et al. 2014). Higher levels of furanic compounds were identified in the grape marc extract biscuits compared to the control. This can be explained by the acidic pH of this material, which is favorable for the formation of these compounds.

Varying yeast amounts have been shown to have an impact on compounds derived from the MR (Birch et al. 2013a; Birch et al. 2013b; Poinot et al. 2008; Zehentbauer and Grosch 1998b), which are associated with "malty", "sweet", and "roasty" attributes, and hence important to the overall aroma of bakery products. The monosaccharide fructose, in the presence of high temperatures, has been shown to have a positive effect on the formation of HMF in cookies and biscuits (Ameur et al. 2007; Nguyen, Van der Fels-Klerx, Peters, and Van Boekel 2016; Zhang et al. 2012). HMF and furfural have also been shown to be influenced by salt (NaCl) content in cookies (Kocadağlı and Gökmen 2016; Van Der Fels-Klerx et al. 2014).

Matrix effect

It is well understood how the removal of key ingredients (fat and sugar) in product formulation can adversely impact on aroma and flavor of baked confectionary (Giarnetti et al. 2015; Struck et al. 2014; Sudha et al. 2007). The food matrix can also significantly influence how flavor and aroma are perceived. On consideration of manipulating the integral high sugar, high fat composition of a confectionary product, it is important to understand how aroma compounds can be retained or released from the matrix when concentrations of these ingredients are altered.

The main function of sucrose in the majority of formulas is to enhance palatability by imparting a sweet, clean taste. Sucrose has proven to have a significant impact on aroma release in sweetened beverages, with studies demonstrating that sugar increases aroma perception (Hansson, Andersson, and Leufvén, 2001; Nahon et al. 1998; Saint-Eve et al. 2009). This effect can be explained by the "salting out" phenomenon, whereby sucrose saturates the solution and as free water is lost due to sugar hydration, aroma compounds are forced into the headspace (Nawar 1971). Headspace analysis of cereal bars showed increasing amounts of glucose solids had a pronounced effect on aroma release for some compounds (acetaldehyde, ethyl butyrate, ethyl methyl butyrate, and limonene) but not others (maltol and methyl cinnamate) (Heenan et al. 2012). As sugar has the ability to increase the aroma intensity of compounds, in theory, when sugar is removed, perception of aroma compounds can also decrease. Aroma addition has been suggested as a tool to compensate for the decline in sensory quality on sucrose reduction in food formulas (Hutchings, Low, and Keast 2018). However, this theory is drawn from liquid and semi-solid models. In order for this concept to apply to sugar reduction in baked confectioneries, more work on aroma-interactions in soft-solid matrices, as found in bakery products, is required (Poinot et al. 2013).

Sugar reduction is a difficult challenge as it is almost inevitable that sweetness perception decreases concurrently with sugar reduction (Biguzzi et al. 2014; Drewnowski, Nordensten, and Dwyer 1998; Martínez-Cervera et al. 2012), leading to diminished consumer acceptance. Fat and sugar are very much intertwined in the role of sensory perception in baked confectionary products. Fat contributes hugely to the texture and mouth-feel of food products. In addition, the perception of fat on consumption can be somewhat hard to define by consumers, with sweetness impression shown to decrease with a decrease of fat in biscuits (Biguzzi et al. 2014; Forker et al. 2012). Cognizance of the relationship between aroma and perception must be taken into account when sugar and fat are reduced so that consumer desirability is not adversely impacted.

Manipulation of components of the matrix can be an innovative way to enhance aroma perception and even improve the quality of reduced fat/sugar products. On variation of particle size distribution in chocolate, Afoakwa et al. (2009) demonstrated that with finer particle sizes, an increase in favorable compounds associated with "cocoa-chocolate-praline" and "caramel-sweet" notes were released into the headspace. Richardson et al. (2018) employed sugar particle size reduction in a chocolate brownie matrix. Replacing standard sugar crystals with a smaller particle size in the formula produced brownies that retained their conventional "sweet" taste and were identified as significantly sweeter than the control. From these findings, the authors postulated that sucrose of smaller particle size can be used in product formulation to produce sugar reduced brownies of acceptable quality.

Precursors of flavour- volatile formation

Aroma is considered a critical determinant to the overall quality of bakery products as it is one of the initial sensory attributes the consumer encounters. Even in small quantities, low aroma threshold compounds can act as a determinant of product quality and consumer preference (Quílez et al. 2006). Aroma compounds can be produced as a result of enzyme activity, fermentation, or through thermal reactions (Pozo-Bayón et al. 2006a). Although the ingredients contribute immensely to the overall flavor perception of the product, it is the thermal reactions that occur during baking that significantly influence the aroma, and thus flavor. The following reactions are thought to generate the most characterizing compounds associated with baked confectionary products.

The Maillard reaction

Maillard reactions are non-enzymatic reactions that occur on heating and have the ability to completely transform the flavor, aroma, and color of food products. The MR is a complex cascade of chemical reactions and has been extensively studied (Hodge 1953; Nursten 1981). It is generally described as occurring in three main stages. The MR is instigated by a condensation reaction between a carbonyl group of a reducing sugar and a free amino group ($-NH^2$) originating from amino acids, peptides, or proteins, in a low moisture, high temperature environment, to produce amines, N-glycosylamine (aldose sugar) or fructosylamine (ketose sugar) (Parliament 1989). These products are colorless and not odor active. As the temperature increases internally in the food product and moisture is driven off, N-glycosylamine or fructosylamine rearrange to form an Amadori or a Heyns product, respectively. Amadori/Heyns products are inherently unstable and subsequently degrade, impacted by the pH of the matrix; this degradation by means of pH is known as dehydration. At pH $\leq$7, 1,2-enolization is promoted to form furfural and HMF, whereas in an alkaline environment (pH $\geq$7), 2,3 enolization occurs forming highly reactive reductones and dehydroreductones (Martins, Jongen, and Van Boekel 2000; Pozo-Bayón et al. 2006a). The temperature, nature of the reactants (amino acid, peptide and sugar), and water activity also strongly influence the rate at which these reactions occur (Van Boekel 2006). Alternatively, Amadori and Heyns products can also undergo cyclization to produce nitrogen-containing heterocyclic compounds, such as pyrroles or pyridines (Jousse et al. 2002). Sugar fragmentation is another possible route of degradation for these products, a complex mechanism involving retro-aldol, hydrolytic, oxidative and amine-induced carbohydrate cleavages resulting in the production of α-dicarbonyl compounds which can recombine to yield HMF and other furans (Nursten 2007; Smuda and Glomb 2013; Taş and Gökmen 2017). The third potential pathway of Amadori/Heyns degradation is through means of Strecker degradation. In relation to the MR, Strecker degradation is brought about by α-dicarbonyls, and induces deamination and decarboxylation of free amino acids, resulting in the production of volatile aldehydes whose structure mimics that of their amino acid counterpart (Rizzi 2008; Yaylayan and Mandeville 1994). Compounds such as 3-methylbutanal, phenylacetaldehyde, and methional are well established as volatile compounds derived from Strecker degradation of leucine, phenylalanine, and methionine, respectively, and can be considered some of the most important products of the MR (Hofmann, Münch, and Schieberle 2000). In addition to aldehydes, aminoketones are also a result of α-dicarbonyl and amino acid reactions. These compounds have the ability to condense into heterocyclic compounds such as pyrazines, pyridines, thiazoles, pyrroles etc. (Shu 1998). As seen in Figure 1, each one of these pathways is capable of producing volatile intermediates that are important aroma compounds which influence the flavor of baked confectionaries. On further condensation, these compounds form polymers known as melanoidins (Zamora and Hidalgo 2005), yielding the characteristic golden brown color of bakery products.

Carmelization

Although the MR receives a lot of attention for the role it plays in the formation of volatile and nonvolatile

