Changes in the volatile profile of skim milk powder prepared under different processing conditions and the impact on the volatile flavor profile of model white chocolate

Stewart, A., Grandison, A., Fagan, C., Ryan, A., Festring, D. and Parker, J. K. (2018) Changes in the volatile profile of skim milk powder prepared under different processing conditions and the impact on the volatile flavor profile of model white chocolate. Journal of Dairy Science, 101 (10). pp. 8822-8836. ISSN 0022-0302 doi: https://doi.org/10.3168/jds.2018-14414 Available at http://centaur.reading.ac.uk/78456/

Changes in the volatile profile of skim milk powder prepared under different processing conditions and the impact on the volatile flavor profile of model white chocolate

STEWART

In this paper we demonstrate that changes in the processing conditions used to manufacture skim milk powder (SMP) can have an impact on the volatile profile of white chocolate. In particular, we have investigated the roles of heat treatment and the drying process on the development of volatile compounds in SMP. Furthermore, we have investigated how the SMPs manufactured under different conditions behave during a typical conching process in a model white chocolate system. The information presented is of use to both the dairy and the confectionery industries in controlling flavor in their products.

Changes in the volatile profile of skim milk powder prepared under different processing conditions and the impact on the volatile flavor profile of model white chocolate

Ashleigh Stewart,[*] Alistair Grandison,[*] Colette Fagan,[*] Angela Ryan,[†] Daniel Festring,[†] Jane K. Parker[*1]

[*] Department of Food and Nutritional Sciences, University of Reading, Reading RG6 6AP, UK

[†] Nestlé Product Technology Centre Confectionery, P.O. Box 204, Haxby Road, York YO91 1XY, UK

[1]Corresponding author: Jane K Parker

Department of Food and Nutritional Sciences

University of Reading, Reading RG6 6AP UK

26 Tel: +44 118 378 7455

27 E-mail: j.k.parker@reading.ac.uk

ABSTRACT

The objective of this work is to determine the extent to which changes in the skim milk powder (SMP) manufacturing process alter the volatile profile of SMP, and whether these changes are carried through to a final product when the SMP is used as an ingredient and subjected to further processing. The manufacture of SMP is a multistage process involving a preliminary concentration step, heat treatment and a drying stage. However, the methods and conditions used by the industry are not standardized, and the inherent variability in the production of SMP has consequences for the end-users, such as the confectionery industry, where the SMP is used as an ingredient during the production of milk chocolate, white chocolate and caramel.

This study investigates the impact of each stage of the manufacturing process on the concentration of reducing sugars and available amino groups (as precursors of the Maillard reaction) as well as on the volatile products of the Maillard reaction and lipid degradation. Eight types of SMP were produced using combinations of different processing conditions: concentration (by evaporation or reverse osmosis), heat treatment (low heat or high heat) and drying (spray-drying or freeze-drying). Maillard precursors were quantified after each processing stage and volatile compounds were extracted using solid-phase microextraction, and analyzed by GC-MS.

The resulting SMPs were incorporated into a model white chocolate system, produced under varying conching conditions. We demonstrate not only that changes in the SMP manufacturing conditions affect the volatile profile of SMP, but also that these differences can be carried through to a final product when the SMP is used to prepare a model white chocolate. Understanding these differences is important to the industry for controlling the flavor of the end product.

53 Key words: manufacture of skim milk powder, flavor, spray dry, freeze dry, chocolate

INTRODUCTION

The manufacture of SMP is a multistage process involving a preliminary concentration step, heat treatment often included to control the functional properties of the final powder (Oldfield et al., 2005), and a drying stage. Since these all involve a rise in temperature, lipid degradation and the Maillard reaction can occur during any of these steps. The severity of the heat treatment applied to milk during milk powder production is classified by industry according to the levels of undenatured whey proteins present i.e. whey protein nitrogen index (WPNI). High heat powder, medium heat powder, and low heat powder have WPNI ranges of < 1.5, 1.5 - 6.0 and > 6.0 mg/g respectively and these can be achieved using a range of different time temperature combinations. Low heat SMP is typically treated at 75 °C for 20 s whereas medium heat conditions range from 85 to105 °C for 1–2 min, and high heat up to 135 °C for 2–3 min (Early, 1998). Given this range of conditions, the extent of the Maillard reaction in SMP is variable. An understanding of the critical control points during the manufacturing process is important to industries that require a consistent product.

The changes in milk powder during storage are well documented (Drake et al., 2006, Driscoll et al., 1985, Hurrell et al., 1983, Karagül-Yüceer et al., 2002, Karagül-Yüceer et al., 2003). Most studies show that the formation of lipid-derived volatiles is prevalent during storage, contributing to the development of off-notes, but both formation and loss of Maillard reaction products were reported, depending on the conditions.

Research on high temperature processes in milk tends to focus on UHT (Celestino et al., 1997, Morales et al., 1992, Romero et al., 2001, Tokuşoğlu et al., 2004, Valero et al., 2001) and sterilization (Contarini et al., 1997). The formation of Maillard intermediates and glycation products during manufacture of dairy products has been studied (Birlouez-Aragon et al., 2004, Cattaneo et al., 2008, Erbersdobler and Somoza, 2007), but the focus of these studies was the reduction in nutritional value as a result of lysine residues becoming

unavailable (Mehta and Deeth, 2016). The development of volatile aroma compounds during the production of milk powder was studied by Drake et al., (2006) who showed that Maillard derived compounds such as 2-acetylpyrrole, 2-acetylthiazole and 2-acetyl-2-thiazoline increased, whereas, there was little change in the profile of the lipid degradation products. However, Li et al. (2012) monitored volatile lipid oxidation compounds during the production of milk powder, and demonstrated that all stages of the process could influence the formation and stability of these volatiles.

Recently, the role in flavor formation of the individual unit operations have been investigated. Falling-film evaporators are used extensively in the dairy industry and evaporation under vacuum results in the milk being heated to a lower temperature. Other concentration methods include membrane separation techniques such as reverse osmosis (Glover, 1985), which operates at high pressure and temperatures below those reached during evaporation. Comparison of reverse osmosis, nanofiltration and ultrafiltration was discussed by Syrios et al. (2011) with regard to stability, pH, calcium content and gel formation. Park and Drake (2016) showed that concentration by reverse osmosis, compared to concentration by evaporation, retained far more of the sweet character of the milk, driven by a greater retention of most volatiles, particularly lactones and furaneol. Maltol however, showed the reverse trend. Park et al. (2016) also showed significant changes in the volatile profile when different spray-drying parameters were employed. They showed that the sweet aromatic note increased as the inlet temperature increased, and this correlated with an increase in some lactones, maltol and vanillin.

Given the significant changes in SMP brought about by different processing conditions, it is important to understand if these changes are reflected in the final products when SMP is used as an ingredient for the manufacture of more complex food products. Caudle et al. (2005) showed a decrease in consumer acceptability of SMP as the storage time increased up to 4

104 years, and when these SMPs were incorporated into ice cream, yogurt and white chocolate
105 (but not hot chocolate) a similar decrease in consumer acceptability was observed. Volatile
106 analysis of the SMP showed an increase in dimethyl sulfide and dimethyl disulfide, and a
107 decrease in maltol. Lloyd et el. (2009b) carried out a similar experimement with stored WMP
108 incorporated in white and dark chocolate and showed a similar decrease in consumer
109 acceptance which was attributed to an increase in lipid degradaton products. Recently,
110 Stewart et al. (2017) showed that the heat treatment applied during SMP manufacture leads to
111 both changes in the aroma profile of the SMP, and flavor changes in white chocolate prepared
112 from the resulting SMPs.
113
114 The aim of this work was to investigate different processing conditions during the production
115 of SMP to determine the key stages for flavor development, and to determine whether these
116 changes are carried through to a final product. Eight types of skim milk powders were
117 produced using combinations of different processing conditions. Maillard precursors (sugars
118 and amino acids) and aroma compounds were quantified after each stage. The SMPs were
119 incorporated into a model white chocolate system and heated to mimic conching to determine
120 the impact of milk processing methods on the flavor profile of a final confectionery product.

121 ## MATERIALS AND METHODS

122 ### *Chemicals*

123 Trehalose, glucose, galactose, lactose and lactulose, L-leucine, sodium hydroxide (50%
124 solution in water; 1.515 g/mL), sodium dodecyl sulfate (SDS), ethanol, o-phthaldialdehyde
125 (OPA), 2-mercaptoethanol, sodium tetraborate buffer solution (pH 9), 1,2-dichlorobenzene,
126 methanol, all aroma chemical, alkanes $C_5 - C_{30}$ and diethyl ether were obtained from Sigma-
127 Aldrich Co. (Dorset, UK). The EZ:Faast amino acid analysis kit was purchased from
128 Phenomenex (Macclesfield, UK).

Preparation of Milk Powders

Raw whole bovine milk (RWM_{RO}) (40 kg) supplied by The University of Reading CEDAR Dairy Farm (CEDAR, Reading, UK) was pasteurized at 72 °C for 15 s and separated using a disc bowl centrifuge. The skimmed pasteurized milk (PM_{RO}) was then concentrated to 20% total solids using reverse osmosis (RO) to produce concentrated milk (CM_{RO}). Half of the concentrated milk was then subjected to a heat treatment stage to give a heated concentrated milk (HCM_{RO}), and no heat treatment was applied to the other half. The concentrated milks was then spray-dried (SD) or freeze dried (FD) to produce the following milk powders (MP): $SDMP_{RO}$, $HSDMP_{RO}$, $HFDMP_{RO}$, $FDMP_{RO}$ and $HFDMP_{RO}$. A second batch of raw whole milk was obtained one week later from the same herd, and the process was repeated concentrating to 20% solids using evaporation (EV) to produce a second set of milks (RWM_{EV}, PM_{EV}, CM_{EV}, HCM_{EV}) and milk powders ($SDMP_{EV}$, $HSDMP_{EV}$, $HFDMP_{EV}$, $FDMP_{EV}$ and $HFDMP_{EV}$).

Reverse Osmosis. Reverse osmosis was carried out at 60 bar outlet pressure using the RO module described previously by Syrios et al. (2011) until the total solids content was 20%, assessed using a Lactoscope (Quadrachem Laboratories Ltd, London, UK). Changes in the protein, fat, lactose and total solid content were previously measured throughout the process(Stewart et al., 2017). The temperature of concentrated milk during RO was 30 °C.

