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Aroma profile development of intermediate chocolate products I. Volatile constituents of block-milk

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Abstract

Block-milk or white crumb is an intermediate product used in the manufacture of white chocolate and milk chocolate and it is produced from a mixture of concentrated milk and sugar. Volatile compounds of block-milk samples at different stages in the manufacturing process were investigated by dynamic headspace GC–MS. The changes in aroma profiles during processing were evaluated using similarity indices and a multidimensional scaling technique. These methods allow a better use of the information contained in the GC data. The results clearly point out the short intense heating step as the key step in the formation of the aroma profile of block-milk. During this step many volatiles are formed due to autoxidative and Maillard reactions. This is consistent with a decrease in the lactose level concomitant with an increase in the lactulose level following the heat treatment, as evaluated by HPLC analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Block-milk; Crumb; Intermediate chocolate products; Dynamic headspace; Aroma profile; Similarity/dissimilarity indices; Maillard chemistry; Flavour formation

1. Introduction

White crumb (or block-milk) and milk crumb (or crumb) are intermediate products used in the manufacture of white and milk chocolate. Milk crumb is produced from a mixture of concentrated milk, sugar and cocoa. Block-milk contains no cocoa.

Crumb and block-milk have undoubtedly been responsible for the great increase in the consumption of white and milk chocolate. Apart from a characteristic flavour, these intermediary products have distinct shelf-life advantages. The processing methods result in a practically sterile, low moisture product with the ingredients intimately mixed. Provided the moisture is kept below 2–3% it can be stored for at least 9 months (Minifie, 1979).

There are many different types of crumb and block-milk making processes in operation, and a large number of them are proprietary (Christiansen, 1976). They all rely on the chemical interaction between the milk proteins and the aldehyde groups of certain sugars. It is called Maillard reaction and the flavour and colour development are related to temperature, time and the presence of water (moisture) (Hodge, 1967).

The research described in this paper is part of a project to improve the manufacturing process of block-milk and crumb and to achieve insight in the key processing steps determining the final aroma of the products. Only the results obtained for block-milk are reported here. The investigation of crumb aroma development will be described in a following paper.

Samples of block-milk were taken at various stages during the manufacturing process. The process conditions were varied to produce different samples. For each sample, measurements were made of the volatile constituents using dynamic headspace GC–MS, and of the sugars using HPLC.

Combined with knowledge about the effect of the process on the production of aroma components, the results described in this paper will give manufacturers more control over the sensory properties of the final product, together with the possibility to change/remove the steps implying large energy expenditure.

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2. Materials and methods

2.1. Block-milk samples

Block-milk samples from various stages of processing were collected. Plastic bottles were filled with the viscous intermediate block-milk products. The samples were frozen using a freeze tunnel (−40°C) and stored at −50°C, until further analysed.

2.2. Isolation of volatiles

Dynamic headspace isolation of volatile compounds was performed in triplo, using Tenax TA 60−80 mesh (Chrompack) as adsorbent packed in glass tubes (177 mm length, 3 mm i.d.) (Luning, de Rijk, Wichers & Roozen, 1994). In a 500 ml glass bottle 10 g of sample and 10 g of volatile-free, deionized water (Milli-Q water purification system, Millipore, Bedford, MA) are added. After connection of the clean Tenax tube the mixture was stirred 2 h at 35°C, while flushed with 30 ml min^{-1} purified nitrogen. For each experiment a system control sample was made by stirring 10 g of Milli-Q water under the same conditions.

2.3. Gas chromatography analytical conditions

Volatile compounds were desorbed (5 min at 250°C) from the Tenax tubes (Tekmar 6016 desorber/autosampler, Interscience, The Netherlands) and via internal trapping at −100°C injected in a capillary column (CP-Wax52CB, 50 m × 0.32 mm i.d., 1.2 μm film thickness). The oven temperature was programmed as follows: 10 min isotherm at 40°C, followed by 3°C min^{-1} to 190°C and 10°C min^{-1} to 250°C and finally 5 min isotherm at 250°C. The gas chromatograph (Fisons 8533, Interscience, The Netherlands) was equipped with a flame ionisation detector (FID). Injection and detection temperatures were 200 and 250°C, respectively.