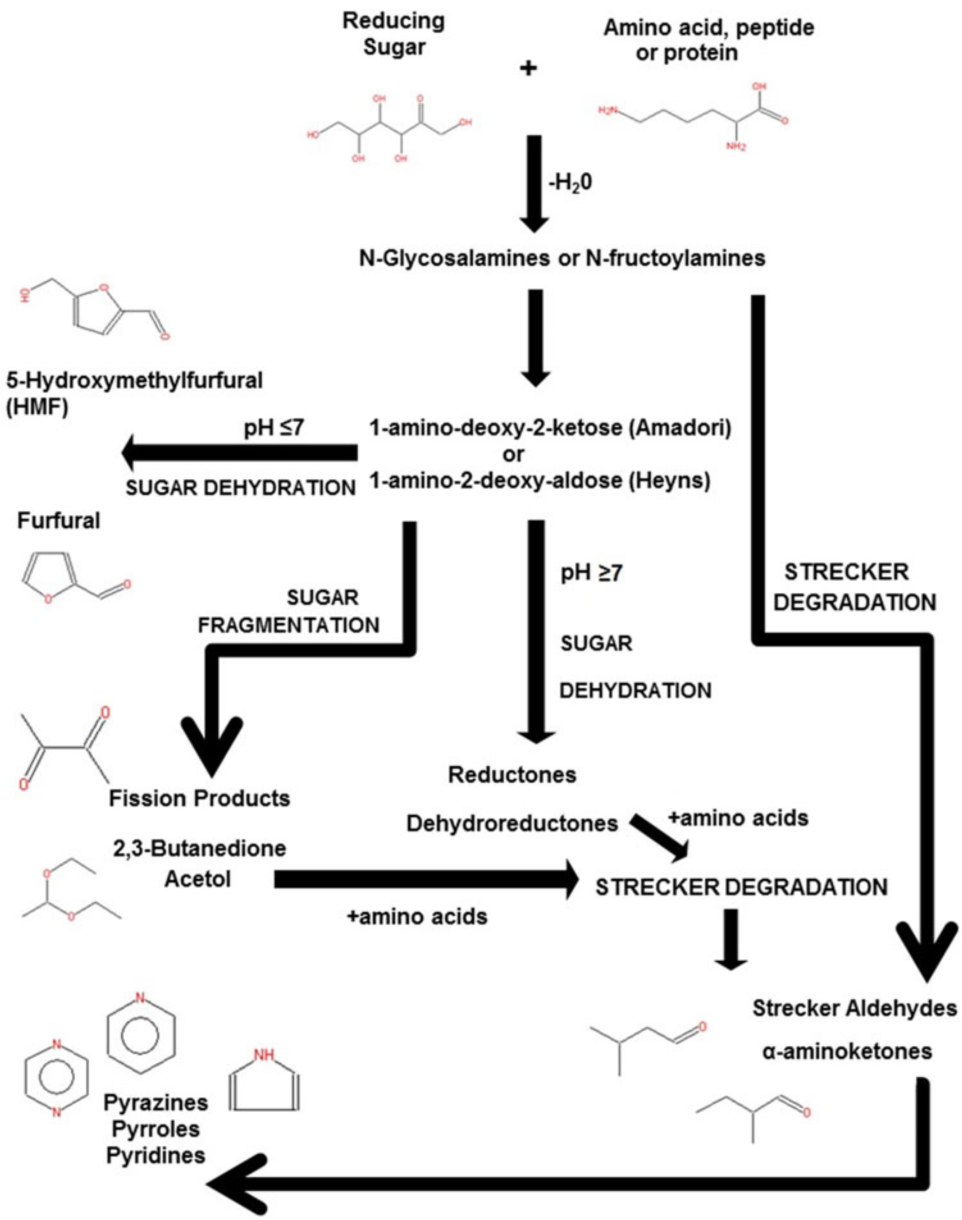

Figure 1. Flavour compound formation. The Maillard reaction(adapted from Pozo-Bayón Guichard, and Cayon 2006a)

compounds during baking, caramelization is also an important contributor to the development of the overall aroma and color of baked products. Caramelization is referred to as the decomposition of sugars and happens at temperatures >120 °C, favored by a pH of <3 or >9, and can be associated with a brown color and "caramel" odor in food (Lee and Lee 1997; Zhang et al. 2012). Isomerization of monosaccharides is generally the initial step in caramelization, where sugar molecules experience enolization, and further degradation reactions lead to the formation of α-dicarbonyls (Kroh 1994). Sugar degradation produces compounds comparable to that of the early stages in the MR, but are produced at a slower rate due to the lack of a catalyst, the amino group (Van Boekel 2006). As the MR relies on the participation of reducing sugars, the extreme temperatures attained on the surface of the product during baking can induce starch and sucrose hydrolysis, thus leading reducing sugars to be available for both MR and caramelization reactions simultaneously (Capuano et al. 2008). As the name suggests, caramelization is associated with aroma compounds associated with a "caramel" odor, which derive from furans, ketones, aldehydes, and lactones, aromatic compounds formed during thermal decomposition of sugars (Paravisini et al. 2015).

Lipid oxidation

Unsaturated lipids are susceptible to LO, a problematic reaction leading to undesirable changes in flavor, nutritional quality, and shelf-life (Waraho, McClements, and Decker 2011). Auto-oxidation is the most common form of LO in bakery products (Maire et al. 2013) and can be described as a free radical chain reaction consisting of three stages; initiation, propagation and termination (Frankel 2014). Margarine and shortenings utilized in baking are an abundant source of oleic, linoleic, and linolenic acid and are thus prone to secondary oxidation. The formation of various aldehydes, ketones, and alcohols are indicators of LO in bakery products and these LO derived compounds can contribute up to a quarter of the volatile profile of bread (Jacobsen 1999; Pico, Bernal, and Gómez 2015). The main pathways of LO occur on ingredient preparation, in the presence of oxygen, at high temperatures of baking, and on storage, with hexanal being the primary marker of LO in sponge cake and other bakery products (Maire et al. 2013; Purcaro, Moret, and Conte 2008).

Processing factors

Processing factors have been shown to influence the formation of volatile compounds generated through thermal reactions in bakery products. Most work to date has focused on furanic compounds such as HMF and furfural, however, other volatile compounds are likely to be affected.

Compounds important to aroma and color development in baked products are produced via thermal reactions, thus baking times and temperatures will have a pronounced effect on their formation and development. Rega et al. (2009) monitored volatile compounds produced during baking a sponge cake over a period of 0–25 minutes. Strecker aldehydes and pyrazines expressed linear behavior and increased with baking time. However, HMF was formed mainly at the end of the baking processed. Longer baking times coupled with higher baking temperatures were shown to have a positive effect on the formation of HMF in sponge cakes (Zhang et al. 2012). This may be reasoned by the longer period for caramelization to occur, which brings about a pH shift in the matrix (slightly acidic), and therefore promotes the formation of this furanic compound. Varying mixing times, baking times, and baking temperatures have been shown to significantly impact the volatile composition of bread, and manipulation of these parameters can yield greater amounts of MR and caramelization volatile compounds (Sabovics, Straumite, and Galoburda 2014).

Volatile analysis of baked cereal products

Gas chromatography (GC)

Sensory analysis acquires useful information on the perception and acceptance of foods but cannot provide information on the compounds responsible for a given flavor perception. Therefore, combining data from both flavor chemistry and sensory science can help identify the compounds responsible for a desired aroma or taste. Gas chromatography mass spectrometry (GC-MS) is a strategic technique used in food analysis to identify potent compounds with the ability to impact on aroma perception, and this information can be used to establish the impact of processes and raw materials on the overall flavor profile, as well as help predict product quality and market acceptance (Paraskevopoulou et al. 2014). The working principle of GC is separation of analytes based on volatility and affinity to a column phase. The analytes elute depending on characteristics such as volatility, molecular weight, vapor pressure, and polarity, and are detected by Mass selective and flame ionization detectors.

To maximize the efficiency and output of the GC instrument, there are a number of aspects that require optimization depending upon the separation required. The type of column is one of the most important considerations. As seen from Table 1, a range of stationary phase columns of various polarities have been utilized in the analysis of baked cereal products. The criteria for the choice of column should suit the chemistry of the compounds extracted. Traditionally most analysis has been undertaken using one-dimensional chromatography, where a single column of selected polarity is used. However, in complex samples, volatiles may co-elute making identification and quantification difficult. The advent of two-dimensional or, comprehensive chromatography, improves separation using two columns of different polarity. In this case, all or part of the eluent of the first column is directed to a second column using modulation (thermal or flow) to create a three-dimensional output. By employing this approach, Matsakidou, Blekas, and Paraskevopoulou (2010) were able to identify 92 compounds from the volatile fraction of Madeira cake.

Flame ionization detector is a popular detector as it has sensitivity for an extensive range of organic compounds, low noise level, excellent linear range, low cost, and excellent durability (Colón and Baird 2004). However, mass spectrometry (MS) has become the detector of choice due to its selectivity, sensitivity, and versatility (Milman 2015). MS operates as a detector through the mechanism of initial molecule ionization followed by resolution of the ionized molecule based on mass-to-charge (m/z) ratio (Croissant, Watson, and Drake 2011). As a result, a mass spectra is created for each compound and therefore enables the identification of compounds in the sample through comparison of library databases and retention indexes.

Chemistry of extraction

Prior to GC analysis, it is necessary to extract volatiles from the sample of interest. Currently no analytical technique can compare to the human nose in terms of sensitivity, therefore it is necessary to concentrate the volatiles during extraction to ensure an optimum representation of the sample is attained (Kilcawley 2017). In addition, compounds responsible for aroma and flavor perception in food range from a diverse mixture of chemical classes of different molecular weight, polarity, and volatility. Hence, the application of the most suitable extraction technique is crucial for creating an accurate depiction of the volatile profile of the product. Implementation of the appropriate extraction technique needs to take into account; type of analysis (trace, target, untargeted, profiling etc.), labor intensity, robustness, flexibility, cost, sample matrix, time, and sample preparation (Ebeler, Terrien, and Butzke 2000; Hyötyläinen and Riekkola 2008). All extraction techniques have advantages and disadvantages, but also an inherent degree of bias. Extraction

Table 1. Extraction techniques utilized in the volatile analysis of baked cereal matrices.