Evaporation. Evaporation was carried out using a single stage rising film evaporator (pressure = 1.8 bar) until a concentration of 20 % total solids was achieved. Milk was concentrated in 10 kg batches and the temperature of the milk during EV was 54–55 °C.

Heat treatment. Half the concentrated milk was subjected to an additional heat treatment of 5 min at 125 °C, achieved by transferring milk to Duran bottles (80 mL) and heating batches of 7 bottles in an autoclave (CertoClav Steriliser, Traun, Austria). No additional heat treatment was applied to the second half of the concentrated milk.

Spray-drying. Spray-drying was carried out using a NIRO spray dryer (Copenhagen, Denmark) with an A/S NIRO atomizer. The inlet air temperature was fixed at 200 °C and the feed flow rate adjusted to give an outlet air temperature of 80–90 °C. The wet bulb temperature during spray drying was 45 -50 °C.

Freeze-drying. Prior to freeze-drying, the milk was frozen at -80 °C for 24 h. Freeze-drying was carried out using a Christ Gamma 2-16 LSC freeze-dryer (120 h, pressure < 0.1 mbar) (Martin Christ, Osterode, Germany).

Preparation of Model White Chocolate

White chocolate was prepared as described by Stewart et al. (2017). The conching process of white chocolate was mimicked using a 250 mL continuously stirred reactor vessel (Atlas Potassium, Syrris Inc., Royston, UK) under different heating conditions. A preliminary study was carried out to test different conching conditions, heating the model white chocolate (produced with commercial SMP) at four temperature/time combinations: 4 h at 50 °C, 4 h at 80 °C, 8 h at 50 °C and 8 h at 80 °C. The two extremes were chosen for a comparison to identify potential differences as a result of conching time and temperature. For each milk powder, two model white chocolates were produced using either mild conching conditions (4 h at 50 °C) or harsh conditions (8 h at 80 °C). Model white chocolate was refrigerated and stored at 4±1 °C prior to analysis. A control white chocolate was also produced containing all ingredients apart from SMP, to confirm that differences observed were as a result of the SMP and not due to other ingredients. This control was conched for 8 h at 80 °C and analyzed under the same conditions as other samples.

Analytical Methods

Prior to analysis, all milk samples were diluted to 8 % solids in water and powder samples were reconstituted in water to 8 % total solids.

Determination of Sugars by Ion Chromatography. An aliquot (400 μL) of each sample was transferred to an Amicon 0.5 mL 3 kDa MWCO filter (Millipore, Watford, UK) and centrifuged for 20 min at 12,000 × g. The filtrate was diluted 200-fold in water and 500 μL of this diluted sample was combined with 500 μL of a 40 g/L trehalose solution. Extracts were analyzed using a Dionex ion chromatography system (Dionex Corp., Sunnyvale, USA), which consisted of an AS50 autosampler, LC25 column oven, GS50 pumps, and an ED50 pulsed amperometric detector, running in internal amperometric mode. Separation was carried out on a Carbopac PA1 column (Dionex Corp., Sunnyvale, USA) (250 x 4 mm i.d.) coupled with a guard column (50 mm × 4 mm i.d.), using an injection volume of 20 μL. A gradient program was set up using water and 200 mM NaOH at a flow rate of 1 ml/min as follows: 40 min at 12 mM NaOH, 5 min at 200 mM NaOH, and finally re-equilibrated for 5 min at 12 mM NaOH. The waveform of the pulsed amperometric detector was as follows: 400 ms at 0.1 V, 20 ms at -2.0 V, 10 ms at 0.6 V, and 60 ms at -0.15 V. Standards of glucose, galactose, lactose and lactulose were used to produce a series of calibration curves, using trehalose as an internal standard, for quantification. Chromeleon software was used to operate the system, as well as for data quantification. All samples were analyzed in triplicate.

Determination of Total Available Amino Groups. Aqueous samples were diluted 5-fold in water, followed by derivatization using OPA and spectrophotometric analysis as described previously by (Brands and Van Boekel, 2001). A calibration curve was obtained from L-leucine, which had been derivatized using the same method. All samples were analyzed in triplicate.

Determination of Free Amino Acids by GC-MS. An aliquot of each aqueous sample (100 μL) was derivatized using the EZ:Faast free amino acid analysis kit for GC-MS (Phenomenex, Macclesfield, UK). GC-MS analysis was carried out as described previously by Elmore et al.(Elmore et al., 2007).

Measurement of Moisture Content and Water Activity (a_w). Moisture content of the skim milk powders was determined by Karl Fischer titration using an Orion AF8 Volumetric Karl Fischer unit (Thermo Scientific, MA, USA). Milk powder samples (0.2 g) were analyzed at room temperature using CombiTitrant 5 (Merck, Darmstadt, Germany) as the titrating agent and methanol as the solvent. The solvent was changed at every replicate and analyses were performed at least in duplicate to give less than 0.08 % difference between readings, which were averaged. The water activity of milk powder samples (0.5 g) was measured at 25 °C using a LabMaster-a_w (Novasina, Lachen, Switzerland).

Microscopy. A small amount of each powder was applied to a microscope slide and observed using a stereoscopic microscope (SZ 60, Olympus, Tokyo, Japan) equipped with a lighting (Highlight 3000, Olympus, UK). Photographic images of each sample were acquired with a digital camera and data capture software (VisiCam 5.0, VWR, Belgium).

Solid-Phase Microextraction/GC-MS (SPME/GC-MS). Volatile compounds were extracted from liquid milk, milk powder and white chocolate samples using an automated SPME/GC-MS system (Agilent), equipped with a DVB/CAR/PDMS Stableflex fiber (Supelco, Bellefonte, USA). Samples (4 g) were weighed into 20 ml glass SPME vials and analyzed using the method detailed previously by Stewart et al. (2015). An internal standard (10 μl of 130.6 μg/ml 1,2-dichlorobenzene in methanol) was added to aqueous samples. No internal standard was added to model white chocolate samples but instrument sensitivity was checked by running a standard of 1,2-dichlorobenzene (10 μl, 130.6 μg/ml in methanol) at regular intervals. All samples were analyzed in triplicate.

Statistical Analysis

One-way analysis of variance (ANOVA) was carried out using XLSTAT Version 2012.4.02 (Addinsoft, Paris, France) and Tukey's honest significant difference (HSD) test was applied to determine which sample means differed significantly at $p = 0.05$.

RESULTS AND DISCUSSION

Milk powder manufacture

The milkpowders were prepared from milk supplied by the University of Reading CEDAR Dairy farm and processed using the equipment available at the University of Reading Food Processing Centre. This allowed us to control the origin and processing of the milk very closely, but, as such, we could not match the manufacturing conditions used in the industry. Although the processing conditions applied to the milk were selected to match industry heating profiles as closely as possible, the heat load on a smaller scale, may be different. A pilot scale can never be fully representative of a full scale industral process but this paper provides the evidence required to move to industrial trials where validation of the results could take place.

Maillard Precursors

Eight different SMPs were produced using a combinations of techniques, which varied in the level of thermal processing applied. Reverse osmosis and evaporation were used to concentrate the milk, followed by spray-drying or freeze-drying. Half the milk was also subjected to a heat treatment of 5 min at 125 °C between the concentration and drying stages. Precursors (sugars, free amino acids and available amino groups) were quantified after each stage of processing to monitor progress of the Maillard reaction. **Table 1** shows the differences in concentration of Maillard precursors throughout the processing of SMP.

It was necessary to use two different batches of raw whole milk (RWM) – one of which was concentrated by evaporation and the other by reverse osmosis. However, the batches were produced < 7 days apart, and analysis of the raw and pasteurized milks showed only minor differences. Batch 2 (EV) contained higher ($p<0.05$) concentrations of sugars and free amino acids in comparison to the first batch (RO). We compared the general trends within the first batch (i.e. whether there was a relative increase or decrease after each step) with the general

253 trends in the second batch, but no quantitative conclusions could be made when directly
254 comparing EV and RO samples.
255 **Sugars**. Lactose is the most abundant component in SMP, comprising approximately
256 50% of the dry weight (Martin et al., 2007), and is known to react at elevated temperatures
257 with free amino groups via the Maillard reaction. **Table 1** shows a loss of lactose during the
258 concentration steps for both RO and EV batches of RWM (loss of 150 and 130 mmol per kg
259 dry weight respectively), and both galactose and glucose also showed losses. One potential
260 route for loss of reducing sugars is via reaction with free amino groups to form a Schiff's
261 base. However, the changes in the concentration of the free amino groups were insufficient to
262 account for the loss of lactose, and no isomerisation to lactulose was observed.
263 The impact of heat treatment was more apparent for lactulose, regardless of the concentration
264 method used. Lactulose was present in samples only after the heat treatment stage and its
265 concentration increased further after spray-drying. Lactulose is formed from the Lobry de
266 Bruyn-Alberda van Ekenstein transformation of lactose during heating, and has been used as
267 a marker for heat treatment in milk (Marconi et al., 2004). Additionally, we noticed that
268 lactulose was not formed after spray-drying alone, as it was not detected in either of the
269 spray-dried milk powders (SDMP) with no heat treatment. This suggests it is the high
270 temperature applied during heat treatment (125 °C) that induces the initial stages of lactose
271 isomerisation, which can then continue during further thermal processing (spray-drying) to
272 form lactulose. These results support the previous use of lactulose as a marker of severity of
273 SMP heat treatment. However work by Berg and Van Boekel (1994) showed that degradation
274 of lactulose to galactose, formic acid and C5/6 compounds occurs after extended heating at
275 high temperatures (> 140 °C).
276 The monosaccharides glucose and galactose were both present at low concentrations in
277 RWM. During processing, we observed an overall decrease in glucose of 30% or more from

RWM to the finished milk powder for all combinations of processing. About 12% was lost during pasteurization (both for RO and EV batches) and there was further loss during heat treatment which was greater for HCM_{EV} than HCM_{RO} and for which we have no explanation. The loss of glucose during freeze-drying of the unheated milk (CM) is more than might be expected and is difficult to explain, whereas upon freeze-drying of the heated milk (HCM), there is no significant change. We observed that the most significant decrease in glucose concentration was from RWM_{EV} to $HSDMP_{EV}$, which represents the powder produced under the most severe combination of processing conditions.