2.4. Gas chromatography–mass spectrometry analytical conditions

Volatile compounds were identified by using a GC–MS (Carlo Erba, Mega 3600, QMD 1000, Interscience, The Netherlands) equipped with a thermal desorption unit (Carlo Erba, Tekmar 5010, automatic desorber, Interscience, The Netherlands). Thermal desorption and GC–MS analytical conditions were identical to those for gas chromatography. Positive ion Electron-Impact Mass Spectra (70 eV) were obtained at a source temperature of 200°C. The scan range was 25–300 amu with a scan rate of 1 s^{-1}. The mass spectra obtained were compared to the *Wiley/NIST Registry of Mass Spectral Data*, the 6th edition (John Wiley and Sons, Inc. New York). Kovats indices were calculated after comparison with a mixture of *n*-alkanes (Merck, >99%).

2.5. High pressure liquid chromatography analytical conditions

The block-milk samples were diluted with milliQ deionized water approximately 20 times. After dilution, the mixture was stirred for about 2 min, centrifuged and filtered using a 20 μm filter. The clear filtrate obtained was used for sugars analysis.

HPLC analyses were carried out using a Waters™ Alliance System, equipped with a Waters® 996 Photodiode Array Detector and a Waters® 410 Refractive Index Detector. The sugars (sucrose, lactose and lactulose) were separated on a High Performance Carbohydrate Column (4.6 mm i.d. × 250 mm) containing 4 μm Nova-Pak spherical silica bonded with trifunctional amino propylsilane. The column was kept at 35°C. The mobile phase used was a mixture of 80% (v/v) acetonitrile and 20% (v/v) water at a flow rate of 1 ml min^{-1}.

2.6. Colour measurements

The colour of the block-milk samples was measured with a Chroma Meter CR-200 (Minolta) colorimeter using the CIELAB uniform colour scale described by L^*, a^*, and b^* parameters (Francis & Clydesdale, 1975). L^* defines lightness, a^* denotes the red/green value and b^* the yellow/blue value. The L^* axis has the following boundaries: $L=100$ (white or total reflection) and $L=0$ (black or total absorption). Along the a^* axis a colour measurement movement in the $-a$ direction depicts a shift toward green; $+a$ movement depicts a shift toward red. Along the b^* axis, $-b$ movement represents a shift towards blue; $+b$ shows a shift towards yellow.

2.7. Data analysis

For data analysis in food research, objective, reliable classification of samples is frequently the major purpose. Samples are grouped according to certain defined criteria of similarity into categories, or clusters. Sometimes, the categories are unknown and the major goal of the analysis is to determine these clusters (unsupervised learning).

In this paper, input data for statistics are constituted by the differences (dissimilarities) of intensities of volatile constituents among samples.

For two chromatograms A and B with N peaks (volatile compounds) the following v_i coordinates

$$v_i = \frac{B_i - A_i}{B_i + A_i} \qquad i \in [1, N] \tag{1}$$

are computed and used to evaluate the differences between pairs of samples, [Eq. (1)]. The B_i and A_i values represent the areas of peak υ_i in the samples B and A, respectively. The υ_i coordinates are calibrated in the $[-1, +1]$ range: a negative value indicates a decrease of volatile intensity and a positive value indicates an increase, respectively. By plotting υ_i for a pair of chromatograms the changes in aroma profile between two samples can be readily identified.

Using the υ_i coordinates computed for every volatile constituent and for every sample pair, the Canberra dissimilarity index, S, was evaluated according to Eq. (2) (Gordon, 1981).

$$S(AB) = \sqrt{\frac{1}{N}\sum_{i=1}^{N} \upsilon_i^2} \tag{2}$$

Eq. (2) represents the dissimilarity of two chromatograms. The $S(AB)$ coefficients vary from 0 to 1: $S(AB)=0$ indicates a perfect match while $S(AB)=1$ indicates absolutely no similarity.