Sample of interest	Extraction technique	Parameters employed	NaCl used in extraction	GC COLUMN	Number of volatiles extracted	Reference
Cookies	**Simultaneous distillation extraction**	**Sample:** 10 g mixed with 40 mL distilled H20 **Solvent:** Dichloromethane **Concentrated 10 times under nitrogen**	N	HP5 ***Non-polar***	14	Prost et al. 1993
Cookies	**Thermal Desorption**	**Adsorbent Material:** Not stated **Purge Time:** 3 min **Desorption Time/ Temp:** 5 mins at 240 °C **Gas/ Desorption Flow:** 200 mL Nitrogen min^{-1} **Temp of Cold Trap:** −20 °C	N	DB-5 ***Non-polar***	5 (Compounds added and recovered)	Heiderich and Reineccius 2001
Sponge Cake	**SAFE**	**Sample:** 20 g **Extraction Time:** 2 hours **Temp:** 30 °C **Solvent:** Dichloromethane	N	DB-Wax ***Polar***	19 (Compounds added and recovered)	Pozo-Bayón et al. 2006b
Sponge Cake	**SAFE**	**Sample:** 70 g mixed with 150 mL distilled H20 **Time:** 2 hours **Temp:** 30 °C **Solvent:** Dichloromethane	N	DB-Wax ***Polar***	77	Pozo-Bayón et al. 2007
Sponge Cake	**Purge and Trap**	**Adsorbent Material:** Tenax Ground cake **Temp:** 25 °C **Purging Gas:** 25 mL/min with Nitrogen **Purge times:** 5, 15, 30 and 60 min and 14 hour	N	DB-Wax ***Polar***	90	Pozo-Bayón et al. 2007
Altamura Bread	**Purge and Trap**	**Adsorbent Material:** Tenax TA **Temp:** 40 °C **Purging Gas:** 40 mL/min with helium **Purge time:** 15 mins	N	Supclowax ***Polar***	89 in crust 74 in crumb	Bianchi et al. 2008
Wheat Bread	**SPME**	**Fibre:** 75 µm DVB/ CAR/ PDMS **Extraction:** 30 mins at 35 °C (shaken with magnetic bar) Bread sample crushed	N	DB-WAX ***Polar***	46	Poinot et al. 2008
Sponge Cake	**Purge and Trap**	**Adsorbent Material:** Tenax	N	DB-Wax ***Polar***		Pozo-Bayón et al. 2008

(*continued*)

Table 1. Continued.

Sample of interest	Extraction technique	Parameters employed	NaCl used in extraction	GC COLUMN	Number of volatiles extracted	Reference
		Temp: 25 °C **Purging Gas:** 25 mL/min with Nitrogen **Purge times:** 5, 15, 30 60 min +14 h			Amylose Interaction Study (looked at 19 compounds)	
Cookies	**Simultaneous distillation extraction**	**Sample:** 100 g +400 mL distilled H20 **Solvent:** Diethyl ether-pentane	N	DB-5 ***Non-polar***	80	Mohsen et al. 2009
Sponge Cake	**SPME**	**Fibre:** 50/30 µm DVB/ CAR/ PDMS and 75 µm CAR/ PDMS and 100 µm PDMS **Extraction:** 30 mins at 50 °C	N	DB-Wax ***Polar***	49 (between 3 fibers)	Rega et al. 2009
Sponge Cake	**SPME**	**Fibre:** 50/30 µm DVB/ CAR/ PDMS **Extraction:** 60 mins at 60 °C (manual) Cake sample cryogenically ground	N	FFAP ***Polar*** and BP-5 ***Non-polar***	92	Matsakidou, Blekas, and Paraskevopoulou 2010
Oat Cake	**SPME**	**Fibre:** 85 µm CAR/ PDMS **Extraction:** 15 mins (temperature not stated)	N	DB-1701 ***Low/ Mid Polar***	36	Cognat et al. 2012
Oat Cake	**Thermal Desorption**	**Adsorbent Material:** Tenax TA **Purge Time:** 1 min **Desorption Time/ Temp:** 5 mins at 240 °C **Gas/ Desorption Flow:** 200 mL Nitrogen min^{-1} **Temp of Cold Trap:** −10 °C	N	DB1701 ***Low/ Mid-polar***	46	Cognat et al. 2012
Pineapple Breads	**SPME**	**Fibre:** 75 µm CAR/ PDMS **Extraction:** 10 mins at 40 °C	Y	DB-5 ***Non-polar***	59	Ying et al. 2012
Sponge Cake	**SPME**	**Fibre:** 75 µm DVB/ CAR/ PDMS **Extraction:** During Baking	N	DB-FFAP ***Polar***	72	Maire et al. 2013
Sponge Cake	**SPME**	**Fibre:** 75 µm CAR/ PDMS **Extraction:** 37°C for 40 mins (agitated at 600 rpm)	Y	HP-5 ***Non-polar***	31	Petisca et al. 2013
Biscuits	**SPME**	**Fibre:** 75 µm CAR/PDMS **Extraction:** 40 °C for 50 mins	Y	HP-Innowax ***Polar***	60	Pasqualone et al. 2014

(*continued*)

Table 1. Continued.

Sample of interest	Extraction technique	Parameters employed	NaCl used in extraction	GC COLUMN	Number of volatiles extracted	Reference
Triticale Bread	**SPME**	**Fibre:** 85 µm CAR/PDMS **Incubation:** 15 mins at 40 °C **Extraction:** 65 mins at 40 °C	N	Elite-WAX ETR ***Polar***	26	Sabovics, Straumite, and Galoburda, 2014
Shortbread Cookies	**SPME**	**Fibre:** 50/30 µm DVB/ CAR/ PDMS **Extraction:** 15 mins at 35 °C	N	HP-Innowax ***Polar***	24	Giarnetti et al. 2015
Biscuits	**SPME**	**Fibre:** 75 µm CAR/PDMS **Extraction:** 40 °C for 50 mins	Y	HP-Innowax ***Polar***	56	Pasqualone et al. 2015
Crackers	**Thermal Desorption**	**Extraction time/ temp:** 20 mins at 30 °C **Purge Time:** 2 min **Desorption Time/ Temp:** 5 mins and 150 °C followed by 5 mins at 300 °C Gas/ Desorption Flow: 50 mL Nitrogen min^{-1} **Temp of Cold Trap:** 30 °C	N	DB-5 ***Non-polar***	49	O'Shea, Kilcawley and Gallagher, 2017

techniques utilized to profile the aroma of baked confectionary products are as follows.

Simultaneous distillation extraction

Simultaneous distillation extraction (SDE) is one of the oldest, widely used methods of volatile extraction and is based on vapor differences over water (Veith and Kiwus 1977). This technique can recover significant amounts of volatiles of different chemical classes with good reproducibly (Chaintreau 2001). Using SDE, Prost et al. (1993) recovered 14 compounds representative of cookie odor, but the technique poorly recovered compounds such as vanillin, γ-butyrolactone, maltol, and 4-(4-hydroxyphenyl)-2-butanone, which are thought to be important constituents to the characteristic cookie odor. Mohsen et al. (2009) applied the same technique and similar parameters in analyzing wheat cookies. The authors were capable of identifying and quantifying γ-butyrolactone and maltol, as well as another 42 volatile aromatic compounds of diverse chemical classes. Although SDE has been widely used in food research, studies in baked matrices are limited. This is probably due to the elevated temperatures associated with distillation, leading to the formation of artifact compounds, particular those relating to the MR (Cai, Liu, and Su 2001; Engel, Bahr, and Schieberle 1999). In addition, solvents utilized in extraction discriminate against compounds of a similar polarity, and hence the recoveries may not provide a true representation of the sample.

Solvent-assisted flavor evaporation

Designed to overcome some of the short comings of SDE, solvent-assisted flavor evaporation (SAFE) is a well-established technique that is suitable for extraction of volatiles from a range of matrices (Drake, Miracle, and McMahon 2010; Mahajan, Goddik, and Qian 2004; Mayuoni-kirshinbaum et al. 2012; Xu, Fan, and Qian 2007). The practicality of the SAFE apparatus allows for reduced loss of highly volatile compounds as the extraction is contained within a single glassware unit and operates at lower temperatures than SDE, thus minimizing the production of artifacts (Engel et al. 1999). On correct application, this method has demonstrated a higher sensitivity than other extraction techniques for compounds related to perceived aroma (Havemose et al. 2007; Majcher and Jeleń 2009; Murat et al. 2012). However, detailed knowledge of the product composition is beneficial to the successful operation of SAFE, as components such as fat and alcohols can interfere with the extraction process (Reineccius 2007).

Pozo-Bayón et al. (2006b) investigated SAFE as a mechanism for quantifying aroma compounds in sponge cake. Nineteen aroma compounds associated with a “rich” and “sweet” character were added to a sponge cake and SAFE recovered all compounds with quantification achieved for 13. Key volatiles such as acetoin, γ-decalactone, and vanillin were quantified, highlighting the suitability of this technique for baked cereal matrices. In a similar study, Pozo-Bayón et al. (2007) employed SAFE to investigate the contribution of egg to the aroma of sponge cake. By combining the use of two extraction techniques, SAFE and Purge and Trap (P&T), the authors were capable of recovering an elaborate volatile profile of 100 compounds. Although it stated the two techniques were complimentary, SAFE had the advantage of isolating 1,2-dimethylbenzene, butan-1-ol, limonene, 2-methyl-dihydro-2(H)-furan-3-one, as well as 19 other compounds, which P&T was unable to recover. However, limitations of this technique include the tendency to favor the extraction of high molecular weight compounds (Thomsen et al. 2014). Solvent extraction techniques by nature retrieve most compounds in the sample, without accounting for the retention effect of the matrix; therefore the sample profile reflects heavier compounds that are bound in the matrix, which may not be truly representative (Kilcawley 2017). Other drawbacks include the copious amounts of solvents used during extraction, leading to the generation of hazardous waste, as well as the length of time the process requires, and the lack of automation.

