

*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*

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

3 STEWART

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

11

12 **CHANGES IN FLAVOR PROFILE OF SKIM MILK POWDER**

13

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

16

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## ABSTRACT

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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

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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 to 105 °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

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

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

100 Given the significant changes in SMP brought about by different processing conditions, it is  
101 important to understand if these changes are reflected in the final products when SMP is used  
102 as an ingredient for the manufacture of more complex food products. Caudle et al. (2005)  
103 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 al. (2009b) carried out a similar experiment 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 degradation 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.

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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.

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## MATERIALS AND METHODS

### *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-phthalaldehyde  
125 (OPA), 2-mercaptoethanol, sodium tetraborate buffer solution (pH 9), 1,2-dichlorobenzene,  
126 methanol, all aroma chemical, alkanes C<sub>5</sub> – C<sub>30</sub> 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).

129 ***Preparation of Milk Powders***

130 Raw whole bovine milk (RWM<sub>RO</sub>) (40 kg) supplied by The University of Reading CEDAR  
131 Dairy Farm (CEDAR, Reading, UK) was pasteurized at 72 °C for 15 s and separated using a  
132 disc bowl centrifuge. The skimmed pasteurized milk (PM<sub>RO</sub>) was then concentrated to 20%  
133 total solids using reverse osmosis (RO) to produce concentrated milk (CM<sub>RO</sub>). Half of the  
134 concentrated milk was then subjected to a heat treatment stage to give a heated concentrated  
135 milk (HCM<sub>RO</sub>), and no heat treatment was applied to the other half. The concentrated milks  
136 was then spray-dried (SD) or freeze dried (FD) to produce the following milk powders (MP):  
137 SDMP<sub>RO</sub>, HSDMP<sub>RO</sub>, HFDMP<sub>RO</sub>, FDMP<sub>RO</sub> and HFDMP<sub>RO</sub>. A second batch of raw whole  
138 milk was obtained one week later from the same herd, and the process was repeated  
139 concentrating to 20% solids using evaporation (EV) to produce a second set of milks  
140 (RWM<sub>EV</sub>, PM<sub>EV</sub>, CM<sub>EV</sub>, HCM<sub>EV</sub>) and milk powders (SDMP<sub>EV</sub>, HSDMP<sub>EV</sub>, HFDMP<sub>EV</sub>,  
141 FDMP<sub>EV</sub> and HFDMP<sub>EV</sub>).

142 ***Reverse Osmosis.*** Reverse osmosis was carried out at 60 bar outlet pressure using the  
143 RO module described previously by Syrios et al. (2011) until the total solids content was  
144 20%, assessed using a Lactoscope (Quadrachem Laboratories Ltd, London, UK). Changes in  
145 the protein, fat, lactose and total solid content were previously measured throughout the  
146 process (Stewart et al., 2017). The temperature of concentrated milk during RO was 30 °C.

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

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

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

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

### 161 ***Preparation of Model White Chocolate***

162 White chocolate was prepared as described by Stewart et al. (2017). The conching process of  
163 white chocolate was mimicked using a 250 mL continuously stirred reactor vessel (Atlas  
164 Potassium, Syrris Inc., Royston, UK) under different heating conditions. A preliminary study  
165 was carried out to test different conching conditions, heating the model white chocolate  
166 (produced with commercial SMP) at four temperature/time combinations: 4 h at 50 °C, 4 h at  
167 80 °C, 8 h at 50 °C and 8 h at 80 °C. The two extremes were chosen for a comparison to  
168 identify potential differences as a result of conching time and temperature. For each milk  
169 powder, two model white chocolates were produced using either mild conching conditions (4  
170 h at 50 °C) or harsh conditions (8 h at 80 °C). Model white chocolate was refrigerated and  
171 stored at 4±1 °C prior to analysis. A control white chocolate was also produced containing all  
172 ingredients apart from SMP, to confirm that differences observed were as a result of the SMP  
173 and not due to other ingredients. This control was conched for 8 h at 80 °C and analyzed  
174 under the same conditions as other samples.