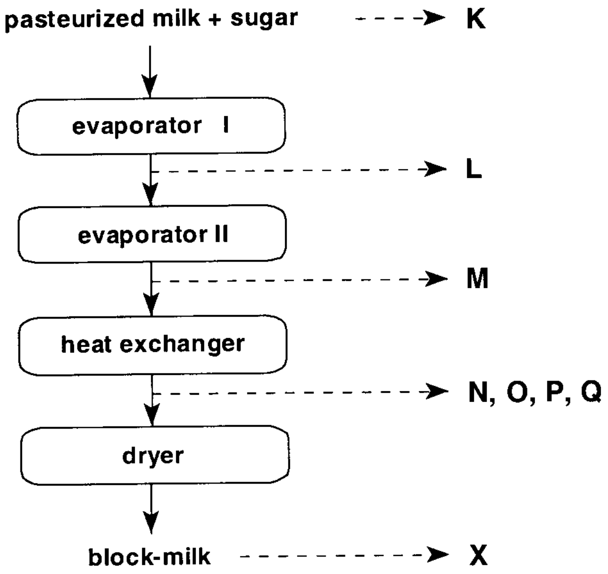

Fig. 1. Overview of the block-milk manufacturing process and the corresponding sampling (dashed arrows).

The S coefficients were analysed by the multidimensional scaling procedure (MDS, SPSS®), since this statistical method was specifically conceived to handle dissimilarities. MDS analyses the dissimilarity data in a way that displays the structure of the distance-like data as a geometrical picture. That is, two similar objects are represented by two points that are close together, and two dissimilar objects are represented by two points that are far apart (Schiffman & Beekert, 1986).

In this way we attempt to utilise the information on data variation to the greatest extent for classification purposes.

3. Results and discussions

3.1. Description of block-milk manufacturing process

The manufacturing process of block-milk and the samples collected and analysed from an industrial plant (Friesland Coberco Dairy Foods, Zwolle, The Netherlands) are presented in Fig. 1 and Table 1.

The mixture of pasteurised whole milk and sugar (88:12 w/w) is concentrated in a set of evaporators until a dry matter content of about 60% (w/w). The resulting paste is subjected to a short, intense heat treatment, considered the key step in the formation of the block-milk aroma profile. After drying to approx. 98% dry matter, milling and sieving, the block-milk powder is packed and stored.

In order to evaluate the influence of the processing parameters upon the aroma profile of block-milk, samples were collected at various stages during the manufacturing. For the main step, the heat exchanger, the process conditions were varied to produce several samples. Thus the samples denoted N,O,P,Q were collected from the same processing step at the same time but at different temperatures (see Table 1). A mild heat treatment was used to produce sample N while sample Q was obtained

Table 1
Samples collected from the block-milk manufacturing process

Sample	Treatment	Colour[a]			Dry matter[b]
		L^*	a^*	b^*	(%, w/w)
K	Pasteurised milk + sugar	78.62	−4.78	4.97	20.5
L	First stage evaporation	74.74	−8.58	12.89	57.9
M	Second stage evaporation	73.43	−8.92	13.89	62.8
N	Mild heat treatment[c]	71.62	−6.94	20.46	63.8
O	Medium heat treatment[c]	61.25	−2.50	25.52	64.3
P	Intense heat treatment[c]	55.67	2.54	28.90	62.4
Q	Severe heat treatment[c]	38.83	13.97	19.60	61.9
X	Drying the severe heat treated product (sample Q)	57.46	6.69	23.04	97.8

[a] Expressed within the CIELAB uniform colour scale (see Materials and methods).
[b] Evaluated using the oven method.
[c] The samples N,O,P,Q were collected from the same processing step at the same time but at different temperatures.