Purge and trap

P&T is a headspace technique that entails purging volatiles from a sample to a highly sorbent material (usually Tenax®) where they are concentrated prior to desorption to the GC (Lee et al. 2001). Some of the attractions to this technique include: a limited sample amount, large volume traps, and a solvent free technique (Pillonel, Bosset, and Tabacchi 2002). P&T has been mainly utilized for the analysis of pollutants in water and air, but has demonstrated successful recoveries in baked cereal matrices (Table 1). Pozo-Bayón et al. (2007) utilized P&T to evaluate the aroma profile of sponge cake, of which 90 compounds were isolated. P&T was capable of identifying 2,3-butanedione (diacetyl), acetoin, 2-ethyl-5-methyl-pyrazine, and δ-decalactone, not detected in SAFE extracts. The aroma of Altumura bread was also successfully characterized using P&T where 89 volatile compounds were identified in the crust, and 78 in the crumb (Bianchi et al. 2008). Purging time is an important parameter in the optimum operation of P&T. Studies in liquid matrices have shown that increasing purging times can actually decrease the rate of compound recovery (Campillo et al. 2004; Salemi et al. 2006). When equilibrium has been reached between sample, headspace, and sorbent material, the sorbent material reaches its full capacity and continuation of purging gas after this point can result in the loss of volatiles.

As seen in Table 1, Pozo-Bayón et al. (2007) utilized a range of different purging times and found 14 hours to be the most effective in extracting volatile compounds from a sponge cake. Similarly, long purging times were effective in studying the interaction of amylose with aroma compounds in a sponge cake (Pozo-Bayón et al. 2008). However, Bianchi et al. (2008) applied a purging time of 15 minutes and retrieved an ample profile of compounds from Altumura bread, comparable to that of Pozo-Bayón et al. (2007).

Complications with this technique can include (i) contamination of the sorbent material from samples (Schmidt 2003), (ii) moisture control, (iii) the catalytic activity occurring on the adsorbent, which can lead to the generation of artifacts compounds (Pillonel et al. 2002), and similarly to SAFE, the length of time needed preform the technique.

Thermal desorption

Similar to the development of P&T, Thermal Desorption (TD) was designed for the analysis of air borne volatiles (Wauters et al. 1979). However, TD is now also widely used to extract aroma compounds from food. The sample is usually incubated and the volatiles are purged dynamically to pre-packed absorbent tubes (usually containing Tenax, or other absorbents such as charcoal or silica gel). The tubes are heated and the volatiles are directly injected into the GC, or further concentrated prior to transfer to the GC. Enhanced sensitivity and efficiency of reusable adsorbent tubes are a significant benefit, but the main appeal is the large adsorption capacity of the tubes (Madruga et al. 2009; Ramírez et al. 2010). This technique has been successful in extracting esters from cookies (Heiderich and Reineccius 2001), characterizing crackers supplemented with barley (O'Shea, Kilcawley, and Gallagher, 2017), as well as differentiating fresh and rancid oat cakes by their volatile profile (Cognat et al. 2012). The main disadvantage associated with TD is moisture control (Pillonel et al. 2002), which may explain the lack of studies utilizing this technique. However, it may be suitable for low moisture biscuit and cookie products, flours etc.

Headspace solid-phase microextraction

Solid-phase microextraction (SPME) is widely utilized for the analysis of volatiles in foods (Cuevas-Glory et al. 2007; Frank, Owen, and Patterson 2004; Ruiz et al. 1998), mainly because it is highly automatable with good reproducibility. The working principle of SPME involves a fused silica fiber that is coated with a stationary phase. The phase can be composed of multiple materials of different polarity to assist in extraction of a wide range of compounds or of single phases for targeted extraction of specific chemical classes, which is accomplished based on polarity, volatility, or molecular weight. The most common types of fibers utilized in literature are comprised of a multi-phase, consisting of a molecular sieve Carboxen (CAR), polar divinylbenzene (DVB), non-polar polydimethylsiloxane (PDMS), or a single phase polyacrylate (PA), which targets very polar analytes. The main application of SPME is in head-space (HS) analysis, where the fiber is exposed to the HS above the sample in a sealed container/vial. Consequently, the volatiles are adsorbed or absorbed onto the fiber through gentle agitation (Kataoka, Lord, and Pawliszyn 2000).

HS-SPME is the most popular technique for volatile extraction of foods, especially in baked cereal analysis (see Table 1). As well as being automatable, HS-SPME is an attractive extraction technique due to the simplicity of sample preparation, solvent free, relatively low cost, and can be targeted towards a wide range of chemical classes (Afoakwa et al. 2009). Rega et al. (2009) evaluated the efficacy of three fibers (50/30 µm DVB/CAR/PDMS, 75 µm CAR/PDMS and 100 µm PDMS) to obtain a representative profile for sponge cake and found that the 50/30 µm DVB/CAR/PDMS extracted the largest quantity of volatile compounds (See Table 2) and the 75 µm CAR/PDMS was capable of isolating high boiling point compounds. It is essential that the appropriate parameters; extraction time, extraction temperature, suitable fiber for compounds of interest, and sample size, are taken into account to ensure optimum results are obtained in SPME analysis (Kataoka et al. 2000).

HS-SPME has been widely utilized for baked cereal products (Cognat et al. 2012; Giarnetti et al. 2015; Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Pasqualone et al. 2014; 2015; Petisca et al. 2013; Poinot et al. 2007; Raffo et al. 2015; Rega et al. 2009; Sabovics et al. 2014; Ying et al. 2012). Poinot et al. (2007) trialed 27 HS-SPME conditions varying in extraction time, extraction temperature and SPME fiber, to optimize the extraction of volatile compounds most representative of bread odor. By permitting a panel of trained judges to compare the odor qualities of collected HS-SPME volatile extracts, the authors were able to conclude that an extraction time of 30 and 60 minutes at 35 °C, using either 50/30 µm DVD/CAR/PDMS or a 75 µm CAR/PDMS fiber, can yield a volatile profile representative of bread odor. Raffo et al. (2015) found an extraction time of 60 minutes at 50 °C (under agitation) with a DVD/CAR/PDMS fiber beneficial for providing a complete volatile profile of wheat bread. Through preliminary work, Matsakidou, Blekas, and Paraskevopoulou (2010) also identified a 60 minute extraction time at 60 °C favorable for the recovery of volatiles representative of cake odor. It is likely that the extensive extraction time and relatively higher extraction temperature contributed to the wide range of volatile compounds identified (92 compounds). Shortbread cookies were examined with a 50/30 µm DVD/CAR/PDMS fiber for 15 minutes at 35 °C, enabling the recovery and identification of 24 volatile compounds (Giarnetti et al 2015). This result seems rather low compared to Mohsen et al. (2009) who were able to identify 42 compounds in cookies using the SDE technique. Pasqualone et al. (2014) utilized a 75 µm CAR/PDMS fiber for the extraction of compounds from biscuits (enriched with grape marc extract) at 40 °C for 50 minutes, and yielded 60 compounds from a wide range of chemical classes; alcohols, aldehydes, ketones, esters, furans etc. The authors employed the same parameters to analyze biscuits enriched with purple wheat, yielding a similar result of 56 compounds (Pasqualone et al. 2015). However, the authors did consider that this fiber was more sensitive to compounds arising from LO, meaning, perhaps the profile depicted by these extraction conditions, was not a true representative of the sample.

On-line extraction of volatile compounds during the baking of sponge cake has been accomplished with SPME (Maire et al. 2013; Rega et al. 2009). By assembling a glass inlet hood from the oven to a refrigerated extraction chamber, volatile compounds generated during baking were captured at different stages throughout the baking process. Utilising this technique, Rega et al. (2009) monitored the development of compounds associated with LO, and the MR, at different time points. By employing the same technique, Maire et al. (2013) demonstrated how varying the flow rate of vapors from the chamber during baking impacted on the extraction of very volatile and semi-volatile compounds. A flow rate of 7.5 L min^{-1} at 40 °C enabled the extraction of a higher volume of compounds and was particularly beneficial in extracting semi volatiles such as pyrans and furans, however, 1 L min^{-1} at 10 °C yielded the extraction of very volatile compounds.

The major downside to SPME is the limited capacity of the fiber. This leads to competition on the fiber and results in the compounds with a higher affinity for the fiber phase displacing more volatile compounds. Fragility of the SPME fiber and the possible carryover of compounds are also potential issues associated with SPME as an extraction technique (Prosen and Zupančič-Kralj 1999).

Potent aroma volatile compounds in baked confectionary

As baked confectionary products exhibit similar formulations and baking procedures, their qualitative volatile profiles can be similar. However, the ratio of individual volatiles will vary significantly, thus impacting on consumer's perceptions (Table 3). The following covers the key volatile classes associated with baked confectionary products.