### 175 ***Analytical Methods***

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

178           **Determination of Sugars by Ion Chromatography.** An aliquot (400  $\mu$ L) of each  
179 sample was transferred to an Amicon 0.5 mL 3 kDa MWCO filter (Millipore, Watford, UK)  
180 and centrifuged for 20 min at 12,000  $\times$  g. The filtrate was diluted 200-fold in water and 500  
181  $\mu$ L of this diluted sample was combined with 500  $\mu$ L of a 40 g/L trehalose solution. Extracts  
182 were analyzed using a Dionex ion chromatography system (Dionex Corp., Sunnyvale, USA),  
183 which consisted of an AS50 autosampler, LC25 column oven, GS50 pumps, and an ED50  
184 pulsed amperometric detector, running in internal amperometric mode. Separation was  
185 carried out on a Carbopac PA1 column (Dionex Corp., Sunnyvale, USA) (250 x 4 mm i.d.)  
186 coupled with a guard column (50 mm  $\times$  4 mm i.d.), using an injection volume of 20  $\mu$ L. A  
187 gradient program was set up using water and 200 mM NaOH at a flow rate of 1 ml/min as  
188 follows: 40 min at 12 mM NaOH, 5 min at 200 mM NaOH, and finally re-equilibrated for 5  
189 min at 12 mM NaOH. The waveform of the pulsed amperometric detector was as follows:  
190 400 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,  
191 galactose, lactose and lactulose were used to produce a series of calibration curves, using  
192 trehalose as an internal standard, for quantification. Chromeleon software was used to operate  
193 the system, as well as for data quantification. All samples were analyzed in triplicate.

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

199           **Determination of Free Amino Acids by GC-MS.** An aliquot of each aqueous sample  
200 (100  $\mu$ L) was derivatized using the EZ:Faast free amino acid analysis kit for GC-MS  
201 (Phenomenex, Macclesfield, UK). GC-MS analysis was carried out as described previously  
202 by Elmore et al.(Elmore et al., 2007).

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

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

215            **Solid-Phase Microextraction/GC-MS (SPME/GC-MS).** Volatile compounds were  
216 extracted from liquid milk, milk powder and white chocolate samples using an automated  
217 SPME/GC-MS system (Agilent), equipped with a DVB/CAR/PDMS Stableflex fiber  
218 (Supelco, Bellefonte, USA). Samples (4 g) were weighed into 20 ml glass SPME vials and  
219 analyzed using the method detailed previously by Stewart et al. (2015). An internal standard  
220 (10  $\mu$ l of 130.6  $\mu$ g/ml 1,2-dichlorobenzene in methanol) was added to aqueous samples. No  
221 internal standard was added to model white chocolate samples but instrument sensitivity was  
222 checked by running a standard of 1,2-dichlorobenzene (10  $\mu$ l, 130.6  $\mu$ g/ml in methanol) at  
223 regular intervals. All samples were analyzed in triplicate.

#### 224 **Statistical Analysis**

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

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## 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 industrial 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

278 RWM to the finished milk powder for all combinations of processing. About 12% was lost  
279 during pasteurization (both for RO and EV batches) and there was further loss during heat  
280 treatment which was greater for HCM<sub>EV</sub> than HCM<sub>RO</sub> and for which we have no explanation.  
281 The loss of glucose during freeze-drying of the unheated milk (CM) is more than might be  
282 expected and is difficult to explain, whereas upon freeze-drying of the heated milk (HCM),  
283 there is no significant change. We observed that the most significant decrease in glucose  
284 concentration was from RWM<sub>EV</sub> to HSDMP<sub>EV</sub>, which represents the powder produced under  
285 the most severe combination of processing conditions.

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

298 **Amino groups.** The OPA spectrophotometric assay used to quantify available amino  
299 groups gives an approximation of the total number of available amino groups, i.e. those not  
300 bound to sugars. The most significant loss we observed was for the high heat spray-dried  
301 powders, with 48 % (139 mmol NH<sub>2</sub>/kg) lost from RWM<sub>EV</sub> to HSDMP<sub>EV</sub> and 59 % (186  
302 mmol NH<sub>2</sub>/kg) lost from RWM<sub>RO</sub> to HSDMP<sub>RO</sub>. These overall losses are of a similar