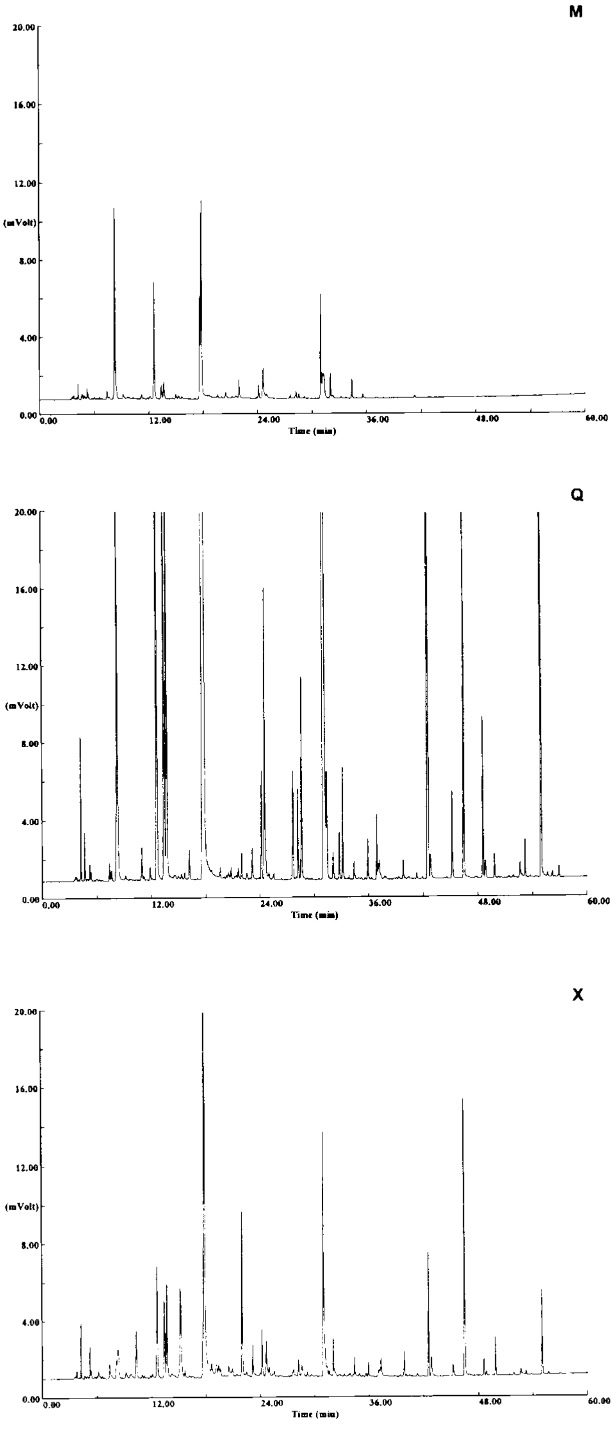

Fig. 2. Gas chromatograms of the block-milk samples M, Q and X. See Table 1 for a description of sample codes.

Table 2
Volatile compounds identified in block-milk samples

Peak no.	Kovats index	Compound (MS identification)	Relative peak area[a] (%)
1	600	Hexane	0.008
2	610	Trimethylamine + 1-hexene	0.09
3	800	Octane	0.05
4	808	Not identified	0.03
5	824	Acetone	1.8
6	881	No identified	0.1
7	885	2,4-Dimethyl-1-heptene + butanal[b]	0.02
8	908	2-Butanone	3.0
9	921	2-Methylbutanal	1.8
10	926	3-Methylbutanal	1.6
11	949	Branched alkane	–
12	956	Branched alkane	0.02
13	963	Alkylcyclohexane	0.1
14	986	2-Pentanone	27.8
15	988	Pentanal	1.8
16	1000	Decane	0.03
17	1006	Branched alkane	–
18	1012	Not identified	0.03
19	1044	2-Methyl-3-butene-2-ol	0.07
20	1068	2,3-Pentadione	0.1
21	1083	Dimethyl disulfide	0.3
22	1090	2-Hexanone + hexanal[b,d]	0.9
23	1192	2-Heptanone + hexanal[b,e]	47.6
24	1218	Pyrazine	0.1
25	1231	4-Octanone	0.3
26	1250	Pentanol + not identified	0.06
27	1272	Not identified	0.006
28	1277	Methylpyrazine + dihydro-2-methyl-3(2H)furanone[b]	0.13
29	1298	Octanal	0.2
30	1379	Not identified	0.02
31	1402	2-Nonanone + dimethyl trisulfide[b,f]	5.2
32	1408	Nonanal	0.1
33	1457	Acetic acid	0.2
34	1483	2-/3-Furaldehyde[c]	1.4
35	1527	1-(2-Furanyl)-ethanone	0.5
36	1532	Formic acid + pyrrole[b]	0.07
37	1616	Not identified	0.06
38	1629	Not identified	0.08
39	1670	2-/3-Furanmethanole[c]	4.1
40	1686	3-Methylbutanoic acid + 2-methylbutanoic acid[b]	0.02
41	1717	Not identified	0.03