Aldehydes

On consumption of baked confectionary products, the perception of "sweet" is un-doubtfully one of the initial attributes perceived during mastication, inherently due to the volume of nonvolatile sucrose present in product formula. However, retronasal olfaction perception of 'sweet' can also result from specific aldehydes, such as benzaldehyde and phenylacetaldehyde, which are associated with "almond", "cherry", "honey", and "floral" notes in biscuit, cookies and cakes (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Mohsen et al. 2009; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009). Egg yolk provides an abundance of amino acids and when subject to the high temperatures of baking, Strecker degradation occurs, resulting in aldehyde formation. Both benzaldehyde and phenylacetaldehyde are products of Strecker degradation of the amino acid phenylalanine (Chu and Yaylayan 2008). 2-Methylpropanal, 3-methylbutanal, and 2-methylbutanal are also Strecker aldehydes considered important to the aroma of baked goods and derive from valine, leucine, and isoleucine, respectively. 2-Methylpropanal has been described as 'sweet', 'mint', and 'floral' by gas chromatography-olfactory (GC-O) evaluation of cakes (Pozo-Bayón et al. 2007; Rega et al, 2009; Maire et al. 2013), whereas 3-methylbutanal and 2-methylbutanal yield a more 'chocolate', "malty" aroma in baked confectionary, with concentrations particularly high in the crust of cakes (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Pozo-Bayón et al. 2007). "Fatty" and "fruity" odors in cake and biscuits derive from aliphatic aldehydes such as octanal, nonanal and decanal (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010;

Table 2. Comparison of different SPME fibers utilized in the volatile extraction of sponge cake (Rega et al. 2009).

Compound	CAR/ PDMS	PDMS	DVB/ CAR/ PDMS
2-Methylpropanal	x		
2-Methylbutanal	x		x
3-Methylbutanal	x	x	x
2-Pentanone	x		x
2,3-Pentanone	x	x	x
Hexanal	x		x
Heptanal	x		x
2-Pentylfuran	x		x
Pentanol	x		x
2-Methylpyrazine	x		x
Octanal	x	x	x
1-Hydroxy-2-propanone	x		x
2,5-Dimethylpyrazine	x	x	x
2,6-Dimethylpyrazine			x
2,3-Dimethylpyrazine	x		x
Nonanal	x		x
Trimethylpyrazine	x	x	x
(E)-2-octenal	x		x
1-octen-3-ol	x		x
Acetic Acid	x	x	x
Furfural	x		x
Decanal	x		x
Benzaldehyde	x		x
(E)-2-nonenal			x
Octanol	x		x
Undecanal	x		x
Acetylpyrazine	x		x
Phenylacetaldehyde	x		x
Butyric Acid	x		x
Furfuryl alcohol	x		x
Nonanol	x		x
Dodecanal	x		x
2-Undecanal	x	x	x
(E,Z)-2,4-Decadienal	x		x
(E,E)-2,4-Decadienal	x		x
Hexanoic acid	x		x
Dimethylsulfone	x		x
2-Acetylpyrrole	x		x
Maltol			x
Pentadecane-2-one			x
Furaneol	x	x	x
Octanoic Acid	x		x
Tetradecanol		x	x
Nonanoic Acid	x		x
2,3-Dihydro-3,5-dihydroxy-6-methyl- 4(H)-pyran-4-one	x	x	x
5-Hydroxymethylfurfural	x	x	x

Mohsen et al. 2009; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009), whose presence is as of result of the auto-oxidation of linoleic or oleic acid (Fullana, Carbonell-Barrachina, and Sidhu, 2004; Whitfield and Mottram 1992). Similarly, hexanal, heptanal, and 2,4-decadienal, markers of auto-oxidation of linoleic acid (Fujisaki, Endo, and Fujimoto 2002), have been reported in bakery products as imparting a "fruity", "herbal", "fresh cut grass" aroma (Giarnetti et al. 2015; Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Mohsen et al. 2009; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009). Methional has been identified as a key contributor to the "roasty" smell of baguettes (Zehentbauer and Grosch 1998a), and is generated from the Strecker degradation of the amino acid methionine (Escudero et al. 2000). Methional contributes a "dusty", "potato-like" odor and is perceived at very low levels in cake products (Maire et al. 2013; Pozo-Bayón et al. 2007; Rega et al. 2009).

Alcohols

Quite a number of alcohols have been identified in cake and biscuit/cookie products (Table 3). As mentioned, LO of the fat promotes the generation of alcohols through degradation of unsaturated fatty acids, particularly polyunsaturated fatty acids due to the presence of multiple double bonds. Depending on the fatty acid, and the point of cleavage, various alcohols of different odor qualities can be produced. Alcohols positively associated with baked confectionary aroma include fatty 2-ethylhexanol, 1-octanol, 1-nonanol, and 1-decanol, identified as having odor qualities described as "orange", "rose", and "sweet" (Maire et al. 2013; Mohsen et al. 2009; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009). Other odor descriptions include "cauliflower", "cardboard", "mushroom/fungal", and are associated with alcohols; 1-pentanol, 1-hexanol, and 1-octen-3-ol, respectively (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009). Linoleic acid is prone to oxidation and thus yields 1-hexanol and 1-octen-3-ol (Paraskevopoulou, Chrysanthou, and Koutidou 2012). Although these compounds may be perceived as unpleasant at high concentrations, in relatively low concentrations they add to the overall dynamic of baked and cereal products, with 1-octen-3-ol identified as a key compound in oat flakes (Klensporf and Jeleń 2008).

Flour is also identified as a contributor to the alcohol profile of baked confectionary (Maire et al. 2013). The process of milling induces the release of free fatty acids and propagates LO reactions, as well as microbial degradation to produce alcohols (Hansen and Hansen 1994). Wheat flour starch has shown to have high levels of 2-ethylhexanol, a degradation product of LO (Sayaslan et al. 2000). This corresponds to Pozo-Bayón et al. (2007) and Maire et al. (2013) identifying this compound in the dough of sponge cakes, indicating this compound originates from the raw material, but formation is potentially promoted during baking preparation.

Ketones

Ketones are generally associated with favorable aromas. The MR and caramelization can contribute some of the most characteristic volatile compounds associated with bakery products. The decomposition of sugar results in diketones such as 2,3-butanedione (diacetyl) and 2,3-pentadione, responsible for "buttery", "caramel", and "butterscotch" notes in sweetened baked goods (Giarnetti et al. 2015; Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Mohsen et al. 2009; Pasqualone et al. 2014; 2015; Pozo-Bayón et al, 2007). As previously mentioned the methyl ketones, 2-butanone, 2-heptanone, 2-nonanone, and 2-undecanone have been identified in cookies (Giarnetti et al. 2015) and are associated with "buttery" and "sweet" attributes. These compounds are generated from β-keto acids in milk fat when exposed to heating (Wong and Patton 1962), and contribute to the aroma of butter (Mallia et al. 2008).

Table 3. Volatile compounds identified in baked confectionary products.

Compound	Odour description	Product	Reference
Alcohols			
Ethanol		Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015
Propanol		Biscuit/Cookie	Pasqualone et al. 2014
Butanol		Cake, Biscuit/Cookie	Pasqualone et al. 2014 Pozo-Bayón et al. 2007
1-Pentanol	Foot, cauliflower, pungent, fusel oil,	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
1-Hexanol	Cardboard, solvent, potatoes, fruity, sweet, green	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
Heptanol	Musty, leafy, violet, herbal, green, sweet, fresh, woody	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
2-Ethylhexanol	Citrus, fresh, floral, oily	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pozo-Bayón et al. 2007
4-Hexen-1-ol		Biscuit/Cookie	Pasqualone et al. 2015
2-Octanol		Cake	Pozo-Bayón et al. 2007
2-Butoxyethanol		Cake	Pozo-Bayón et al. 2007
1-Methoxy-2-propanol		Cake	Pozo-Bayón et al. 2007
1-Octen-3-ol	Mushroom, musty,fungal, earthy	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
2,6-Dimethyl-2,7-octadien-1,6-diol		Cake	Matsakidou et al. 2010
1-(2-Methoxypropoxy)-2-propanol		Cake	Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
1-Octanol	Waxy, green, orange, aldehydic, fatty, rose	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
1-Nonanol	Fresh, clean, fatty, floral, rose, orange, dusty, wet,	Cake, Biscuit/Cookie	Maire et al. 2013 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Decanol	Floral, fatty, orange, sweet, clean, watery	Cake	Maire et al. 2013
Dodecanol	Earthy, soapy, waxy, fatty, honey, coconut	Cake	Maire et al. 2013
Octadecanol		Cake	Maire et al. 2013
1-Penten-3-ol		Cake	Matsakidou et al. 2010
α-Terpineol		Cake	Pozo-Bayón et al. 2007
Borneol		Cake	Pozo-Bayón et al. 2007
1-(2-butoxyethoxy)ethanol		Cake	Pozo-Bayón et al. 2007
Benzyl alcohol		Cake, Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
2-Phenylethanol		Cake, Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
Hexadecanol	Waxy, floral	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007
Tetradecanol		Cake	Rega et al. 2009
2-Methylcyclopentyl alcohol		Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015
Aldehydes			
Acetaldehyde	Pungent, fresh, aldehydic, refreshing, green	Cake	Maire et al. 2013 Matsakidou et al. 2010

(continued)

Table 3. Continued.