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

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

315 Figure 1 shows variation in the concentration of lysine which demonstrated a significant  
316 decrease in concentration during thermal processing. Lysine residues in milk proteins are  
317 considered to be the most important for the Maillard reaction in milk powder due to the free  
318 and highly reactive  $\epsilon$ -amino group, but free lysine also has an additional  $\alpha$ -amino  
319 group(O'Brien, 2003) which can participate. This is supported by the results of this study, as  
320 free lysine concentration can be seen to decrease ( $p<0.05$ ) with increased heating, likely to be  
321 the result of the Maillard reaction with lactose. There was a decrease in lysine concentration  
322 after concentration by both reverse osmosis and evaporation and, although only the decrease  
323 from reverse osmosis was statistically significant, the trend was the same for evaporation.  
324 However, the decrease from PM to HCM was significant for both concentration methods.  
325 There was generally little difference observed between batches concentrated by EV and RO,  
326 compared to the bigger changes in Maillard precursors which took place during the heat  
327 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

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

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

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

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

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

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

384 During the subsequent concentration, comparison of RO and EV showed that  $CM_{RO}$   
385 contained more aldehydes (particularly hexanal) and acids compared to  $CM_{EV}$ , although the  
386 differences were not always significant. This is consistent with Park and Drake (2016) who  
387 showed that RO retained in general more aldehydes, lactones and acids. During the  
388 subsequent heating step, the aldehydes tended to decrease, and we attribute this to their  
389 volatile nature, suggesting that they are lost by volatilisation quicker than they are formed.

390 However, this was not the case for 2-heptanone and 2-nonanone, which demonstrated a  
391 consistent increase with each additional processing stage and a significant increase after heat  
392 treatment. The longer chain ketones (2-decanone and 2-undecanone) and 2-pentylfuran were  
393 almost exclusively formed during the heating step. The trends were consistent across the  
394 samples regardless of concentration method.

395 Free fatty acids (FFAs) have been identified as major contributors to the flavor of milk fat by  
396 Schieberle et al. (1993) and were detected in all RWM samples. They have also been reported  
397 in SMP (Karagül-Yüceer et al., 2001), although our results show that most were removed  
398 when the milk was first pasteurised and skimmed, consistent with Drake et al. (2006).

399 Concentration by RO led to an increase in FFA concentration which continued with heat  
400 treatment, although levels were much lower than those observed in the starting RWM.

401 Without a double bond, saturated FFAs are less reactive than unsaturated FFAs and as a  
402 result are likely to be more heat-stable at lower heating temperatures, such as those applied

403 during the concentration step. As part of the pasteurization step, the milk was skimmed by  
404 centrifugation immediately followed by pasteurization. It is possible that the large decrease in  
405 FFA concentration between RWM and PM could be due to the separation process and the  
406 removal of FFA with the milk fat. This would result in an initial decrease in concentration  
407 followed by an increase as they are formed via lipid oxidation during further processing.  
408 The effect of thermal processing is most apparent for volatile compounds formed as a result  
409 of thermal degradation and the Maillard reaction. Sulfur compounds and Maillard reaction  
410 products (MRPs) were detected only in heat-treated samples and generally in larger amounts  
411 for samples concentrated by RO, although the differences between RO and EV were not  
412 significant in most cases.

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

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

426 Considering that the EV batch had a slightly higher concentrations of Maillard precursors  
427 (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<sub>EV</sub> and HCM<sub>RO</sub>, and the general trend was for there to be fewer MRPs  
430 in HCM<sub>EV</sub>. 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 et 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<sub>EV</sub>. This supports previous work by Li et al.  
451 (2012), which concluded that heat treatment of milk prior to concentration and spray-drying

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

463 Hexanoic acid was only detected in RO samples and although there was no difference  
464 between heat treatments the freeze-dried samples had significantly higher concentrations than  
465 their spray-dried equivalents. Conversely, octanoic acid was detected in both EV and RO  
466 samples but only the EV samples showed significant differences, as a result of both drying  
467 method and heat treatment. Loss of volatile fatty acids during conching was shown to take  
468 place by Hoskin and Dimick (1979) and spray-drying of milk powder could yield similar  
469 results. The temperature of milk particles during spray-drying (wet bulb temperature) was 45  
470 – 50 °C and in combination with the evaporation of water this could have led to the lower  
471 concentration of FFAs in SDMP compared to FDMP produced from the same HCM.