[a] Relative peak area for sample Q (see Fig. 2).
[b] Both components present.
[c] Mass spectra are similar.
[d] Mass spectral analysis indicates 70% 2-hexanone and 30% hexanal.
[e] Mass spectral analysis indicates > 99% 2-heptanone.
[f] Mass spectral analysis indicates > 99% 2-nonanone.

after a severe heat treatment. The final product, X, was obtained by drying sample Q.

3.2. Analysis of aroma profile. Volatiles formation

The gas chromatography data obtained for the block-milk samples indicated a good reproducibility of the dynamic headspace technique. The coefficients of variation for the three replicates (CV = (standard deviation × 100/mean) were less than 15%. Characteristic chromatograms for the block-milk samples M, Q, and X are presented in Fig. 2

Of a total of 41 peaks separated, 30 peaks were identified as shown in Table 2. The compounds identified

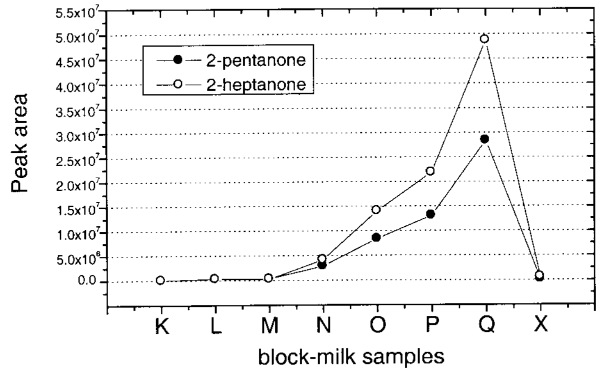

Fig. 3. Evolution of some volatiles compounds during block-milk processing.

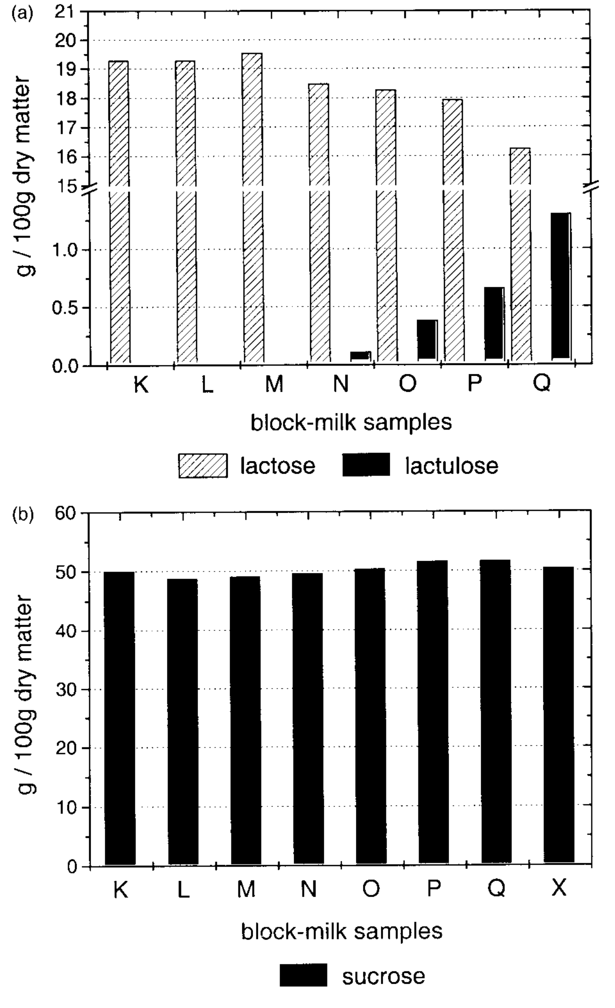

Fig. 4. Sugar content of block-milk samples: (a) lactose and lactulose, (b) sucrose.