We found that the loss of galactose during pasteurization (13%) (both RO and EV) was similar to that for glucose but, in contrast to glucose, we found a five-fold increase in galactose concentration after heat treatment for both HCM_{EV} and $HCM_{RO.}$ During the Maillard reaction of lactose with an ε-amino group, the glucose moiety is the reducing sugar which participates in the first stage of the Maillard reaction. It may remain bound to protein, or further degrade to form volatile flavor compounds (Van Boekel, 1998) during which an intact galactose unit is cleaved off. This explains why there was an increase in galactose concentration after the heat treatment step, but no equivalent increase for glucose. Consistent with this explanation, we also noticed small increases ($p<0.05$) in galactose but not glucose when the concentrated milks were spray dried, and this change in galactose was less or insignificant when the concentrated milks were freeze-dried. This is consistent with the higher temperatures reached in the spray-drying process compared to the freeze-drying.

Amino groups. The OPA spectrophotometric assay used to quantify available amino groups gives an approximation of the total number of available amino groups, i.e. those not bound to sugars. The most significant loss we observed was for the high heat spray-dried powders, with 48 % (139 mmol NH_2/kg) lost from RWM_{EV} to $HSDMP_{EV}$ and 59 % (186 mmol NH_2/kg) lost from RWM_{RO} to $HSDMP_{RO}$. These overall losses are of a similar

magnitude to the losses of lactose which are 170 and 190 mmol respectively. Lactose binds to amino groups during the Maillard reaction to form the Amadori rearrangement product, making these amino groups unavailable and not quantified by this technique. Therefore it makes sense that the concentration of available amino groups decreased with increased heating.

There was little correlation between the level of thermal processing and the total concentration of free amino acids. Although free amino acids are involved in the Maillard reaction at elevated temperatures, there may also be a small degree of proteolysis during processing, releasing free amino acids from the casein or whey protein. Free amino acids are also regenerated by the Maillard reaction during rearrangement of the Amadori rearrangement product to deoxyosones. This would explain the insignificant changes to the total free amino acid concentration.

Figure 1 shows variation in the concentration of lysine which demonstrated a significant decrease in concentration during thermal processing. Lysine residues in milk proteins are considered to be the most important for the Maillard reaction in milk powder due to the free and highly reactive ε-amino group, but free lysine also has an additional α-amino group(O'Brien, 2003) which can participate. This is supported by the results of this study, as free lysine concentration can be seen to decrease ($p<0.05$) with increased heating, likely to be the result of the Maillard reaction with lactose. There was a decrease in lysine concentration after concentration by both reverse osmosis and evaporation and, although only the decrease from reverse osmosis was statistically significant, the trend was the same for evaporation. However, the decrease from PM to HCM was significant for both concentration methods. There was generally little difference observed between batches concentrated by EV and RO, compared to the bigger changes in Maillard precursors which took place during the heat treatment, and to a lesser extent during spray drying.

328 ***Physical Properties of Skim Milk Powders***

329 The moisture content and water activity (a_w) values measured for each powder are shown in
330 Figure 2. It can be seen that FD powders consistently had higher moisture contents and a_w,
331 compared to SD samples. With the exception of HSDMP concentrated by RO, heat-treated
332 samples had a slightly lower moisture content and a_w than the corresponding unheated
333 samples.

334 Commercial milk powders are produced with a moisture content of 2-4 % (Smit, 2003) to
335 prevent deterioration by bacterial growth or processes such as the Maillard reaction and lipid
336 oxidation, which would also change the flavor profile of the product. Freeze-dried powders in
337 this study had a moisture content of ~ 5-6%, making them more susceptible to deterioration
338 and subsequent flavor formation. The higher moisture content and a_w had a significant impact
339 on flavor formation after incorporation of the powders into a model white chocolate system,
340 which is discussed below.

341 Substantial differences can be seen in the surface structure of the powders by microscopy
342 (Figure 3.), which agree with previous findings by Miao and Roos (2004). Whereas spray-
343 dried samples were spherical with a smooth surface, freeze-dried powders were irregular in
344 shape with a surface resembling broken-glass. Despite clear differences in surface structure,
345 lactose is highly likely to be in the amorphous state in both powders as water is removed
346 faster than crystallisation can occur during spray-drying, and lactose molecules are unable to
347 move themselves into a crystalline arrangement in a frozen matrix prior to freeze-drying.
348 Therefore, though the solid state of lactose is unlikely to be different as a result of the
349 different drying methods, the particle size and shape may have influenced the rate of Maillard
350 reaction taking place. In addition, the higher moisture content of the FDMPs are more likely
351 to allow reactants to come into contact with one another. The optimum moisture content for
352 the Maillard reaction in SMP is 7% (Franzen et al., 1990) above which the system is diluted

and reactants are less likely to come into contact. The FDMPs are closer to this optimum moisture content, which is likely to enhance the Maillard reaction in those powders during further processing.

Volatile Compounds in Intermediate Milk Products (RWM, CM, PM, HCM)

The volatile compounds identified in samples by SPME/GC-MS are shown in Table 2 for raw, pasteurized, concentrated and heat-treated samples. (The reconstituted milk powders are shown in Table 3 and discussed below).

Lipid-derived volatiles. Of the 22 volatile compounds identified, 11 were products of lipid oxidation, primarily straight-chain aldehydes (pentanal, hexanal, heptanal, octanal, nonanal and decanal) and methyl ketones (2-heptanone, 2-nonanone, 2-decanone and 2-undecanone). These compounds have all been identified previously in heated milk (Vazquez-Landaverde et al., 2005) and SMP (Bassette and Keeney, 1960, Shimamura and Ukeda, 2012, Walker, 1972), although they are generally considered to contribute off-notes to SMP flavor. Autoxidation of lipids in milk is catalyzed by both light and heat and therefore any processing stage that applies heat and exposes the milk to light would be expected to increase the concentration of lipid oxidation products.

Interestingly, only 2 of these were identified in the volatile profile of RWM whereas 9 were identified in the pasteurized milk (PM). This could be due to the different flavor release properties of the RWM, which contains 4% fat compared to the other samples which had a fat content of <0.1. The higher fat content can decrease the partitioning of the lipophilic aldehydes and ketones into the headspace. It could also be due to the (relatively mild) processing conditions applied during pasteurization (15 s at 72 °C) initiating the oxidative process. Vazquez-Landaverde et al., (2005) compared by SPME/GC-MS the volatile profile of commercial pasteurised milk at 0, 1, 2 and 3% fat content, and found that there was no consistent or significant decrease in the concentration of these volatiles in the headspace as

the fat content increased, suggesting that the lack of these compounds in the headspace of RWM is not due to differences in the flavor release. However, they also reported the presence of these compounds in the raw milk as well as the pasteurised samples, with few significant differences between them, suggesting that they are not formed during pastuerization. However, these observation were made in commercial samples whereas ours have all been prepared from the same two batches of raw milk.

During the subsequent concentration, comparison of RO and EV showed that CM_{RO} contained more aldehydes (particularly hexanal) and acids compared to CM_{EV}, although the differences were not always significant. This is consistent with Park and Drake (2016) who showed that RO retained in general more aldehydes, lactones and acids. During the subsequent heating step, the aldehydes tended to decrease, and we attribute this to their volatile nature, suggesting that they are lost by volatilisation quicker than they are formed. However, this was not the case for 2-heptanone and 2-nonanone, which demonstrated a consistent increase with each additional processing stage and a significant increase after heat treatment. The longer chain ketones (2-decanone and 2-undecanone) and 2-pentylfuran were almost exclusively formed during the heating step. The trends were consistent across the samples regardless of concentration method.

Free fatty acids (FFAs) have been identified as major contributors to the flavor of milk fat by Schieberle et al. (1993) and were detected in all RWM samples. They have also been reported in SMP (Karagül-Yüceer et al., 2001), although our results show that most were removed when the milk was first pasteurised and skimmed, consistent with Drake et al. (2006). Concentration by RO led to an increase in FFA concentration which continued with heat treatment, although levels were much lower than those observed in the starting RWM. Without a double bond, saturated FFAs are less reactive than unsaturated FFAs and as a result are likely to be more heat-stable at lower heating temperatures, such as those applied

during the concentration step. As part of the pasteurization step, the milk was skimmed by centrifugation immediately followed by pasteurization. It is possible that the large decrease in FFA concentration between RWM and PM could be due to the separation process and the removal of FFA with the milk fat. This would result in an initial decrease in concentration followed by an increase as they are formed via lipid oxidation during further processing.

The effect of thermal processing is most apparent for volatile compounds formed as a result of thermal degradation and the Maillard reaction. Sulfur compounds and Maillard reaction products (MRPs) were detected only in heat-treated samples and generally in larger amounts for samples concentrated by RO, although the differences between RO and EV were not significant in most cases.

Maillard reaction products. The first stage of the Maillard reaction in milk involves the reaction of lactose with lysine ε-amino groups in proteins to form the Amadori rearrangement product (ARP) lactulosyllysine. This ARP can break down via different pathways to give large numbers of volatile flavor compounds. At low pH, dehydration of the ARP leads to the formation of 2-furfural.The presence of 2-furfural in both HCM samples confirms that the Maillard reaction is taking place to a greater degree under the most severe processing conditions (5 min at 125 °C). Two furan derivatives, 2-furfural and 2-furanmethanol, were previously identified in SMP by Shiratsuchi et al. (1994) but were not thought to contribute to the flavor of milk due to their low concentrations and high odor thresholds (2 and 3 mg/kg respectively (Buttery and Ling, 1995)).

In summary, MRPs were only detected in samples that had undergone the heat treatment step and there was no clear differences between flavor formation in samples concentrated by RO or EV.