Compound	Odour description	Product	Reference
2-Methylpropanal	Fresh, sweet, mint, floral	Cake, Biscuit/Cookie	Maire et al. 2013 Mohsen et al. 2009 Pozo-Bayón et al. 2007 Rega et al. 2009
2-Methylbutanal	Musty, cocoa, coffee, nutty,malty	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
3-Methylbutanal	Chocolate, ethereal, aldehydic, peach, fatty, malty	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Pentanal		Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015
2-Pentenal		Biscuit/Cookie	Mohsen et al. 2009
Hexanal	Floral, fruity, herbal, cut grass, green, sweaty	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Methional	Musty, tomato, potato,earthy, vegetable, creamy	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007 Rega et al. 2009
(*E*)-2-Hexenal		Biscuit/Cookie	Mohsen et al. 2009, Pasqualone et al. 2014 Pasqualone et al. 2015
3-Hexenal		Biscuit/Cookie	Mohsen et al. 2009
Heptanal	Fresh, green, sweet, herbal	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
(E)-2-Heptenal		Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2014 Pasqualone et al. 2015
(Z)-4-Heptenal		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Mohsen et al. 2009
Octanal	Floral, citrus, fruit, orange peel	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
(*E*)-2-Octenal	Fried, Fatty, Unpleasant	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pozo-Bayón et al. 2007 Rega et al. 2009
Benzaldehyde	Sweet, bitter, almond, sharp, cherry	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al,2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Phenylacetaldehyde	Rose, honey, floral, flowers, sweet, cocoa	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Nonanal	Aldehydic, waxy, citrus, orange, green, peel	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010

(*continued*)

Table 3. Continued.

Compound	Odour description	Product	Reference
			Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
2-Nonenal	Vegetable, solvent, floral, musty, cucumber, green	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2015 Rega et al. 2009
(*E,E*)-2,4-Heptadienal	Fatty, green, oily, aldehydic, cake, cinnamon	Cake, Biscuit/Cookie	Maire et al. 2013 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015
Decanal	Floral, fruity, sweet, waxy, orange, peel, citrus	Cake	Maire et al. 2013 Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
(*E*)-2-Decenal	Waxy, fatty, earthy, coriander, green, mushroom	Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Pasqualone et al. 2015
(*E,E*)-2,4-Decadienal	Rice, cooked, baked, fried potato, fatty, pumpkin nut, meat	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
(E,Z)-2,4-Decadienal	Fried oil, cooked, fatty, geranium, green	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007 Rega et al. 2009
2,4-Nonadienal		Biscuit/Cookie	Pasqualone et al. 2015
(*E,E*)-2,4-Nonadienal		Biscuit/Cookie	Mohsen et al. 2009 Pasqualone et al. 2014
2-Dodecanal	Vegetable, floral, fatty, clean	Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2014 Pasqualone et al. 2015 Rega et al. 2009
2-Undecanal	Floral, bud, soapy, citrus, green, fatty, fresh laundry	Cake	Maire et al. 2013 Rega et al. 2009
Methylbenzaldehyde		Cake	Pozo-Bayón et al. 2007
Tridecanal	Fresh, clean, soapy, citrus, petal, waxy, grapefruit peep	Cake	Maire et al. 2013
Octadecanal	Oily	Cake	Maire et al. 2013
Vanillin	Sweet, vanilla, creamy, chocolate	Cake	Maire et al. 2013
Pyrazines			
Pyrazine		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Mohsen et al. 2009
Methylpyrazine		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al. 2010 Mohsen et al2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
2,5-Dimethylpyrazine	Solvent, hospital, perfumed rice, cake crust	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
2,6-Dimethylpyrazine	Cake, roasted, bread crust, rice, walnut, praline	Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
Ethylpyrazine		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Pasqualone et al. 2014 Pozo-Bayón et al. 2007
2,3-Dimethylpyrazine	Earthy, potatoes, green pea, perfumed rice, cake, crust, nutty, peanut butter, walnut, caramel, leather	Cake	Maire et al. 2013 Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
2-Ethyl-6-methylpyrazine	Roasted, burnt	Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007

(*continued*)

Table 3. Continued.

Compound	Odour description	Product	Reference
			Rega et al. 2009
2-Ethyl-5-methylpyrazine		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Rega et al. 2009
Trimethylpyrazine	Herbal, earthy, potatoes, roasted, cake	Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
Vinylpyrazine		Cake	Pozo-Bayón et al. 2007
3-Ethyl-2,5-dimethylpyrazine		Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Mohsen et al. 2009
2-Ethyl-3,5-dimethylpyrazine		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Pozo-Bayón et al. 2007
2-Methyl-6-vinylpyrazine	Vegetables, potato	Cake	Pozo-Bayón et al. 2007
2-Methyl-5-vinylpyrazine		Cake	Pozo-Bayón et al. 2007
3,5-Diethyl-2-methylpyrazine		Cake	Pozo-Bayón et al. 2007
Dimethyl-2-vinylpyrazine (isomer)	Pungent, herbal, potatoes	Cake	Pozo-Bayón et al. 2007
Acetylpyrazine	Hazelnut, praline, cake	Cake	Pozo-Bayón et al. 2007 Rega et al. 2009
2-Methyl-5-(2-propenyl)-pyrazine		Cake	Matsakidou et al. 2010
2-Acetyl-5-methylpyrazine		Cake	Pozo-Bayón et al. 2007
2-Acetyl-6-methylpyrazine		Cake	Pozo-Bayón et al. 2007
Benzopyrazine		Cake	Pozo-Bayón et al. 2007
Ketones			
Acetone		Biscuit/Cookie	Giarnetti et al. 2015
2,3-Butanedione (Diacetyl)	Butter, fruity, caramel, butterscotch	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pozo-Bayón et al. 2007
2-Butanone		Biscuit/Cookie	Giarnetti et al. 2015 Mohsen et al. 2009 Pasqualone et al. 2015
2-Pentanone		Cake, Biscuit/Cookie	Mohsen et al. 2009 Pasqualone et al. 2015 Rega et al. 2009
2,3-Pentanedione	Pungent, sweet, butter, creamy, caramel, nutty	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pozo-Bayón et al. 2007 Rega et al. 2009
Hydroxyacetone (1-Hydroxy-2-propanone)		Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Acetoin (3-Hydroxy-2-butanone)		Cake, Biscit/Cookie	Giarnetti et al. 2015 Pozo-Bayón et al. 2007
2-Heptanone		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
1-Octen-3-one	Herbal, mushroom, earthy, musty	Cake	Maire et al. 2013
2-Octanone		Cake	Matsakidou et al. 2010 Rega et al. 2009
3-Octen-2-one		Cake	Matsakidou et al. 2010
2-Nonanone		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al. 2010 Pozo-Bayón et al. 2007
2-Decanone		Cake	Maire et al. 2013 Matsakidou et al. 2010 Pozo-Bayón et al. 2007
2,3-Methyloctanone		Cake	Matsakidou et al. 2010 Rega et al,2009
2-Pentadecanone		Cake	Rega et al. 2009
2-Undecanone		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al. 2010
2-Dodecanone		Cake	Matsakidou et al. 2010
6-Methyl-5-hepten-2-one		Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007
(*E*,*E*)-3,5-Octadiene-2-one		Cake, Biscuit/Cookie	Pozo-Bayón et al. 2007 Mohsen et al.,2009 Pasqualone et al.,2015

(*continued*)

Table 3. Continued.

Compound	Odour description	Product	Reference
Acetophenone		Cake	Pozo-Bayón et al. 2007
Acids			
Acetic acid	Unpleasant, earthy, sharp, pungent, sour, vinegar	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Formic acid	Pungent, vinegar	Cake	Maire et al. 2013
Propanoic acid		Biscuit/Cookie	Pasqualone et al. 2015
Butanoic acid	Sweat, fish, unpleasant	Cake, Biscuit/Cookie	Mohsen et al. 2009 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Pentanoic acid		Cake	Pozo-Bayón et al. 2007
Hexanoic acid	Mild, sour, fatty, sweat, cheese, rancid	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Heptanoic acid		Cake	Pozo-Bayón et al. 2007
Octanoic acid	Fatty, acid, sour	Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
2-Hexenoic acid		Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2015
2,4-Hexadienoic acid		Biscuit/Cookie	Giarnetti et al. 2015 Pasqualone et al. 2014 Pasqualone et al. 2015
Nonanoic acid	Waxy, dirty, cheese, cultured dairy	Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Decanoic acid	Unpleasant, rancid, sour, fatty, citrus	Cake, Biscuit/Cookie	Maire et al. 2013 Mohsen et al. 2009 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
Dodecanoic acid	Fatty, coconut, bay oil	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007
Benzoic acid	Faint, balsm	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007
Dodecanoic acid	Fatty, coconut, bay oil	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007
Hexadecanoic acid	Slightly fatty, waxy	Cake	Maire et al. 2013
Furans			
2-Methylfuran	Sweet, pungent, caramel, burnt	Biscuit/Cookie	Pasqualone et al. 2014
2-Pentylfuran	Earthy, vegetable, beany, metallic	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Dihydro-2-methyl-3(2H)-furanone	Roasted, biscuit, hazelnut, nutty	Cake, Biscuit/Cookie	Mohsen et al. 2009 Pozo-Bayón et al. 2007
Furaneol (Strawberry Furanone)	Caramel-like, spice, cake, sweet, cotton candy, strawberry, sweet, fruity	Cake, Biscuit/Cookie	Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Rega et al. 2009
2-Furanmethanol	Sweet caramel, burnt	Cake, Biscuit/Cookie	Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009
Furfural	Earthy, potatoes, green pea, parfumed rice, cake, crust, sweet, woody, almond, fragrant, bready	Cake, Biscuit/Cookie	Giarnetti et al. 2015 Maire et al. 2013 Matsakidou et al. 2010 Mohsen et al. 2009 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007 Rega et al. 2009

(*continued*)

Table 3. Continued.