Table 3
Distance between the block-milk samples using Canberra dissimilarity index[a]

Sample	K	L	M	N	O	P	Q	X
K	0	**0.21**[b]	0.20	0.30	0.50	0.56	0.72	0.68
L		0	**0.13**	0.29	0.45	0.52	0.77	0.60
M			0	**0.27**	**0.49**	**0.55**	**0.74**	0.63
N				0	0.31	0.42	0.68	0.61
O					0	0.2	0.58	0.51
P						0	0.52	0.50
Q							0	**0.64**
X								0

[a] See Table 1 for a description of sample codes.

[b] The bold values correspond to the processing steps presented in Fig. 1.

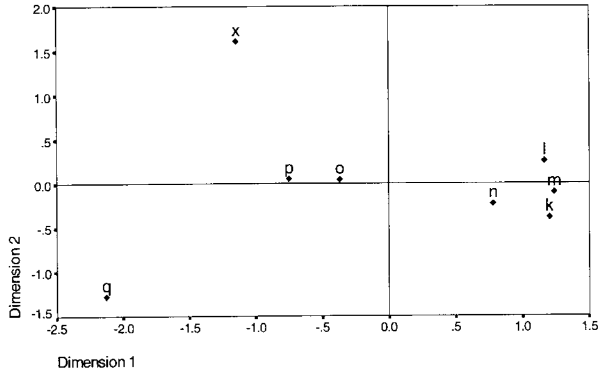

Fig. 5. The first two dimensions of multidimensional scaling of GC distances between block-milk samples. See Table 1 for a description of sample codes.

included hydrocarbons, aldehydes, ketones, alcohols, organic acids, N- and S-containing compounds.

Many of these compounds have been described for various heat-treated milk samples and milk powders (Badings, 1991; Jeon, Thomas & Reineccius, 1978; Shiratsuchi, Yoshimura, Shimoda, Noda & Osajima, 1995) as well as in a lactose–casein model system during browning (Ferreti & Flanagan, 1971). Using aroma extract dilution analysis (AEDA) several compounds listed in Table 2 were evaluated as key odorants in milk chocolate (Schnermann & Schieberle, 1997).

Going from the raw material (sample K) to the final product (sample X) the aroma profile is changing. The general trend is an increase of volatile intensities with the heat treatment and then a decrease after the drying process as is presented in Fig. 3 for 2-pentanone and 2-heptanone.

Several hydrocarbons, namely C_8–C_{10} alkanes and alkenes, were identified. Their origin in block-milk products is uncertain. They might originate from contamination of the equipment (e.g. mineral oil).

The aldehydes and ketones represent the largest amount of volatile compounds found in the heat-treated block-milk samples (see Table 2). The alkanals and alkenals with more than six carbon atoms are typical products of lipid oxidation. Autoxidation products are formed from unsaturated fatty acids by nonenzymatic autocatalitic oxidation reactions resulting in the formation of hydroperoxides. These hydroperoxides may undergo secondary oxidation to form products such as aldehydes and ketones. The latter group contains many important flavour compounds, with specific odour and usually very low flavour threshold values (Badings, 1991). The autoxidative mechanisms of the unsaturated fatty acids lead to the complete inferior homologous series of aldehydes (Loury, 1972; Paquette, Kupranycz & van de Voort, 1985).