Considering that the EV batch had a slightly higher concentrations of Maillard precursors (Table 1) and the EV process involved higher temperatures than the RO process (RO = 35 °C,

428 EV = 55 °C), it is interesting to find that there were only two significant differences in MRPs
429 when comparing HCM_{EV} and HCM_{RO}, and the general trend was for there to be fewer MRPs
430 in HCM_{EV}. Therefore it seems likely that the difference in temperature between the two
431 methods was not sufficient to cause significant differences in flavor compounds formed from
432 the Maillard reaction.
433 Dimethyl disulfide and dimethyl trisulfide were previously identified as key contributors to
434 the heated flavor of UHT milk by Al-Attabi et al. (2008) and can be formed by the Strecker
435 degradation of methionine during thermal processing. Similarly, 3-methylbutanal and 2-
436 methylbutanal are Strecker aldehydes formed from leucine (Ramshaw and Dunstone, 1969)
437 and isoleucine (Griffith and Hammond, 1989) respectively. Both have previously been
438 identified in raw, pasteurized and UHT milk (Vazquez-Landaverde et al., 2005) as well as in
439 milk powder (Hall et al., 1985, Lloyd et al., 2009a,b).
440 ***Volatile Compounds in Skim Milk Powders***
441 Table 3 shows the volatile compounds identified in reconstituted milk powders, and
442 comparison with samples from the early processing stages reveals that the majority of
443 compounds appear in both sample sets and aldehydes and ketones remain the most abundant
444 group of compounds.
445 ***Lipid-derived volatiles.*** The first thing to observe is that the low solids content prior
446 to spray drying (20% compared to 40-50% typically used in industry), may have promoted
447 lipid oxidation as discussed by Park at al. (2016). We observed a significant difference in the
448 concentration of lipid-derived aldehydes in EV powders, with spray-dried powders
449 consistently having a higher concentration than freeze-dried, thus the highest concentration of
450 lipid-derived aldehydes was found in $HSDMP_{EV}$. This supports previous work by Li et al.
451 (2012), which concluded that heat treatment of milk prior to concentration and spray-drying

results in accelerated formation of aldehydes and ketones. A similar trend was not observed for all RO powders or for other lipid oxidation products, such as methylketones. Comparison of $HSDMP_{EV}$ and $HSDMP_{RO}$ revealed that 11 of the lipid-derived compounds were higher in the powders prepared by EV. This is unlikely to be related to differences between the batches of milk, since the profiles of the lipid-derived volatiles before concentration were very similar (apart from hexanal which was higher in RO). We suggest that the milk is more prone to lipid oxidation during the evaporation stage where they are exposed to light and oxygen as well as mild thermal conditions. Once initiated, the oxidation continues during heating and spray drying. We suggest that RO is likely to be a more effective concentration method to limit the formation of lipid oxidation products during manufacture of SMP, particularly if it is heated and spray-dried.

Hexanoic acid was only detected in RO samples and although there was no difference between heat treatments the freeze-dried samples had significantly higher concentrations than their spray-dried equivalents. Conversely, octanoic acid was detected in both EV and RO samples but only the EV samples showed significant differences, as a result of both drying method and heat treatment. Loss of volatile fatty acids during conching was shown to take place by Hoskin and Dimick (1979) and spray-drying of milk powder could yield similar results. The temperature of milk particles during spray-drying (wet bulb temperature) was 45 – 50 °C and in combination with the evaporation of water this could have led to the lower concentration of FFAs in SDMP compared to FDMP produced from the same HCM.

Maillard reaction products. Significant differences were seen between powders for sulfur compounds and MRPs, which were generally at higher concentrations or only present in heated samples, consistent with Drake et al. 2006. Dimethyl trisulfide is one of the compounds which is likely to contribute to the flavor profile of the heated treated powders (Stewart et al., 2017). It was only detected in the heat treated milks and in the powders

produced from the heat treated milks, and there was no difference between the products prepared by EV or RO. The less odor active dimethyl disulfide showed a similar trend. Two Maillard-derived compounds, benzaldehyde and 3-hydroxy-2-methyl-4H-pyran-4-one (maltol), were significantly affected by the combination of concentration, heat treatment and drying methods used. Karagül-Yüceer et al. (2001) previously identified maltol in SMP of various heat treatments, but a higher intensity was perceived in the high heat-treated powder. Maltol is derived from the Maillard reaction of disaccharides such as lactose at high temperatures (Patton, 1950, Yaylayan and Mandeville, 1994) and was only detected after the most severe processing ($HSDMP_{EV}$). It is one of the compounds reported by Stewart et al., (2017) which are likely to contribute to the more caramel-like flavor in the heat treated powders.

The amount of benzaldehyde detected correlated with the level of thermal processing applied and its concentration was in the following order: HSDMP > HFDMP > SDMP, with none detected in FDMP. Benzaldehyde can be formed from the thermal reaction of lactose with phenylalanine (Ramshaw and Dunstone, 1969), and has been identified previously in stored milk powder (Parks and Patton, 1961). Benzaldehyde was detected in a significantly larger amount in HSDMP concentrated by EV: over 8 times that of the next highest concentration. However, based on the results of Stewart et al., (2017), it is unlikely to contribute to the flavor of the SMP.

Model White Chocolate

To evaluate the effect of different milk powder processing conditions after incorporation into a confectionery product, a series of model white chocolate samples was produced under different conching conditions. For this study, each milk powder was used to produce one batch of model white chocolate conched under normal conditions (4 h at 50 °C) and one batch produced under more extreme heating conditions (8 h at 80 °C). Twenty-five volatile

502 compounds were monitored by SPME GC-MS. The volatile profile of the products conched
503 at 80 °C are shown in Table 4, but those conched at 50 °C showed very few significant
504 differences between the samples and the full data are not shown. Apart from the short chain
505 acids which tended to show no significant difference across the 8 products, the volatiles fall
506 into two groups according to their overall trends across the 80 °C samples.

507 **Lipid-derived volatiles**. The lipid degradation products all followed a pattern similar
508 to that shown for 2-heptanone (Figure 4). This included 2-pentanone, 2-nonanone as well as
509 hexanal, heptanal, octanal and nonanal. Although we cannot account for differences in flavor
510 release, the fact that there was no significant difference across the set of samples conched at
511 50 °C, suggests that the differences observed at 80 °C are not just a result of different flavour
512 release properties of the samples. The increase in these lipid-derived compounds at 80 °C is
513 consistent with (Counet et al., 2002) who showed an increase in 2-heptanone at high
514 temperature conching. The samples made with freeze-dried SMP showed an increase in lipid-
515 derived compounds when compared to the spray-dried equivalents, and we attribute that to
516 the increase in moisture content of the freeze dried material. Within the products made with
517 spray-dried SMP, there were no significant differences where different milk processing
518 conditions had been used, consistent with the data from the SMPs.

519 **Maillard reaction products**. This comprises a group of Maillard sugar breakdown
520 products: 2-furfural, 2-furanmethanol, methyl 2-furoate and maltol, but interestingly not the
521 pyrazines and Strecker aldehydes which generally require high temperature processing for
522 their formation. These sugar degradation products all follow the trend shown in Figure 4 for
523 maltol. Again we see the highest concentrations present in those samples containing freeze-
524 dried SMP, and attribute this to the increase in moisture. Franzen et al. (1990) found 7% to be
525 the optimum moisture content for the Maillard reaction in SMP. The milk powders produced
526 in this study had moisture contents in the range of 2.7 – 6.1 % (a_w 0.15 – 0.25), which is

527 below the optimum, and once incorporated into the fat phase of the white chocolate the
528 overall moisture content would be lower again. Thus the slightly higher moisture content of
529 the freeze-dried SMP (Figure 2) moves the system closer to the browning-critical moisture
530 content, thus promoting the formation of these Maillard-derived compounds.
531 However, we also observe that those samples containing freeze-dried SMP, where the milk
532 had been concentrated by evaporation rather than reverse osmosis, contain 10-20 times more
533 maltol and other sugar degradation products. We suggest that this can only be due the
534 formation of precursors as a result of the mild heat treatment applied during the evaporation
535 stage. This is supported by theloss of sugars and free amino groups at this stage - there being
536 a significant loss of free amino groups in the EV cocnetrated milk but not the RO
537 concentrated milk (Table 1). However, we observe the effect of the heat treatment applied to
538 the milk in the set of products made from spray-dried SMP. The concentration of maltol is
539 significantly higher when the additional heat treatment was applied, and 2-furfural, 2-
540 furanmethanol, acetic acid and hydroxypropanone all followed a similar trend. This is
541 consistent with the differences found in the constituent SMPs (Table 3).
542
543 **CONCLUSIONS**
544 Overall, this work highlights the importance of the combinations and interactions of the
545 model processes chosen for each stage of SMP and confectionery manufacture, on the
546 development of volatile aroma compounds in model white chocolate. Use of evaporation as a
547 drying method seemed to initiate lipid oxidation, which resulted in significantly higher lipid-
548 derived volatiles in the milk powder when further heat treatment was applied.
549 For production of Maillard-derived compounds in SMP, heat treatment was the most
550 important processing stage, and was the first stage at which MRPs were identified. The
551 application of further heat during spray-drying led to increased levels of MRPs compared to

freeze-dried samples. The concentration method seemed to have very little influence on the Maillard reaction, except that maltol, an important aroma compound, was only found in the high heat, spray-dried powder that had been concentrated using evaporation.

The volatile profile of the white chocolate was shown to be driven by a number of factors which include moisture content of the SMP, method of concentration and the application of heat. The interrelation of these mechanism is complex, but here we show that changes in these unit operations can quite significantly alter the volatile profile, in particular the combination of concentration by evaporation when the moisture content of the SMP is somewhat higher than is typically used within the industry. In general, we have shown that these stages of processing are interdependent, and early stages of SMP manufacture can have an impact of the volatile profile of model white chocolate. The results of this investigation are potentially useful for the dairy and confectionery industries in controlling the volatile profile of their final product.

ACKNOWLEDGEMENTS

This research was funded by the Biotechnology and Biological Sciences Research Council (BB/J500860/1) and Nestlé PTC York through a CASE studentship.

REFERENCES

Al-Attabi, Z., B. D'arcy, and H. Deeth. 2008. Volatile sulphur compounds in UHT milk. Critical Reviews in Food Science and Nutrition 49(1):28-47.

Bassette, R. and M. Keeney. 1960. Identification of Some Volatile Carbonyl Compounds from Nonfat Dry Milk. Journal of Dairy Science 43(12):1744-1750.

Berg, H. E. and M. A. J. S. Van Boekel. 1994. Degradation of lactose during heating of milk. 1. Reaction pathways. Netherlands Milk and Dairy Journal.

Birlouez-Aragon, I., M. Pischetsrieder, J. Leclere, F. Morales, K. Hasenkopf, R. Kientsch-Engel, C. Ducauze, and D. Rutledge. 2004. Assessment of protein glycation markers in infant formulas. Food Chemistry 87(2):253-259.

Brands, C. M. J. and M. A. J. S. Van Boekel. 2001. Reactions of Monosaccharides during Heating of Sugar−Casein Systems: Building of a Reaction Network Model. Journal of Agricultural and Food Chemistry 49(10):4667-4675.

Buttery, R. G. and L. C. Ling. 1995. Volatile Flavor Components of Corn Tortillas and Related Products. Journal of Agricultural and Food Chemistry 43(7):1878-1882.

Cattaneo, S., F. Masotti, and L. Pellegrino. 2008. Effects of overprocessing on heat damage of UHT milk. European food research and technology 226(5):1099-1106.