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

477 produced from the heat treated milks, and there was no difference between the products  
478 prepared by EV or RO. The less odor active dimethyl disulfide showed a similar trend.  
479 Two Maillard-derived compounds, benzaldehyde and 3-hydroxy-2-methyl-4H-pyran-4-one  
480 (maltol), were significantly affected by the combination of concentration, heat treatment and  
481 drying methods used. Karagül-Yüceer et al. (2001) previously identified maltol in SMP of  
482 various heat treatments, but a higher intensity was perceived in the high heat-treated powder.  
483 Maltol is derived from the Maillard reaction of disaccharides such as lactose at high  
484 temperatures (Patton, 1950, Yaylayan and Mandeville, 1994) and was only detected after the  
485 most severe processing (HSDMP<sub>EV</sub>). It is one of the compounds reported by Stewart et al.,  
486 (2017) which are likely to contribute to the more caramel-like flavor in the heat treated  
487 powders.

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

#### 496 ***Model White Chocolate***

497 To evaluate the effect of different milk powder processing conditions after incorporation into  
498 a confectionery product, a series of model white chocolate samples was produced under  
499 different conching conditions. For this study, each milk powder was used to produce one  
500 batch of model white chocolate conched under normal conditions (4 h at 50 °C) and one  
501 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 the loss of sugars and free amino groups at this stage - there being  
536 a significant loss of free amino groups in the EV concentrated 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

552 freeze-dried samples. The concentration method seemed to have very little influence on the  
553 Maillard reaction, except that maltol, an important aroma compound, was only found in the  
554 high heat, spray-dried powder that had been concentrated using evaporation.  
555 The volatile profile of the white chocolate was shown to be driven by a number of factors  
556 which include moisture content of the SMP, method of concentration and the application of  
557 heat. The interrelation of these mechanism is complex, but here we show that changes in  
558 these unit operations can quite significantly alter the volatile profile, in particular the  
559 combination of concentration by evaporation when the moisture content of the SMP is  
560 somewhat higher than is typically used within the industry. In general, we have shown that  
561 these stages of processing are interdependent, and early stages of SMP manufacture can have  
562 an impact of the volatile profile of model white chocolate. The results of this investigation are  
563 potentially useful for the dairy and confectionery industries in controlling the volatile profile  
564 of their final product.