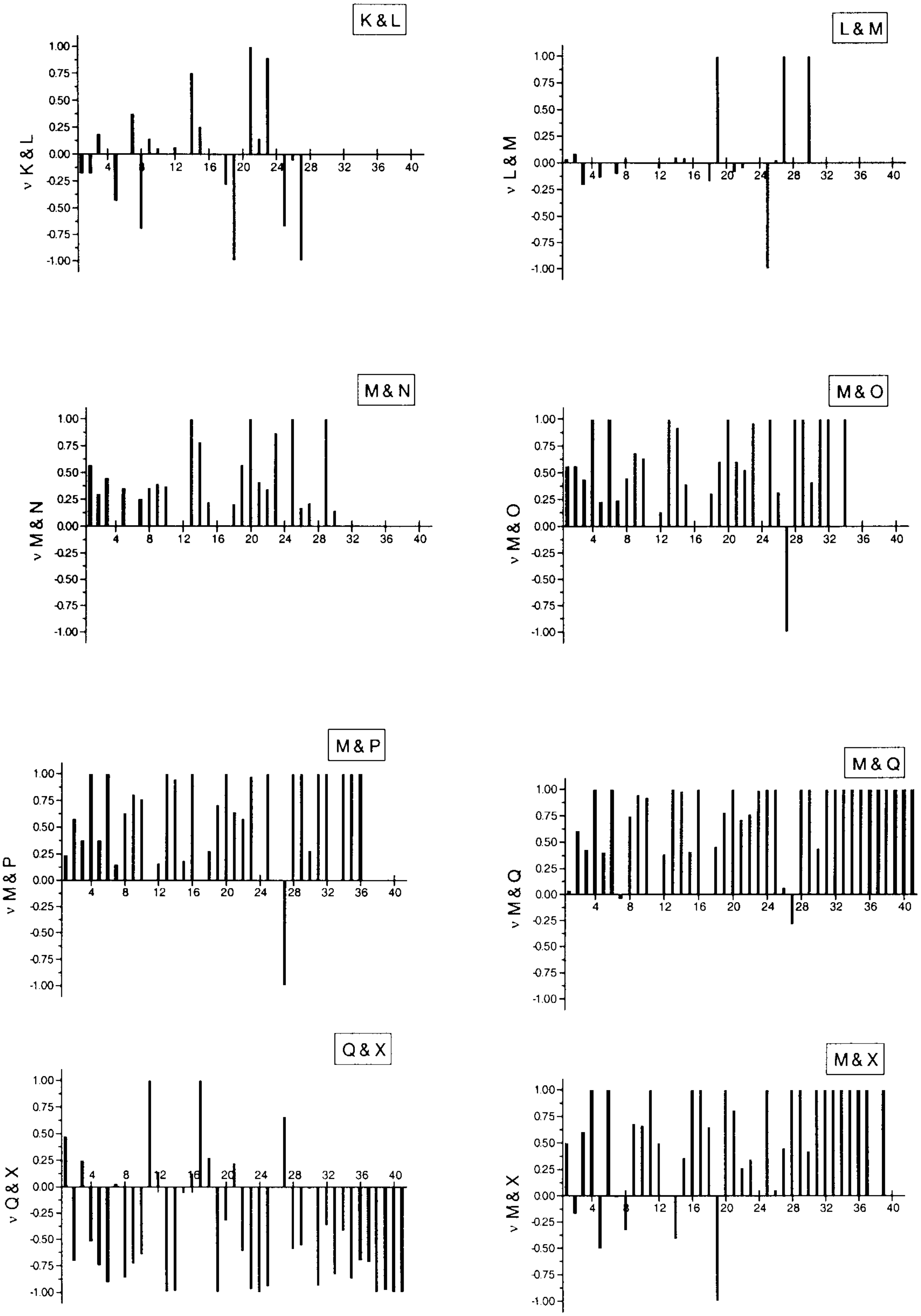

Fig. 6. Development of block-milk aroma profile during processing. Positive lines indicate an increase while negative lines indicate a decrease of volatile intensities, as described in Material and methods. For process description and sample codes see Fig. 1 and Table 1.

Among the identified ketones, methylketones were the most abundant. They were proposed to be derived from free and esterified fatty acids, which were first oxidized to β-keto acids and then decarboxylated into the corresponding methylketones (Forss, 1979; Hawke, 1966).

Acetone is a well-known product of carbohydrate fragmentation and dehydration during the nonenzymatic browning reactions (Weenen, 1998). Sulfur compounds like dimethyl disulfide and dimethyl trisulfide can be formed by heat from β-lactoglobulin, a milk protein.

Several heterocyclic compounds such as furan and pyrazine derivatives were identified: 2-/3-furanmethanol, 1-(2-furanyl)-ethanol, dihydro-2-methyl-3(2H)furanone, pyrazines, which are known as products of nonenzymatic browning reactions (Hodge, 1967).