585 Caudle, A. D., Y. Yoon, and M. Drake. 2005. Influence of Flavor Variability in Skim Milk
586 Powder on Consumer Acceptability of Ingredient Applications. Journal of Food Science
587 70(7):s427-s431.
588 Celestino, E. L., M. Iyer, and H. Roginski. 1997. Reconstituted UHT-treated milk: Effects of
589 raw milk, powder quality and storage conditions of UHT milk on its physico-hemical
590 attributes and flavour. International Dairy Journal 7(2):129-140.
591 Contarini, G., M. Povolo, R. Leardi, and P. M. Toppino. 1997. Influence of Heat Treatment
592 on the Volatile Compounds of Milk. Journal of Agricultural and Food Chemistry 45(8):3171-
593 3177.
594 Counet, C., D. Callemien, C. Ouwerx, and S. Collin. 2002. Use of gas chromatography-
595 olfactometry to identify key odorant compounds in dark chocolate. Comparison of samples
596 before and after conching. Journal of Agricultural and Food Chemistry 50(8):2385-2391.
597 Drake, M. A., R. E. Miracle, A. D. Caudle, and K. R. Cadwallader. 2006. Relating sensory
598 and instrumental analysis. Pages 23-55 in Sensory-directed flavor analysis. R. Marsili, ed.
599 Taylor and Francis, FLBoca raton, FL.
600 Driscoll, N., C. Brennand, and D. Hendricks. 1985. Sensory quality of nonfat dry milk after
601 long-term storage. Journal of Dairy Science 68(8):1931-1935.
602 Early, R. 1998. Technology of Dairy Products. Springer.
603 Elmore, J. S., D. S. Mottram, N. Muttucumaru, A. T. Dodson, M. A. Parry, and N. G.
604 Halford. 2007. Changes in free amino acids and sugars in potatoes due to sulfate fertilization
605 and the effect on acrylamide formation. Journal of Agricultural and Food Chemistry
606 55(13):5363-5366.
607 Erbersdobler, H. F. and V. Somoza. 2007. Forty years of furosine–Forty years of using
608 Maillard reaction products as indicators of the nutritional quality of foods. Molecular
609 nutrition & food research 51(4):423-430.
610 Franzen, K., R. K. Singh, and M. R. Okos. 1990. Kinetics of nonenzymatic browning in dried
611 skim milk. Journal of Food Engineering 11(3):225-239.
612 Glover, F. 1985. Ultrafiltration and reverse osmosis for the dairy industry. National Institute
613 for research in Dairying.
614 Griffith, R. and E. G. Hammond. 1989. Generation of Swiss cheese flavor components by the
615 reaction of amino acids with carbonyl compounds. Journal of Dairy Science 72(3):604-613.
616 Hall, G., J. Andersson, H. Lingnert, and B. Olofsson. 1985. Flavor changes in whole milk
617 powder during storage. Journal of Food Quality 7(3):153-190.
618 Hoskin, J. and P. Dimick. 1979. Volatile fatty acid changes during the conching of chocolate.
619 Pages 23-32 in Proc. Proceedings of the 33rd PMCA production conference.
620 Hurrell, R. F., P. A. Finot, and J. E. Ford. 1983. Storage of milk powders under adverse
621 conditions. 1. Losses of lysine and of other essential amino acids as determined by chemical
622 and microbiological methods. British Journal of Nutrition 49(Copyright (C) 2012 American
623 Chemical Society (ACS). All Rights Reserved.):343-354.
624 Karaguel-Yueceer, Y., K. R. Cadwallader, and M. Drake. 2002. Volatile Flavor Components
625 of Stored Nonfat Dry Milk. J. Agric. Food Chem. 50(Copyright (C) 2018 American Chemical
626 Society (ACS). All Rights Reserved.):305-312.
627 Karaguel-Yueceer, Y., M. A. Drake, and K. R. Cadwallader. 2003. Aroma characterization of
628 fresh and stored nonfat dry milk. in Freshness and shelf life of foods. Vol. 836. K. R.
629 Cadwallader and H. Weenen, ed. ACS symposium series, Washington DC.
630 Karagül-Yüceer, Y., K. R. Cadwallader, and Drake. 2002. Volatile Flavor Components of
631 Stored Nonfat Dry Milk. Journal of Agricultural and Food Chemistry 50(2):305-312.
632 Karagül-Yüceer, Y., M. Drake, and K. R. Cadwallader. 2001. Aroma-Active Components of
633 Nonfat Dry Milk. Journal of Agricultural and Food Chemistry 49(6):2948-2953.

Li, Y., L. Zhang, and W. Wang. 2012. Formation of aldehyde and ketone compounds during production and storage of milk powder. Molecules 17(8):9900-9911.
Lloyd, M. A., M. A. Drake, and P. D. Gerard. 2009. Flavor Variability and Flavor Stability of U.S.-Produced Whole Milk Powder. Journal of Food Science 74(7):S334-S343.
Lloyd, M. A., J.S. Hess and M.A. Drake. 2009. Effect of nitrogen flushing and storage temperature on flavor and shelf-life of wjole milk powder. Journal of Dairy Science 92:2409-2422.
Marconi, E., M. C. Messia, A. Amine, D. Moscone, F. Vernazza, F. Stocchi, and G. Palleschi. 2004. Heat-treated milk differentiation by a sensitive lactulose assay. Food Chemistry 84(3):447-450.
Martin, G., R. Williams, and D. Dunstan. 2007. Comparison of casein micelles in raw and reconstituted skim milk. Journal of Dairy Science 90(10):4543-4551.
Mehta, B. M. and H. C. Deeth. 2016. Blocked lysine in dairy products: Formation, occurrence, analysis, and nutritional implications. Comprehensive Reviews in Food Science and Food Safety 15(1):206-218.
Miao, S. and Y. Roos. 2004. Comparison of Nonenzymatic Browning Kinetics in Spray-dried and Freeze-dried Carbohydrate-based Food Model Systems. Journal of Food Science 69(7):322-331.
Morales, F. J., C. Romero, and S. Jimenez-Perez. 1992. An enhanced liquid chromatographic method for 5-hydroxymethylfurfural determination in UHT milk. Chromatographia 33(Copyright (C) 2012 American Chemical Society (ACS). All Rights Reserved.):45-48.
O'Brien, J. 2003. Non-Enzymatic Degradation Pathways of Lactose and Their Significance in Dairy Products. in Advanced Dairy Chemistry, Volume 3: Lactose, Water, Salts and Minor Constituents. 3rd ed. P. Fox and P. McSweeney, ed. Kluwer Academic/Plenum.
Oldfield, D., M. Taylor, and H. Singh. 2005. Effect of preheating and other process parameters on whey protein reactions during skim milk powder manufacture. International Dairy Journal 15(5):501-511.
Park, C. W. and M. Drake. 2016. Condensed milk storage and evaporation affect the flavor of nonfat dry milk. J. Dairy Sci. 99(Copyright (C) 2018 American Chemical Society (ACS). All Rights Reserved.):9586-9597.
Park, C. W., M. A. Stout, and M. A. Drake. 2016. The effect of spray-drying parameters on the flavor of nonfat dry milk and milk protein concentrate 70%. J. Dairy Sci. 99(Copyright (C) 2018 American Chemical Society (ACS). All Rights Reserved.):9598-9610.
Parks, O. W. and S. Patton. 1961. Volatile carbonyl compounds in stored dry whole milk. Journal of Dairy Science 44(1):1-9.
Patton, S. 1950. The Isolation of Maltol from Heated Skim Milk. Journal of Dairy Science 33(2):102-106.
Ramshaw, E. and E. Dunstone. 1969. Volatile compounds associated with the off-flavour in stored casein. Journal of Dairy Research 36(02):215-223.
Romero, C., F. J. Morales, and S. Jiménez-Pérez. 2001. Effect of storage temperature on galactose formation in UHT milk. Food research international 34(5):389-392.
Schieberle, P., K. Gassenmeier, H. Guth, A. Sen, and W. Grosch. 1993. Character impact odour compounds of different kinds of butter. Lebensmittel-Wissenschaft & Technologie 26(4):347-356.
Shimamura, T. and H. Ukeda. 2012. Maillard reaction in milk—effect of heat treatment. Pages 147-158 in Milk protein. InTechOpen Science. W. L. Hurley, ed.
Shiratsuchi, H., M. Shimoda, K. Imayoshi, K. Noda, and Y. Osajima. 1994. Volatile Flavor Compounds in Spray-Dried Skim Milk Powder. Journal of Agricultural and Food Chemistry 42(4):984-988.
Smit, G. 2003. Dairy processing: Improving quality. Elsevier.

684 Stewart, A., A. S. Grandison, A. Ryan, D. Festring, L. Methven, and J. K. Parker. 2017. The
685 impact of the skim milk powder manufacturing process on the flavor of model white
686 chocolate. J. Agric. Food. Chem.
687 Stewart, A., A. S. Grandison, A. Ryan, and J. K. Parker. 2015. Investigating the Maillard
688 reaction of milk powder in a low-moisture system. Pages 245-248 in Proceedings of XIV
689 Weurman Flavour Research Symposium. A. D. Taylor and D. S. Mottram, ed. Context
690 Products Ltd., Packington, UK, Cambridge, UK.
691 Syrios, A., M. Faka, A. S. Grandison, and M. J. Lewis. 2011. A comparison of reverse
692 osmosis, nanofiltration and ultrafiltration as concentration processes for skim milk prior to
693 drying. International Journal of Dairy Technology 64(4):467-472.
694 Tokusoglu, O., A. S. Akalin, and M. K. Unal. 2004. A rapid high performance liquid
695 chromatographic detection of furosine (.vepsiln.-N-2-furoylmethyl-L-lysine) in pasteurized
696 and UHT milks. Milchwissenschaft 59(Copyright (C) 2012 American Chemical Society
697 (ACS). All Rights Reserved.):502-505.
698 Valero, E., M. Villamiel, B. Miralles, J. Sanz, and I. Martínez-Castro. 2001. Changes in
699 flavour and volatile components during storage of whole and skimmed UHT milk. Food
700 Chemistry 72(1):51-58.
701 Van Boekel, M. A. J. S. 1998. Effect of heating on Maillard reactions in milk. Food
702 Chemistry 62(4):403-414.
703 Vazquez-Landaverde, P. A., G. Velazquez, J. A. Torres, and M. C. Qian. 2005. Quantitative
704 Determination of Thermally Derived Off-Flavor Compounds in Milk Using Solid-Phase
705 Microextraction and Gas Chromatography. Journal of Dairy Science 88(11):3764-3772.
706 Walker, N. J. 1972. Flavour defects in edible casein and skim-milk powder: I. The role of
707 Maillard browning. Journal of Dairy Research 39(02):231-238.
708 Yaylayan, V. A. and S. Mandeville. 1994. Stereochemical control of maltol formation in
709 Maillard reaction. Journal of Agricultural and Food Chemistry 42(3):771-775.
710