Compound	Odour description	Product	Reference
2-Acetylfuran	Sweet, balsam, almond, cocoa, caramel, coffee	Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2014 Pozo-Bayón et al. 2007
5-Hydroxymethylfurfural (HMF)	Fatty, musty, waxy, caramel	Cake, Biscuit/Cookie	Maire et al. 2013 Pasqualone et al. 2015 Rega et al. 2009
5-Methylfurfural	Biscuit, chocolate, roasted, cake, spice, caramel, maple	Cake, Biscuit/Cookie	Maire et al,2013 Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
2-Ethyl-5-methylfuran		Biscuit/Cookie	Mohsen et al. 2009
5H-furan-2-one		Cake, Biscuit/Cookie	Giarnetti et al,2015 Matsakidou et al. 2010 Pozo-Bayón et al. 2007
Alkanes			
Octane	Gasoline	Cake	Maire et al. 2013
Decane		Cake	Matsakidou et al. 2010
Dodecane	Alkane	Cake	Maire et al. 2013
Hexadecane		Cake	Maire et al. 2013
Tridecane		Cake	Matsakidou et al. 2010
Tetracosane		Cake	Maire et al. 2013
Tetradecane	Mild Waxy	Cake	Maire et al. 2013 Matsakidou et al. 2010
Pentadecane	Waxy	Cake	Maire et al. 2013
Esters			
Ethyl Acetate		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Pasqualone et al. 2014 Pasqualone et al. 2015
Butyl Acetate		Cake	Matsakidou et al. 2010
Ethyl Butanoate		Cake	Pozo-Bayón et al. 2007
Ethyl Hexanoate	Vegetable, floral, fruity	Cake	Pozo-Bayón et al. 2007
2-Ethylhexanoic acid		Cake	Pozo-Bayón et al. 2007
Methyl Benzoate		Biscuit/Cookie	Pasqualone et al. 2015
Ethyl Benzoate		Biscuit/Cookie	Pasqualone et al. 2015
Methyl Decanoate		Biscuit/Cookie	Pasqualone et al. 2015
Methyl Dodecanoate		Biscuit/Cookie	Mohsen et al. 2009
Ethyl Decanoate		Biscuit/Cookie	Mohsen et al. 2009
Isopropyl Tetradecanoate		Cake	Pozo-Bayón et al. 2007
Ethyl Octanoate	Fruity, wine, waxy, sweet, apricot, banana, brandy	Cake	Maire et al. 2013
Lactones			
γ-Butyrolactone		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Mohsen et al. 2009 Pozo-Bayón et al. 2007
γ-Hexalactone		Cake	Pozo-Bayón et al. 2007
γ-Octalactone		Cake	Pozo-Bayón et al. 2007
γ-Nonalactone		Cake	Pozo-Bayón et al. 2007
γ-Decalactone		Cake	Pozo-Bayón et al. 2007
δ-Decalactone		Cake, Biscuit/Cookie	Mohsen et al2009. Pozo-Bayón et al. 2007
Sulfur Compounds			
Dimethyl Disulphide	Sulfurous, vegetable, cabbage, onion	Cake	Maire et al. 2013 Pozo-Bayón et al. 2007
Dimethyl Trisulfide	Solvent, gas, wastewater, pungent	Cake	Pozo-Bayón et al. 2007
Dimethyl Sulfone		Cake	Pozo-Bayón et al. 2007
2-Acetyl-2-thiazoline		Cake	Pozo-Bayón et al. 2007 Rega et al. 2009
2-Acetylthiazole	Hazelnut, popcorn	Cake	Matsakidou et al. 2010 Pozo-Bayón et al. 2007
Benzothiazole		Biscuit/Cookie	Pasqualone et al. 2014
Aromatic Hydrocarbons			
Toulene		Cake	Maire et al. 2013
Pentylbenzene		Biscuit/Cookie	Pasqualone et al,2014
2-Methyl-propenylbenzene		Biscuit/Cookie	Pasqualone et al. 2014
Hexylbenzene		Biscuit/Cookie	Pasqualone et al. 2014
Octylbenzene		Biscuit/Cookie	Pasqualone et al. 2014
Phenolic Compounds			
Phenol		Cake, Biscuit/Cookie	Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007
2-Methoxyphenol (Guaiacol)		Cake	Pasqualone et al. 2014 Pasqualone et al. 2015 Pozo-Bayón et al. 2007

(*continued*)

Table 3. Continued.

Compound	Odour description	Product	Reference
2-Methoxy-4-vinylphenol		Cake	Pozo-Bayón et al. 2007
Pyrroles			
1-H-Pyrrole		Cake, Biscuit/Cookie	Matsakidou et al. 2010 Mohsen et al2009
2-Acetylpyrrole		Cake	Matsakidou et al. 2010 Mohsen et al2009 Pozo-Bayón et al. 2007, Rega et al. 2009
2-Acetyl-1-pyrroline	Popcorn	Biscuit/Cookie	Mohsen et al. 2009
Terpenes			
Verbenone		Cake	Pozo-Bayón et al. 2007
D-Limonene		Cake, Biscuit/Cookie	Giarnetti et al. 2015 Matsakidou et al,2010 Pasqualone et al. 2014 Pozo-Bayón et al. 2007
Pyran			
2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one		Cake, Biscuit/Cookie	Maire et al,2013 Matsakidou et al. 2010 Mohsen et al. 2009 Rega et al. 2009
Maltol	Caramel, sweet, cotton candy, jam, fruity	Cake	Maire et al. 2013 Matsakidou et al. 2010 Rega et al. 2009
Pyridines			
N-acetyl-4(H)-pyridine	Walnut, popcorn	Cake	Matsakidou et al. 2010
Lactams			
N-Methyl-2-pyrrolidine(NMP)		Cake	Pozo-Bayón et al. 2007

Pyrazines

Similar to wheat bread, cake is composed of a crust and a crumb that are distinguishable by the quantitative differences of their volatile profile. The crust of cake is a concentrated source of thermal reactions, and therefore generates a greater quantity of heat derived compounds such as pyrazines; compounds responsible for the "roasted", "caramel", and "nutty" odors in baked confectionary. Pyrazines are formed through the Strecker degradation of α-aminoketones during the high temperatures of baking, with formation being promoted in an alkaline pH (Jousse et al. 2002). A range of pyrazines have been identified in the crust and crumb of cakes (see Table 3), with 2,5-dimethylpyrazine, 2,6-dimethlypyrazine, 2,3-dimethylpyrazine, trimethylpyrazine, and 2-methyl-6-vinylpyrazine having high odor activity and noted to be the main contributors to the characteristic "roasty" and "perfumed rice" aroma of sponge cake (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Pozo-Bayón et al. 2007; Rega et al. 2009). Some pyrazines have high odor thresholds, thus requiring their concentration to be quite high before their "roasty", "nutty" aroma can be perceived in cereal products (Bredie et al. 1998). "Biscuit like" 2-ethyl-5-methylpyrazine has been identified in cookies (Mohsen et al. 2009), as well as odor active 2,5-dimethylpyrazine and trimethylpyrazine (Giarnetti et al. 2015). It appears the abundance of pyrazine compounds is not as prominent in biscuits and cookies, compared to that of cake (Table 3). However, this could be a repercussion of the extraction technique and parameters taken to isolate these compounds (Pasqualone et al. 2015), thus more research is required to understand pyrazine contribution to biscuit/cookie aroma.

Furans

Furan and its derivatives are widespread in foods and beverages, with quantities present depending on heat exposure. These compounds generate interest due to their ability to thrive in low moisture systems, with formation favored in acidic environments (Kroh 1994). The low moisture content of biscuit/cookie structures accelerates caramelization and Maillard reactions, enhancing the concentration of furans (Ameur et al. 2007). Similar to pyrazines, the crusts of cakes reflect higher concentrations of furan compounds compared to the crumb (Matsakidou, Blekas, and Paraskevopoulou 2010; Pozo-Bayón et al. 2007). Furans have low odor thresholds and significantly contribute to the delicate aroma of bakery products. Fresh biscuits have been associated "sweet", "toasted", and "caramel" attributes (Heenan et al. 2009), elucidated by the presence of furfural and HMF. Furanic compounds are described as the most potent compounds in biscuits and cookies, yielding a desirable "bready", "almond", "pungent", and "sweet" aroma (Giarnetti et al. 2015; Mohsen et al. 2009; Pasqualone et al. 2014; 2015). Pyrolysis of hexose and pentose induce the formation of HMF and furfural, respectively (Petisca et al. 2014). Levels of furans have been shown to be significantly higher in fresh cookies compared to those after storage (Mohsen et al. 2009), demonstrating their importance in cookie aroma. Furaneol, 2-pentylfuran, and 2-furanmethanol have been identified in high amounts in the crust and crumb of sponge cakes (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Rega et al. 2009). Furaneol significantly contributes to sweet tasting fruits such as strawberries and pineapples, contributing a sweet taste and "burnt sugar", "caramel" aroma (Chen and Sidisky 2011; Elss et al. 2005; Sanz, Richardson, and Pérez 1995). Lipoxygenase-catalysed oxidation of linoleic acid can produce 2-pentylfuran which is associated with an “earthy” “beany” aroma (Vara-Ubol, Chambers, and Chambers 2004). Oxidation of flour lipids can also contribute to levels of 2-pentyl furan (Birch, Petersen, and Hansen 2013). “Caramel-like” aroma derives from 2-furanmethanol, a compound associated with products exposed to high temperatures, with significant levels identified in coffee and chocolate (Afoakwa et al. 2009; Nebesny et al. 2007). It is apparent that furan and its derivatives are important to the perceived aroma of baked confectionary products.