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**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.) <sup>a</sup>				available amino groups (mmol NH <sub>2</sub> /kg dry wt.) <sup>b</sup>	total free amino acids (mmol/kg dry wt.) <sup>c</sup>
		galactose	glucose	lactose	lactulose		
Reverse osmosis							
RWM <sub>RO</sub>	Raw whole milk	3.6 ± 0.04 <sup>e</sup>	4.8 ± 0.05 <sup>i</sup>	940 ± 19 <sup>h</sup>	nd <sup>a</sup>	314 ± 6.7 <sup>a</sup>	6.76 <sup>cd</sup>
PM <sub>RO</sub>	Pasteurized milk	3.1 ± 0.08 <sup>d</sup>	4.2 ± 0.07 <sup>g</sup>	950 ± 19 <sup>hi</sup>	nd <sup>a</sup>	304 ± 11 <sup>ab</sup>	6.68 <sup>cde</sup>
CM <sub>RO</sub>	Concentrated milk	2.4 ± 0.12 <sup>c</sup>	3.1 ± 0.08 <sup>cd</sup>	790 ± 16 <sup>cde</sup>	nd <sup>a</sup>	289 ± 18 <sup>abc</sup>	5.82 <sup>fg</sup>
FDMP <sub>RO</sub>	Freeze-dried milk powder	2.1 ± 0.04 <sup>b</sup>	1.7 ± 0.14 <sup>a</sup>	780 ± 16 <sup>cd</sup>	nd <sup>a</sup>	279 ± 15 <sup>abc</sup>	6.14 <sup>def</sup>
SDMP <sub>RO</sub>	Spray-dried milk powder	3.5 ± 0.09 <sup>e</sup>	3.0 ± 0.21 <sup>cd</sup>	730 ± 15 <sup>a</sup>	nd <sup>a</sup>	228 ± 13 <sup>efg</sup>	6.01 <sup>ef</sup>
HCM <sub>RO</sub>	Heat-treated concentrated milk	15 ± 0.4 <sup>j</sup>	2.7 ± 0.08 <sup>b</sup>	900 ± 18 <sup>g</sup>	31 ± 0.6 <sup>c</sup>	142 ± 5.9 <sup>h</sup>	5.78 <sup>fg</sup>
HFDMP <sub>RO</sub>	Heat-treated freeze-dried milk powder	16.8 ± 0.2 <sup>k</sup>	2.9 ± 0.14 <sup>bc</sup>	780 ± 16 <sup>cd</sup>	33 ± 0.7 <sup>d</sup>	135 ± 12 <sup>h</sup>	5.95 <sup>f</sup>
HSDMP <sub>RO</sub>	Heat-treated spray-dried milk powder	17.2 ± 0.2 <sup>l</sup>	3.1 ± 0.14 <sup>cd</sup>	750 ± 15 <sup>ab</sup>	42 ± 0.8 <sup>f</sup>	128 ± 7.5 <sup>h</sup>	4.19 <sup>h</sup>
Evaporation							
RWM <sub>EV</sub>	Raw whole milk	4.0 ± 0.1 <sup>f</sup>	5.2 ± 0.1 <sup>j</sup>	970 ± 19 <sup>i</sup>	nd <sup>a</sup>	290 ± 7.5 <sup>abc</sup>	7.91 <sup>a</sup>
PM <sub>EV</sub>	Pasteurized milk	3.5 ± 0.13 <sup>e</sup>	4.5 ± 0.08 <sup>h</sup>	1100 ± 21 <sup>j</sup>	nd <sup>a</sup>	313 ± 22 <sup>a</sup>	7.69 <sup>ab</sup>
CM <sub>EV</sub>	Concentrated milk	1.8 ± 0.09 <sup>a</sup>	4.6 ± 0.07 <sup>h</sup>	840 ± 17 <sup>f</sup>	nd <sup>a</sup>	260 ± 3 <sup>cde</sup>	5.20 <sup>g</sup>
FDMP <sub>EV</sub>	Freeze-dried milk powder	2.0 ± 0.07 <sup>ab</sup>	3.3 ± 0.11 <sup>e</sup>	820 ± 16 <sup>ef</sup>	nd <sup>a</sup>	273 ± 6 <sup>bcd</sup>	6.22 <sup>def</sup>
SDMP <sub>EV</sub>	Spray-dried milk powder	2.9 ± 0.08 <sup>d</sup>	3.7 ± 0.08 <sup>f</sup>	830 ± 17 <sup>f</sup>	nd <sup>a</sup>	237 ± 22 <sup>def</sup>	6.70 <sup>cd</sup>
HCM <sub>EV</sub>	Heat-treated concentrated milk	8.7 ± 0.23 <sup>g</sup>	3.1 ± 0.18 <sup>de</sup>	760 ± 15 <sup>bc</sup>	22 ± 0.4 <sup>b</sup>	194 ± 8.1 <sup>g</sup>	7.13 <sup>bc</sup>
HFDMP <sub>EV</sub>	Heat-treated freeze-dried milk powder	9.8 ± 0.12 <sup>h</sup>	3.0 ± 0.04 <sup>cd</sup>	830 ± 17 <sup>f</sup>	22 ± 0.5 <sup>b</sup>	203 ± 10 <sup>fg</sup>	5.64 <sup>fg</sup>
HSDMP <sub>EV</sub>	Heat-treated spray-dried milk powder	12 ± 0.1 <sup>i</sup>	1.8 ± 0.08 <sup>a</sup>	800 ± 16 <sup>de</sup>	35 ± 0.7 <sup>e</sup>	151 ± 11 <sup>h</sup>	5.57 <sup>fg</sup>

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  $\pm$  standard deviation. nd = not detected. Means in same column that contain none of the same letters are significantly different ( $p = 0.05$ )

<sup>a</sup> Quantification using a Dionex ion chromatography system without derivatization

<sup>b</sup> Derivatization using the EZ:Faast free amino acid analysis kit followed by quantification by GC-MS

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

965	benzaldehyde	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	28 ± 12 <sup>a</sup>	nd <sup>b</sup>	nd <sup>b</sup>	nd <sup>b</sup>	20 ± 15 <sup>a</sup>
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<sup>a</sup> Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C<sub>5</sub>-C<sub>25</sub>

<sup>b</sup> Compounds identified by comparing the LRI value and mass spectral data with a reference collection (NIST 08)

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

<sup>a</sup> Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C<sub>5</sub>-C<sub>25</sub>

<sup>b</sup> Compounds identified by comparing the LRI value and mass spectral data with authentic samples

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

<sup>a</sup> Linear retention index on DB-5 column, calculated from a linear equation between each pair of straight chain alkanes C<sub>5</sub>-C<sub>25</sub>