Table 1. Concentration of sugars, free amino acids and available amino groups in samples after each stage of milk powder production (per kg dry weight), concentrated by either evaporation or reverse osmosis

code	sample	sugars (mmol/kg dry wt.) [a]				available amino groups (mmol NH_2 / kg dry wt.) [b]	total free amino acids (mmol/kg dry wt.) [c]
		galactose	glucose	lactose	lactulose		
Reverse osmosis							
RWM_{RO}	Raw whole milk	3.6 ± 0.04^{e}	4.8 ± 0.05^{i}	940 ± 19^{h}	nd^{a}	314 ± 6.7^{a}	6.76^{cd}
PM_{RO}	Pasteurized milk	3.1 ± 0.08^{d}	4.2 ± 0.07^{g}	950 ± 19^{hi}	nd^{a}	304 ± 11^{ab}	6.68^{cde}
CM_{RO}	Concentrated milk	2.4 ± 0.12^{c}	3.1 ± 0.08^{cd}	790 ± 16^{cde}	nd^{a}	289 ± 18^{abc}	5.82^{fg}
$FDMP_{RO}$	Freeze-dried milk powder	2.1 ± 0.04^{b}	1.7 ± 0.14^{a}	780 ± 16^{cd}	nd^{a}	279 ± 15^{abc}	6.14^{def}
$SDMP_{RO}$	Spray-dried milk powder	3.5 ± 0.09^{e}	3.0 ± 0.21^{cd}	730 ± 15^{a}	nd^{a}	228 ± 13^{efg}	6.01^{ef}
HCM_{RO}	Heat-treated concentrated milk	15 ± 0.4^{j}	2.7 ± 0.08^{b}	900 ± 18^{g}	31 ± 0.6^{c}	142 ± 5.9^{h}	5.78^{fg}
$HFDMP_{RO}$	Heat-treated freeze-dried milk powder	16.8 ± 0.2^{k}	2.9 ± 0.14^{bc}	780 ± 16^{cd}	33 ± 0.7^{d}	135 ± 12^{h}	5.95^{f}
$HSDMP_{RO}$	Heat-treated spray-dried milk powder	17.2 ± 0.2^{l}	3.1 ± 0.14^{cd}	750 ± 15^{ab}	42 ± 0.8^{f}	128 ± 7.5^{h}	4.19^{h}
Evaporation							
RWM_{EV}	Raw whole milk	4.0 ± 0.1^{f}	5.2 ± 0.1^{j}	970 ± 19^{i}	nd^{a}	290 ± 7.5^{abc}	7.91^{a}
PM_{EV}	Pasteurized milk	3.5 ± 0.13^{e}	4.5 ± 0.08^{h}	1100 ± 21^{j}	nd^{a}	313 ± 22^{a}	7.69^{ab}
CM_{EV}	Concentrated milk	1.8 ± 0.09^{a}	4.6 ± 0.07^{h}	840 ± 17^{f}	nd^{a}	260 ± 3^{cde}	5.20^{g}
$FDMP_{EV}$	Freeze-dried milk powder	2.0 ± 0.07^{ab}	3.3 ± 0.11^{e}	820 ± 16^{ef}	nd^{a}	273 ± 6^{bcd}	6.22^{def}
$SDMP_{EV}$	Spray-dried milk powder	2.9 ± 0.08^{d}	3.7 ± 0.08^{f}	830 ± 17^{f}	nd^{a}	237 ± 22^{def}	6.70^{cd}
HCM_{EV}	Heat-treated concentrated milk	8.7 ± 0.23^{g}	3.1 ± 0.18^{de}	760 ± 15^{bc}	22 ± 0.4^{b}	194 ± 8.1^{g}	7.13^{bc}
$HFDMP_{EV}$	Heat-treated freeze-dried milk powder	9.8 ± 0.12^{h}	3.0 ± 0.04^{cd}	830 ± 17^{f}	22 ± 0.5^{b}	203 ± 10^{fg}	5.64^{fg}
$HSDMP_{EV}$	Heat-treated spray-dried milk powder	12 ± 0.1^{i}	1.8 ± 0.08^{a}	800 ± 16^{de}	35 ± 0.7^{e}	151 ± 11^{h}	5.57^{fg}

All samples (except RWM) were adjusted or reconstituted to 8 % total solids content prior to analysis. The total solids content of the raw whole milk was 12%. Results are the mean of three replicate analyses ± standard deviation. nd = not detected. Means in same column that contain none of the same letters are significantly different (p = 0.05)

[a] Quantification using a Dionex ion chromatography system without derivatization

[b] Derivatization using the EZ:Faast free amino acid analysis kit followed by quantification by GC-MS

[c] Derivatization using OPA assay and spectrophotometric analysis

Table 2 Volatile compounds (SPME-GC/MS) in raw whole milk (RWM), pasteurized milk (PM), concentrated milk (CM) and heated concentrated milk (HCM) concentrated using reverse osmosis or evaporation

LRI [a]	Compound [b]	Relative concentration (μg/L)[c]							
		Reverse Osmosis				Evaporation			
		RWM_{RO}	PM_{RO}	CM_{RO}	HCM_{RO}	RWM_{EV}	PM_{EV}	CM_{EV}	HCM_{EV}
Lipid oxidation products									
697	pentanal	nd ^{b}	3.1 ± 0.95 ^{ab}	1.6 ± 1.1 ^{ab}	4.1 ± 2.4 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	2.6 ± 1.5 ^{ab}
801	hexanal	54 ± 1.6 ^{b}	330 ± 80 ^{a}	94 ± 60 ^{b}	59 ± 31 ^{b}	11 ± 0.26 ^{b}	49 ± 19 ^{b}	5.2 ± 2.7 ^{b}	4.5 ± 2.9 ^{b}
901	heptanal	nd ^{c}	40 ± 11 ^{a}	24 ± 7.8 ^{ab}	27 ± 6.3 ^{ab}	nd ^{c}	39 ± 15 ^{a}	6.3 ± 3.4 ^{b}	7.1 ± 4.5 ^{b}
1002	octanal	nd ^{c}	18 ± 5.2 ^{a}	6.1 ± 4 ^{bc}	9.7 ± 5 ^{abc}	nd ^{c}	16 ± 6.1 ^{ab}	2.8 ± 1.4 ^{c}	7.2 ± 4.8 ^{abc}
1103	nonanal	nd ^{b}	52 ± 15 ^{a}	17 ± 10 ^{ab}	17 ± 8.6 ^{ab}	nd ^{b}	18 ± 29 ^{ab}	11 ± 5.7 ^{b}	9.8 ± 7.2 ^{b}
1205	decanal	nd ^{a}	8 ± 10 ^{a}	0.86 ± 0.82 ^{a}	2 ± 1.2 ^{a}	nd ^{a}	nd ^{a}	nd ^{a}	nd ^{a}
889	2-heptanone	3.4 ± 0.66 ^{b}	1.6 ± 0.28 ^{b}	4.4 ± 2.9 ^{b}	120 ± 56 ^{a}	3.3 ± 0.52 ^{b}	1.9 ± 0.86 ^{b}	5.1 ± 2.8 ^{b}	100 ± 66 ^{a}
1090	2-nonanone	nd ^{c}	1.4 ± 0.34 ^{c}	1.1 ± 0.79 ^{c}	75 ± 36 ^{a}	nd ^{c}	3.1 ± 1.8 ^{bc}	1.2 ± 0.64 ^{c}	54 ± 37 ^{ab}
1191	2-decanone	nd ^{b}	nd ^{b}	nd ^{b}	1.5 ± 0.63 ^{ab}	nd ^{b}	nd ^{b}	nd ^{b}	1.7 ± 1.4 ^{a}
1293	2-undecanone	nd ^{b}	nd ^{b}	nd ^{b}	19 ± 10 ^{a}	nd ^{b}	2.6 ± 1.7 ^{b}	nd ^{b}	13 ± 9.6 ^{ab}
992	2-pentylfuran	nd ^{a}	nd ^{a}	nd ^{a}	51 ± 26 ^{a}	nd ^{a}	nd ^{a}	nd ^{a}	240 ± 310 ^{a}
Free fatty acids									
781	butanoic acid	26 ± 3.7 ^{a}	nd ^{c}	nd ^{c}	0.42 ± 0.72 ^{c}	40 ± 1.7 ^{b}	nd ^{c}	nd ^{c}	nd ^{c}
969	hexanoic acid	98 ± 16 ^{b}	nd ^{c}	4.2 ± 2.4 ^{c}	16 ± 12 ^{c}	170 ± 22 ^{a}	nd ^{c}	nd ^{c}	nd ^{c}
1161	octanoic acid	63 ± 4.3 ^{b}	nd ^{d}	1.7 ± 1.3 d	29 ± 20 ^{c}	87 ± 7.8 ^{a}	6.1 ± 1.3 d	nd ^{d}	3 ± 2.2 d
Sulfur compounds									
748	dimethyl disulfide	nd ^{b}	nd ^{b}	nd ^{b}	24 ± 13 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	15 ± 9.3 ^{ab}
978	dimethyl trisulfide	nd ^{b}	nd ^{b}	nd ^{b}	58 ± 29 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	25 ± 20 ^{ab}
Maillard reaction products									
643	3-methylbutanal	nd ^{b}	nd ^{b}	nd ^{b}	3.3 ± 2.4 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	1.5 ± 0.91 ^{ab}
655	2-methylbutanal	nd ^{b}	nd ^{b}	nd ^{b}	3.4 ± 1.6 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	nd ^{b}
835	2-furfural	nd ^{b}	nd ^{b}	nd ^{b}	11 ± 9 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	6 ± 4.2 ^{ab}
854	2-furanmethanol	nd ^{b}	nd ^{b}	nd ^{b}	120 ± 59 ^{a}	nd ^{b}	nd ^{b}	nd ^{b}	58 ± 31 ^{b}

965	benzaldehyde	nd [b]	nd [b]	nd [b]	28 ± 12 [a]	nd [b]	nd [b]	nd [b]	20 ± 15 [a]

[a] Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C_5-C_{25}

[b] Compounds identified by comparing the LRI value and mass spectral data with a reference collection (NIST 08)