Other compounds

Although the above chemical classes may dominate the profile of baked confectionary, many others can impact greatly on the perceived aroma of cakes, biscuits and cookies. Maltol, a pyran compound, is considered important to the aroma of cakes (Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Rega et al. 2009), yielding a “cotton candy” odor at low concentrations. This compound is a well-known product of the MR, with 2,3-dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one acting as a precursor (Yaylayan and Mandeville 1994). N-Acetyl-4(H)-pyridine and 2-acetylthiazole have been identified in cake crust and associated with a “walnut”, “hazelnut”, “popcorn” aroma (Matsakidou, Blekas, and Paraskevopoulou 2010), where 2-acetyl-1-pyrroline yields a “popcorn aroma” and has been identified in cookies (Mohsen et al. 2009). This compound is known to give rice its characteristic aroma (Buttery et al. 1983). Ethyl esters of fatty acids, ethyl octanoate, and ethyl hexanoate, have also been identified in cake (Maire et al. 2013; Pozo-Bayón et al. 2007) and offer “sweet”, “apricot”, “floral”, and “fruity” notes.

Baked confectionary in general are associated with having pleasant aroma, however, depending on ingredient preparation, or thermal processes, unfavorable compounds with low odor threshold can form. Although present in low quantities, carboxylic acids can be detected in baked confectionary ranging in a variety of unpleasant odors (Table 3). Hexanoic acid, octanoic acid, and nonanoic acid, auto-oxidation products of their corresponding aldehydes (Paradiso et al. 2008), have been identified in cakes, biscuits, and cookies (Giarnetti et al. 2015; Maire et al. 2013; Matsakidou, Blekas, and Paraskevopoulou 2010; Pasqualone et al. 2014; 2015; Pozo-Bayón et al. 2007; Rega et al. 2009) and yield a “fatty”, “rancid”, “cheese” aroma, risking deterioration to the sensory properties of these products. LO is the main precursor of off flavors and taints in many foods; therefore it is optimum to manage the cascade of reactions to retain the desirable aroma and flavor of bakery products (Maire et al. 2013).

Relating volatile compounds to sensory data

The aim of sensory analysis is to gain an insight into the way food is perceived by humans using visual, olfactory, taste, touch, and auditory responses. It is beneficial for all those involved in product development to have knowledge and understanding of the types of sensory methodologies available. Application of the most suitable sensory method can aid evaluation of new and reformulated products, and yield insights into product acceptability. Although information on volatiles gives a comprehensive insight into the compounds that may affect aroma and flavor, it can only provide an estimate on how consumers may perceive a product; therefore it is of utmost benefit to use volatile information in conjunction with sensory analysis to obtain a better understanding of the relationship between aroma and sensory perception.

There are many sensory tests available to evaluate a food product, with the most suitable depending on the information required. Considerations such as complexity of the test, cost, resources, and training or commitment from panelists, must be all taken into account when choosing an appropriate sensory test (Lawless and Heymann 2010).

Sensory acceptance testing, through the use of hedonic scales, is a popular choice for consumer research as they are easily understood and panelists do not require in depth training. Hedonic scales normally assess the degree of liking or disliking of sensory attributes such as appearance, odor, taste, aroma, texture, and are popularly utilized to assess food and beverages (O’Sullivan 2016). Hedonic scales have been extensively utilized in many studies to evaluate reformulated baked confectionary (Cavalcante and Silva 2015; Eslava-Zomeño et al. 2016; Giarnetti et al. 2015; Karp et al. 2016; Matsakidou, Blekas, and Paraskevopoulou 2010; Mohsen et al. 2009; Onacik-Gür et al. 2016; Serin and Sayar 2016; Wardy et al. 2018; Zahn et al. 2010). However, this type of sensory method can yield ambiguous information and can be difficult to correlate with volatile information.

Descriptive analysis is the most complete and informative tool for assessing the sensory attributes of food products (Lawless and Heymann 2010). Methodologies under this category include; Flavour Profile Method (Caul 1957), Texture Profile Method (Brandt, Skinner, and Coleman 1963), QDA (Stone et al. 2004), as well as general descriptive analysis. These are extensively utilized for their comprehensive evaluation of food and beverages (Murray, Delahunty, and Baxter 2001). In short, all descriptive analysis techniques involve the same principle steps. Initially, the generation of an agreed list of sensory attributes that best describe the product is developed. This is followed by panelist training; the selected attributes are defined using product references or standards, helping the assessors to distinguish clearly between attributes (O’Sullivan 2016). Subsequently, the panelists are permitted to assess the intensity of each attribute in respect to the product. Training and commitment of panelists is crucial for the success of this technique.

When trying to understand the intricate make-up of flavor, descriptive analysis used in conjunction with volatile analysis can elucidate relationships between aroma compounds and flavor perception. Utilising this strategy, Cognat et al. (2014) identified specific volatiles related to particular off-flavors perceived by panelists when monitoring oat biscuits over time, providing important information regarding product quality throughout shelf-life. Without complimenting volatile data with sensory analysis, it is impossible to know if the product continues to have approval on the market. The concentrations of volatile compounds that form the aroma fraction of bread are highly susceptible to changes in processes and ingredients, however, combining sensory and chemical information have proven effective in characterizing individual aroma profiles of similar breads (Heenan et al. 2009; Poinot et al. 2007). QDA has also been used to validate volatile information from reformulated biscuits and cookies (Pasqualone et al. 2014; 2015; Giarnetti et al. 2015).

In order to define a true relationship between volatile and sensory data, chemometric methods are often employed. Combining the principle concepts of multivariate statistical techniques, mathematics, and computer science, chemometrics enables important correlations to be realized between sensory attributes and volatile compounds through a simplistic, visual aid (Zielinski et al. 2014). Principal component analysis (PCA) is frequently used and attempts to identify the prominent factors (variables) that best explain the variance in a large data set (Kallithraka et al. 2001). PCA has been utilized to relate volatile compounds in different bread aroma extracts to sensory results (Poinot et al. 2007) as well as relating volatile compounds to color data in biscuits supplemented with grape marc extract (Pasqualone et al. 2014). Partial least square (PLS) analysis another popular technique utilized to make connections between instrumental and sensory data. Depending on the information sought, PLS may be considered superior to PCA as this takes into consideration the correlation between the dependent variable and the independent variables.

GC-O utilizes the human nose as a detection device to aid in the identification of odor active fractions of a chromatograph (Wardencki, Chmiel, and Dymerski 2013). Although compounds may be present in large concentrations, it is dependent on their odor threshold whether they are relevant to the aroma quality of a product. GC-O is a preeminent technique for determining odor thresholds of key volatiles, but has limitations. Sensory perception is often a combination of multiple volatiles rather than individual compounds. Volatiles need to be extracted/concentrated and therefore some compounds may be lost, underestimated or overestimated depending upon procedures used. Extraction methods, SAFE and SPME, have successfully been able to identify the odor active compounds which relate to the traditional aroma of a sponge cake (Matsakidou, Blekas, and Paraskevopoulou 2010; Pozo-Bayón et al. 2007; Rega et al. 2009). GC-O can be time consuming as human assessors require selection and training, with most approaches requiring multiple sessions (Delahunty, Eyres, and Dufour 2006; Zellner et al. 2008). However, on successful of application of this technique, the important volatiles responsible for the characteristic odor in a product can be established.

Conclusions and future work

Characterizing the volatile aroma compounds in baked confectionary provides a basis for improving the quality of reduced fat/reduced sugar formulas. It is evident that the raw materials of baked confectionary have a major impact on flavor perception, and modification of these ingredients can have a significant impact on sensory quality. Although a small percentage of volatiles transfer directly from the raw materials, thermal degradation of components in the formula generates the most potent and characterizing compounds. Aldehydes, alcohols, pyrazines, ketones, and furans are by far the most prominent and potent compounds that appear to influence the sensory appeal of baked confectionary products. LO also appears to be an important contributor to the volatile profile of these products, and therefore reducing fat content or, changing lipid types, is likely to have implications for flavor perception and shelf-life. Further research is required in relation to how the sensory impact of the inclusion or exclusion of the fundamental raw materials influence the volatile profile and sensory character of baked confectionary. This challenge would be best achieved using a chemometric approach to analyze sensory and flavor chemical data. In addition, the application of GC-O to determine the odor activity of key volatile compounds could also be useful in determining their direct impact on sensory perception and how they are influenced by production formulation changes.

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