<sup>b</sup> Compounds identified by comparing the LRI value and mass spectral data with authentic standard

<sup>c</sup> 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

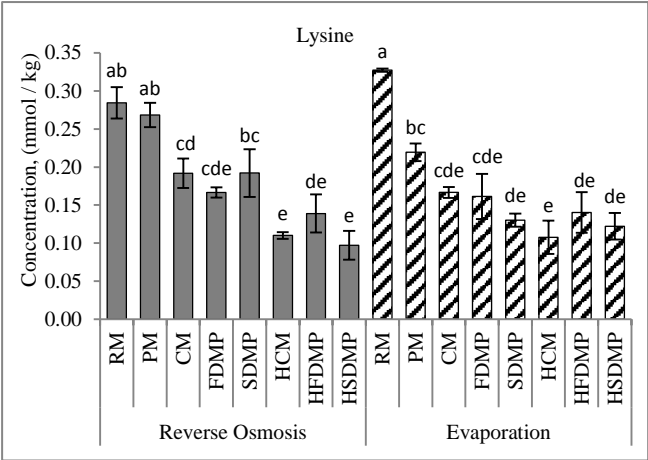
**Figure 1.** Variation in the concentration of lysine during processing of skim milk powder (SMP) using two different concentration methods: reverse osmosis and evaporation. RWM: raw milk, PM: pasteurized milk, CM: concentrated milk, HCM: heat treated concentrated milk, SDMP: spray-dried milk powder, 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  $\pm$  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  $\pm$  standard deviation as error bars. Number above each bar denotes the water activity ( $a_w$ ).

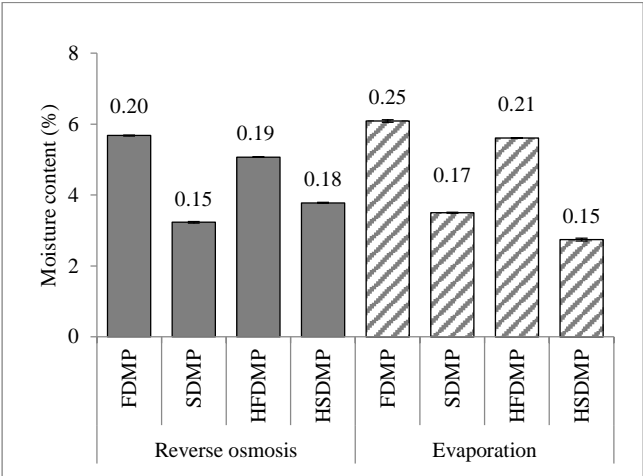
**Figure 3.** Optical micrographs of heated spray-dried milk powder (HSDMP) or freeze-dried milk powder (HFDMP) produced from milk concentrated by reverse osmosis (RO) or evaporation (EV). (A) HSDMP<sub>RO</sub>, (B) HSDMP<sub>EV</sub>, (C) HFDMP<sub>RO</sub>, and (D) HFDMP<sub>EV</sub>

**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  $\pm$  standard deviation as error bars. Bars not labelled with the same letters are significantly different ( $p = 0.05$ )

STEWART FIGURE 1

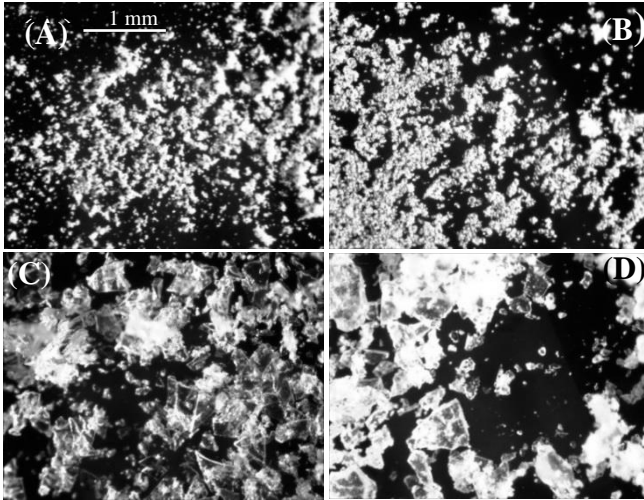


STEWART FIGURE 2





STEWART FIGURE 3



STEWART FIGURE 4