[c] Relative concentration = peak area of compound x concentration of internal standard (ISTD) / peak area of ISTD. Internal standard: 10 µl of 130.6 µg/ml in methanol, nd: not detected. Means of triplicate analyses ± standard deviation, means within the same row not labelled with the same letters are significantly different (p = 0.05)

Table 3 Volatile compounds (SPME-GC/MS) in heated/unheated spray-dried milk powder (HSDMP/SDMP) or freeze-dried milk powder (HFDMP/FDMP) made from milk concentrated by reverse osmosis or evaporation

LRI [a]	Compound [b]	Relative concentration (μg/L) [c]							
		Reverse Osmosis				Evaporation			
		$FDMP_{RO}$	$SDMP_{RO}$	$HFDMP_{RO}$	$HSDMP_{RO}$	$FDMP_{EV}$	$SDMP_{EV}$	$HFDMP_{EV}$	$HSDMP_{EV}$
Lipid oxidation products									
697	pentanal	1 ± 0.37 ^{bc}	0.9 ± 0.4 ^{bc}	nd ^{c}	nd ^{c}	nd ^{c}	1.5 ± 0.29 ^{b}	nd ^{c}	5.2 ± 1.3 ^{a}
801	hexanal	65 ± 16 ^{a}	37 ± 13 ^{b}	14 ± 4.4 ^{c}	7.6 ± 6.9 ^{c}	1.4 ± 0.39 ^{c}	11 ± 2.6 ^{c}	1.6 ± 0.42 ^{bc}	37 ± 7.6 ^{b}
901	heptanal	16 ± 11 ^{b}	15 ± 5.1 ^{b}	nd ^{b}	nd ^{b}	2.7 ± 0.73 ^{b}	25 ± 5.6 ^{b}	6.2 ± 1.3 ^{b}	130 ± 28 ^{a}
1002	octanal	4.1 ± 2.5 ^{b}	4.1 ± 0.92 ^{b}	4.9 ± 1.3 ^{b}	7.8 ± 0.34 ^{b}	2.8 ± 2 ^{b}	14 ± 3.5 ^{b}	6.5 ± 1.5 ^{b}	100 ± 24 ^{a}
1103	nonanal	15 ± 8.6 ^{b}	32 ± 5.4 ^{b}	14 ± 3.5 ^{b}	44 ± 1.3 ^{b}	8.9 ± 1.3 ^{b}	44 ± 12 ^{b}	17 ± 4.2 ^{b}	120 ± 32 ^{a}
1205	decanal	2.2 ± 1.8 ^{b}	nd ^{b}	nd ^{b}	0.99 ± 0.047 ^{b}	nd ^{b}	2.8 ± 0.8 ^{b}	0.66 ± 0.24 ^{b}	10 ± 2.8 ^{a}
889	2-heptanone	2.1 ± 1 ^{b}	3.5 ± 2.7 ^{b}	9.1 ± 4.2 ^{b}	3.2 ± 0.31 ^{b}	1.6 ± 0.64 ^{b}	6.6 ± 1.7 ^{b}	43 ± 12 ^{a}	13 ± 3 ^{b}
1090	2-nonanone	2.4 ± 1.7 ^{d}	nd ^{d}	17 ± 4.8 ^{bc}	8.1 ± 0.8 ^{cd}	2.4 ± 3.2 ^{d}	5.7 ± 1.8 ^{d}	33 ± 7.8 ^{a}	21 ± 5.2 ^{b}
1191	2-decanone	nd ^{c}	nd ^{c}	nd ^{c}	nd ^{c}	nd ^{c}	0.77 ± 0.33 ^{b}	0.98 ± 0.31 ^{b}	1.9 ± 0.42 ^{a}
1293	2-undecanone	nd ^{c}	nd ^{c}	7.9 ± 3 ^{ab}	4.2 ± 0.5 ^{bc}	nd ^{c}	nd ^{c}	9.3 ± 2.2 ^{a}	10 ± 2.8 ^{a}
992	2-pentylfuran	nd ^{b}	nd ^{b}	21 ± 5.8 ^{b}	13 ± 2 ^{b}	nd ^{b}	12 ± 2.5 ^{b}	44 ± 11 ^{a}	60 ± 18 ^{a}
Free fatty acids									
969	hexanoic acid	7.3 ± 2.8 ^{ab}	2 ± 0.77 ^{bc}	7.8 ± 4 ^{a}	3.3 ± 2.4 ^{abc}	nd ^{c}	nd ^{c}	nd ^{c}	nd ^{c}
1161	octanoic acid	1.2 ± 0.67 ^{c}	0.29 ± 0.26 ^{c}	1.7 ± 0.92 ^{c}	0.91 ± 0.41 ^{c}	nd ^{c}	5.1 ± 2 ^{b}	0.77 ± 0.41 ^{c}	15 ± 1.7 ^{a}
Sulfur compounds									
748	dimethyl disulfide	nd ^{b}	nd ^{b}	6.8 ± 1.6 ^{ab}	13 ± 6.4 ^{a}	nd ^{b}	1.5 ± 0.42 ^{b}	5.5 ± 1.8 ^{b}	6.4 ± 0.23 ^{ab}
978	dimethyl trisulfide	nd ^{b}	nd ^{b}	16 ± 2.8 ^{a}	27 ± 9 ^{a}	nd ^{b}	nd ^{b}	16 ± 4.9 ^{a}	25 ± 4.2 ^{a}
Maillard reaction products									
643	3-methylbutanal	nd ^{c}	1.4 ± 0.37 ^{b}	0.93 ± 0.78 ^{bc}	5.1 ± 0.59 ^{a}	nd ^{c}	1.6 ± 0.41 ^{b}	nd ^{c}	1.5 ± 0.26 ^{b}
655	2-methylbutanal	nd ^{d}	2.2 ± 0.51 ^{c}	nd ^{d}	8.5 ± 1.1 ^{a}	nd ^{d}	2.4 ± 0.7 ^{bc}	nd ^{d}	3.7 ± 0.54 ^{b}
835	2-furfural	nd ^{d}	nd ^{d}	2.6 ± 1.8 ^{c}	5.6 ± 1.1 ^{b}	nd ^{d}	nd ^{d}	2.5 ± 0.76 ^{c}	16 ± 0.57 ^{a}
854	2-furanmethanol	nd ^{b}	nd ^{b}	20 ± 13 ^{ab}	21 ± 6.7 ^{ab}	nd ^{b}	nd ^{b}	38 ± 18 ^{a}	15 ± 4.4 ^{b}
965	benzaldehyde	nd ^{b}	1.7 ± 1 ^{b}	8.8 ± 0.99 ^{b}	11 ± 2.5 ^{b}	nd ^{b}	11 ± 2.7 ^{b}	11 ± 3.5 ^{b}	94 ± 21 ^{a}
1116	maltol	nd ^{b}	nd ^{b}	nd ^{b}	nd ^{b}	nd ^{b}	nd ^{b}	nd ^{b}	1.8 ± 0.52 ^{a}

[a] Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C_5-C_{25}

[b] Compounds identified by comparing the LRI value and mass spectral data with authentic samples

[c] Relative concentration = peak area of compound x concentration of internal standard (ISTD) / peak area of ISTD. Internal standard: 10 µl of 130.6 µg/ml in methanol, nd: not detected. Means of triplicate analyses ± standard deviation, means within the same row not labelled with the same letters are significantly different (p = 0.05)

Table .4 Volatile compounds (SPME-GC/MS) in model white chocolate produced from skimmed milk powders produced using different processing conditions, conched for 8 h at 80 °C