The colour measurements presented in Table 1 show a decrease of L^* values of block-milk samples during processing together with a positive shift of both a^* and b^* parameters. These changes, translated visually by a change of block-milk colour from milk-white (sample K) to light-brown (sample X), are indicative for advanced and final Maillard reactions.

The lactose and lactulose content of the block-milk products is presented in Fig. 4(a). Lactose is not only a reactant in the Maillard reactions but is also a subject of isomerization and degradation reactions. One of the resulting reaction products of the isomerization is lactulose (a disaccharide of galactose and fructose). The actual level of lactulose can be considered as an indicator related to the heat-induced reactions. From the kinetic studies of lactose reactions in milk it was shown that at temperatures above 100°C, isomerization reactions are far more important from a quantitative point of view than the Maillard reactions (van Boekel, 1998). From Fig. 4(a) one can see that the level of lactulose is increasing with the heat-treatment. However, the loss of lactose was higher than the formation of lactulose. It can be assumed that the remaining loss is a result of further degradation of lactose (including Maillard reactions) other than via lactulose formation.

There is no clear trend of the level of sucrose for block-milk samples [see Fig. 4(b)]. Due to the high concentration of sucrose in the block-milk (approx. 50 g/100 g dry matter) minute changes are difficult to assess.

3.3. *The effects of processing steps on volatiles formation*

The effects of the different processing steps on the volatile formation were evaluated by analysing the GC data of block-milk samples using dissimilarity indices. The distance or proximity matrix based on Canberra dissimilarity index is presented in Table 3. The bold values correspond to the processing steps presented in Fig. 1.

The result of applying multidimensional scaling using the distance matrix presented in Table 3 is displayed in Fig. 5. This plot gives an overview of the relationships between the samples.

An inspection of the S distances (Table 3) and MDS plot (Fig. 5) reveals a close similarity between the K, L and M samples. The N, O, P, and Q samples collected after the heat exchanger are different compared to the initial samples and they are also different amongst themselves. The final product, sample X, seems to be rather different from the other samples.

In order to describe in more detail the information depicted in Fig. 5 and to monitor the influence of the manufacturing process on the development of the block-milk aroma profile the ν_i coordinates between different pairs of block-milk samples were computed as described in Material and Methods. The results are presented in Fig. 6.

During the initial steps, the mixture of pasteurised milk and sugar is concentrated to a dry matter content of approx. 60%. No major changes occurred during these initial steps suggesting no relevant contribution to the final aroma profile of block-milk (Fig. 6, K & L and L & M plots).

From Fig. 6 it can be concluded that the short and intense heating treatment is the key step for developing the aroma profile of block-milk. During this step many volatile compounds are formed, mainly due to autoxidative and Maillard reactions. Several samples produced at different temperatures were analysed. As can be seen from Fig. 6 (M & N, M & O, M & P and M & Q plots), the different temperatures are reflected predominantly in the "quantity" and not in the "quality" of the aroma profile. By increasing the temperature the total amount of volatiles increases while the aroma profile remains more or less the same.

During the final step, the drying, the total amount of volatiles has been decreased (some of the volatiles disappeared) but essentially the final product, X, has a similar aroma profile as the N–Q intermediary products (Fig. 6, Q & X plot). A comparison of samples M (before the heat exchanger) and X (the final product, after drying) confirms the importance of the heating step in developing the final aroma profile of the block-milk, (Fig. 6, M & X plot).

4. Conclusions

In the preparation of block-milk many volatiles are formed as a result of heat-induced reactions. The changes in block-milk aroma profile during processing were evaluated using similarity indices based on gas chromatographic data and a multidimensional scaling technique. These methods allow a better use of the information contained in GC data.

The results obtained indicated the short intense heating step as the key step in the formation of the aroma profile of block-milk. During this step many volatiles are formed due to autoxidative and advanced Maillard reactions. This is consistent with a decrease in the lactose level concomitant with an increase in the lactulose level following the heat treatment, as evaluated by HPLC analysis. Final Maillard reactions and sugar caramelizations are reflected in the colour changes of block-milk during processing.

Acknowledgements

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