LRI [a]	compound [b]	peak area ($x10^5$) [c]							
		Reverse Osmosis				Evaporation			
		FDMP	SDMP	HFDMP	HSDMP	FDMP	SDMP	HFDMP	HSDMP
<600	acetic acid	140 ± 0.25 ^{de}	34 ± 1 ^{ab}	150 ± 3.1 ^{e}	74 ± 8 ^{bc}	260 ± 25 ^{f}	58 ± 2.8 ^{abc}	310 ± 6 ^{g}	150 ± 23 ^{e}
642	3-methylbutanal	6.8 ± 0.68 ^{cd}	4.3 ± 0.48 ^{abc}	6.3 ± 0.29 ^{bcd}	4.2 ± 0.63 ^{abc}	4.6 ± 0.59 ^{abc}	4.6 ± 1.7 ^{abc}	4 ± 1 ^{ab}	3 ± 0.037 ^{a}
649	1-hydroxy-2-propanone	13 ± 1.1 ^{ab}	2.2 ± 0.073 ^{a}	35 ± 2.9 ^{c}	18 ± 4.8 ^{b}	53 ± 3 ^{d}	4.4 ± 1.9 ^{a}	71 ± 3.3 ^{e}	11 ± 1.3 ^{ab}
654	2-methylbutanal	12 ± 0.65 ^{a}	5.1 ± 0.63 ^{a}	nd	11 ± 0 ^{a}	nd	6.1 ± 2.2 ^{a}	nd	6.8 ± 1.4 ^{a}
677	propanoic acid	11 ± 4.6 ^{a}	7.5 ± 3.3 ^{a}	14 ± 3.8 ^{a}	10 ± 6 ^{a}	9 ± 1.2 ^{a}	8.8 ± 5.8 ^{a}	7.2 ± 1.6 ^{a}	11 ± 0.71 ^{a}
684	2-pentanone	31 ± 3.1 ^{f}	11 ± 0.061 ^{abc}	24 ± 0.85 ^{def}	11 ± 1.6 ^{abc}	26 ± 3.1 ^{ef}	15 ± 7.1 ^{bcd}	20 ± 1 ^{cde}	12 ± 0.73 ^{abc}
698	pentanal	360 ± 6.5 ^{abc}	550 ± 52 ^{d}	340 ± 46 ^{abc}	350 ± 66 ^{abc}	330 ± 2.3 ^{abc}	450 ± 85 ^{bcd}	270 ± 7.5 ^{a}	290 ± 40 ^{ab}
782	butanoic acid	190 ± 0.59 ^{c}	67 ± 7.5 ^{a}	120 ± 7.3 ^{b}	70 ± 12 ^{a}	120 ± 8.2 ^{b}	71 ± 9.6 ^{a}	110 ± 6.3 ^{b}	120 ± 20 ^{b}
800	hexanal	82 ± 3.7 ^{ab}	65 ± 3.3 ^{a}	70 ± 9.3 ^{ab}	52 ± 10 ^{a}	100 ± 2 ^{b}	70 ± 17 ^{ab}	74 ± 8.5 ^{ab}	51 ± 5 ^{a}
830	3-methylbutanoic acid	6 ± 0 ^{a}	5.4 ± 0 ^{a}	5.2 ± 0 ^{a}	5 ± 0 ^{a}	nd	5 ± 0 ^{a}	3.4 ± 0 ^{a}	3.5 ± 0 ^{a}
833	2-furfural	5.1 ± 0.9 ^{a}	0.55 ± 0.13 ^{a}	3.3 ± 0.31 ^{a}	2 ± 0.56 ^{a}	60 ± 0.86 ^{c}	1.5 ± 0.8 ^{a}	26 ± 6.4 ^{b}	3.7 ± 0.28 ^{a}
852	2-furanmethanol	31 ± 1 ^{a}	1.6 ± 0.27 ^{a}	53 ± 12 ^{a}	9.8 ± 1.4 ^{a}	780 ± 53 ^{c}	3.3 ± 0 ^{a}	540 ± 190 ^{b}	9.8 ± 2.3 ^{a}
870	pentanoic acid	16 ± 0.31 ^{a}	12 ± 4.2 ^{a}	13 ± 3.7 ^{a}	15 ± 0.51 ^{a}	16 ± 0.12 ^{a}	20 ± 2.6 ^{a}	10 ± 0.17 ^{a}	16 ± 4 ^{a}
889	2-heptanone	88 ± 2 ^{fg}	41 ± 3 ^{cd}	67 ± 12 ^{def}	38 ± 8.2 ^{bcd}	100 ± 11 ^{g}	51 ± 18 ^{de}	72 ± 13 ^{ef}	41 ± 4.6 ^{cd}
900	heptanal	14 ± 0.2 ^{bc}	7.8 ± 0.25 ^{ab}	9.7 ± 0.97 ^{abc}	6.3 ± 2 ^{a}	16 ± 1.7 ^{c}	9.2 ± 4.6 ^{abc}	10 ± 2.5 ^{abc}	6.8 ± 2.1 ^{ab}
913	dimethyl sulfone	95 ± 2.6 ^{e}	30 ± 0.76 ^{abc}	71 ± 6.4 ^{de}	37 ± 4.8 ^{bc}	190 ± 4.5 ^{g}	46 ± 9.9 ^{cd}	130 ± 22 ^{f}	46 ± 0.52 ^{cd}
956	(E)-2-heptenal	5.9 ± 0.71 ^{a}	2.4 ± 0.12 ^{a}	3.8 ± 1.4 ^{a}	3.7 ± 1.3 ^{a}	21 ± 6.2 ^{b}	7.1 ± 0.75 ^{a}	12 ± 9.5 ^{ab}	4.7 ± 1.1 ^{a}
965	benzaldehyde	3.3 ± 0.56 ^{ab}	2.1 ± 0.73 ^{ab}	2.8 ± 1.1 ^{ab}	1.6 ± 0.13 ^{a}	11 ± 0.86 ^{c}	3.4 ± 1.3 ^{ab}	4.6 ± 0.55 ^{b}	1.7 ± 0.046^{ab}
966	hexanoic acid	68 ± 1.7 ^{d}	20 ± 4.5 ^{abc}	37 ± 6.3 ^{bc}	16 ± 2.6 ^{ab}	74 ± 3.5 ^{d}	21 ± 6.3 ^{abc}	39 ± 16 ^{c}	29 ± 6.2 ^{abc}
1001	octanal	11 ± 0.8 ^{bc}	7 ± 0.34 ^{abc}	8.9 ± 1.9 ^{abc}	6.5 ± 1.3 ^{ab}	19 ± 1 ^{d}	8.7 ± 1.4 ^{abc}	12 ± 3.4 ^{c}	7.3 ± 0.96 ^{abc}
1085	methyl 2-furoate	nd	nd	nd	nd	26 ± 4.5 ^{a}	nd	12 ± 8.4 ^{a}	nd
1088	tetramethylpyrazine	nd	0.64 ± 0.26 ^{a}	0.88 ± 0 ^{a}	0.56 ± 0.018 ^{a}	nd	0.81 ± 0 ^{a}	nd	0.71 ± 0.006^{a}
1089	2-nonanone	25 ± 1.8 ^{de}	8.2 ± 0.068^{abc}	17 ± 4 ^{cd}	7.8 ± 1.3 ^{abc}	32 ± 3.1 ^{e}	12 ± 2.8 ^{abc}	16 ± 5 ^{bcd}	9.1 ± 0.93 ^{abc}
1102	nonanal	49 ± 4.9 ^{bc}	21 ± 1.3 ^{ab}	35 ± 4.7 ^{ab}	18 ± 2 ^{a}	72 ± 24 ^{c}	26 ± 3.7 ^{ab}	31 ± 9.4 ^{ab}	18 ± 1.9 ^{a}
1114	maltol	17 ± 0.88 ^{a}	nd	15 ± 0 ^{a}	2.6 ± 2.2 ^{a}	310 ± 3.2 ^{c}	nd	120 ± 18 ^{b}	1.8 ± 0.13 ^{a}

[a] Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C_5-C_{25}

[b] Compounds identified by comparing the LRI value and mass spectral data with authentic standard

[c] Peak area from SPME/GC-MS, nd: not detected. Means of triplicate analyses ± standard deviation, means within the same row not labelled with the same letters are significantly different (p = 0.05). FDMP: freeze-dried milk powder, SDMP: spray-dried milk powder, HFDMP: heat-treated freeze-dried milk powder, HSDMP: heat-treated freeze-dried milk powder

FIGURE CAPTIONS

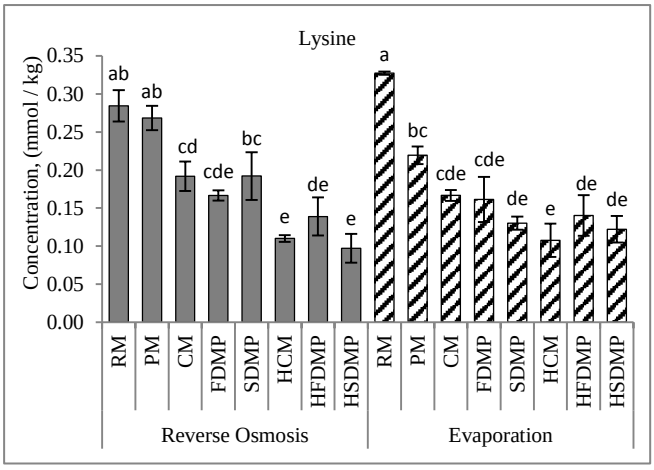
Figure 1. Variation in the concentration of lysine during processing of skim milk powder (SMP) using two different concentration methods: reverse osmosis and evaporation. RWM: raw milk, PM: pasteurized milk, CM: concentrated milk, HCM: heat treated concentrated milk, SDMP: spray-dried milk powder, HSDMP: heat treated spray-dried milk powder, FDMP: freeze-dried milk powder, HFDMP: heat treated freeze-dried milk powder. All samples were made up to 8 % total solids content prior to analysis. Results are the mean of three replicate analyses ± standard deviation (error bars). Bars not labelled with the same letters are significantly different (p = 0.05).

Figure 2. Moisture content (%) of milk powder samples, determined by Karl Fischer titration. Mean of duplicate analyses ± standard deviation as error bars. Number above each bar denotes the water activity (a_w).

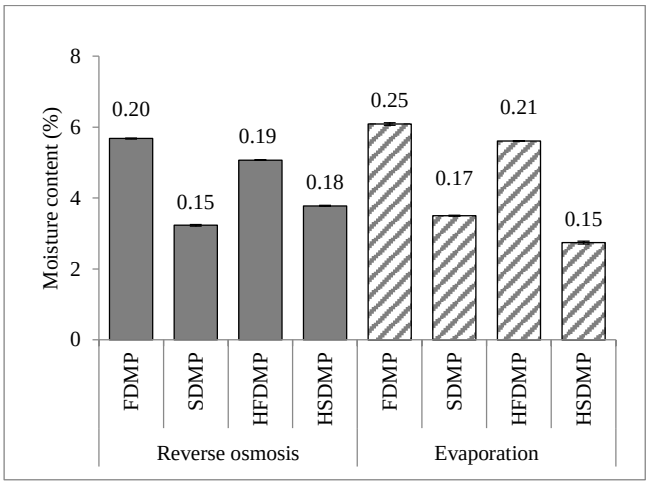
Figure 3. Optical micrographs of heated spray-dried milk powder (HSDMP) or freeze-dried milk powder (HFDMP) produced from milk concentrated by reverse osmosis (RO) or evaporation (EV). (A) $HSDMP_{RO}$, (B) $HSDMP_{EV}$, (C) $HFDMP_{RO}$, and (D) $HFDMP_{EV}$

Figure 4. Comparative analysis (SPME-GC/MS) of (a) 2-heptanone and, (b) maltol in model white chocolate containing skimmed milk powder produced with different combinations of processing conditions: Concentration by reverse osmosis or evaporation, low or high heat treatment (H: high heat treatment) and drying by either freeze-drying (FD) or spray-drying (SD). Mean of triplicate analyses shown ± standard deviation as error bars. Bars not labelled with the same letters are significantly different (p = 0.05)

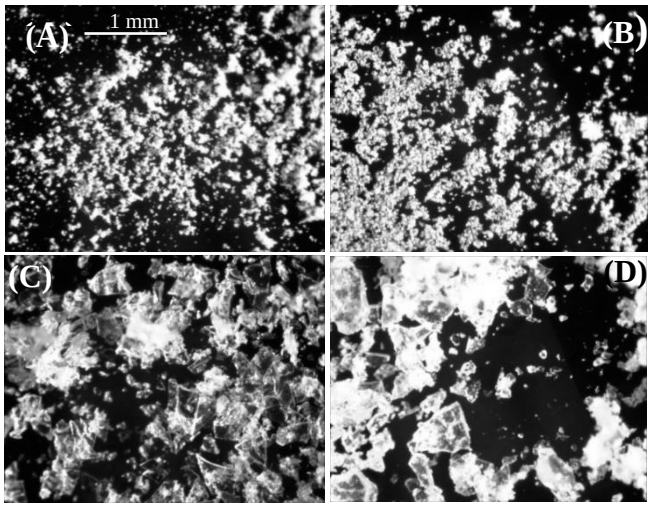
STEWART FIGURE 1



STEWART FIGURE 2



STEWART FIGURE 3



STEWART FIGURE 4