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Changes in flavour and volatile components during storage of whole and skimmed UHT milk

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Abstract

Six batches of commercial UHT milk, submitted to direct treatment, three whole and the other three skimmed milk, were stored at 25±2°C for 4 months. Non-casein nitrogen (NCN) and sensorial analysis were carried out on packs opened every month. Volatile composition was analysed every 15 days, using a purge-and-trap concentrator coupled on-line to a GC–MS instrument. NCN increased during storage; the increase was greater in skimmed milk samples. Sensory characteristics were slightly better in the whole samples, although the scores decreased for both groups in the third month. Quantification of about 40 volatile components in whole milks showed no changes until 90 days (the legal shelf-life in Spain); the main change was the increase of methyl ketones. New components appeared in skimmed samples after 65 days storage; they could be related to both proteolysis and Maillard reaction. This is consistent with the poorer sensory quality found in skimmed milk samples.

1. Introduction

UHT processing involves the heating of milk to a high temperature during a short time in order to obtain a product with a long shelf life at room temperature. During the process, most bacteria are inactivated but heat-stable enzymes of native or bacterial origin can survive and give rise, during storage, to both gelation and off-flavours (bitter, stale and oxidised) (Burton, 1988). Gelation and bitterness are usually related to protein breakdown (Harwalkar, 1982). UHT milk odour has a "cooked" note in the freshly prepared samples, which afterwards evolves to a "flat" character (Mehta, 1980). Other objectionable off-flavours can then begin to develop.

Different factors affecting the evolution of volatile components in UHT milk during storage have been studied, including exposure to fluorescent light (Mehta & Basette, 1979), oxygen (Early & Hansen, 1982), copper (Leland, Reineccius & Lahiff, 1987) and storage temperature (Gaafar, 1991). Most of these factors favour lipid oxidation, giving rise to stale and "oxidised" flavours, caused by formation of aldehydes and ketones. Other changes that occur as a consequence of UHT milk storage have been widely studied over recent years (Bansal & Sharma, 1995; Bassette & Jeon, 1983; Christensen & Reineccius, 1992; Contarini, Povolo, Leardi & Topino, 1997; Jeon, Thomas & Reineccius, 1978; Rerkrai, Jeon & Bassette, 1987).

On the other hand, the fat content of milk can influence the shelf life of stored UHT milk. López-Fandiño, Olano, Corzo and Ramos (1993) and García-Risco, Ramos and López-Fandiño (1999) reported that UHT skimmed milk deteriorates more than UHT whole milk during storage at room temperature: proteolysis and off-flavour development were higher in samples submitted to the direct process (steam injection). Although the mechanisms involved are still unclear, the explanation seems to be related to a lower activity of the proteases in the case of whole UHT milk. However, the influence of fat content on volatile composition during the storage of UHT milk at room temperature has not been described.

As part of a project addressing the effect of fat content on proteolysis development in direct UHT milk, the evolution of volatile components during the shelf-life of several commercial samples has been studied.

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2. Materials and methods

2.1. Samples

Six batches consisting of 24 packs (Tetra Brik™) of commercial UHT milk from three different brands (1, 2 and 3) were purchased. Packs (1 l capacity) were filled without headspace and all were of identical design and geometry. Batches W1, W2 and W3 were 3% fat, while batches S1, S2, S3 corresponded to skimmed samples (< 0.5%fat). Both types of milk were processed by the direct treatment. Samples were stored at 25±2°C for 4 months. Every 15 days, two packs of each batch were opened and analysed in duplicate.

2.2. Analytical determinations

An estimation of the intensity of heat proccessing was carried out from the determination of lactulose and furosine formation, as well as undenatured β-lactoglobulin.

Lactulose determination was performed by gas chromatographic analysis of the trimethylsilyl derivatives of the free carbohydrate fraction using a 3 m long×1.0 mm inside diameter stainless steel column (Chrompack, Middelburg, The Netherlands) packed with 2% OV-17 on nonsilanized 120/140 Volaspher A-2 (Merck, Darmstadt, Germany), following the method described by Olano, Calvo and Reglero (1986). Calibration was performed using phenyl-β-glucoside as internal standard (Sigma Chemical CO., St. Louis, USA).

For furosine determination, 2 ml of milk were hydrolysed with 6 ml of 10.6 M HCl and analysed by RP-HPLC, according to the method of Resmini, Pellegrino and Batelli (1990), using a C8 column (250×4.6 mm inside diameter, Alltech Furosine-dedicated; Alltech Associates, Laarne, Belgium) with a linear binary mobile phase gradient. Calibration was performed by the external standard method using pure furosine (Neosystem Laboratories, Strasbourg, France) as standard.

Undenatured β-lactoglobulin was determined in the soluble fraction at pH 4.6 by RP-HPLC using a PLRP-S 8 μm column, (3 nm, 150×4.6 mm inside diameter) (Polymer Laboratories, Church Stretton, UK) with a linear binary mobile phase gradient (Resmini, Pellegrino, Hogenboom & Andreini, 1989). Calibrations were performed by the external standard method and curves were constructed with commercial standards of whey proteins (Sigma Chemical CO., St. Louis, USA).

The extent of proteolysis was estimated by measuring non-casein nitrogen (NCN) at pH 4.6 by the Kjeldahl method (IDF, 1993).

Volatile compounds were isolated from milk with an HP-7695 Purge & Trap concentrator coupled to a HP-5890 gas chromatograph (Hewlett-Packard, Avondale, PA) with a mass detector HP-5971A. Operating conditions were as follows: 25 ml of sample containing 0.25 μg internal standard (ethyl pentanoate) were purged at 45°C with 35 ml/min helium for 15 min. Volatiles were adsorbed on a 30 cm×32 mm trap containing a mixture of Carbosieve-SIII (0.05 g) and Carbopack-B 60/80 (0.2 g) and then thermally desorbed at 220°C for 5 min. A cryofocusing module was used to concentrate the band arriving at the capillary column. The transfer line and the valve were maintained at 150°C. A fused silica (50 m×0.22 mm×0.25 μm) capillary column coated with BP-20 (SGE, Ringwood, Australia), was used, with helium as the carrier gas at a flow rate of 1 ml/min. Column temperature was held at 40°C for 15 min and then programmed at 3°C/min up to 180°C for 10 min. Tentative identifications of volatile components were from peak retention times and mass spectral data. Identification was confirmed by using standard compounds when available. Semiquantitative measurements were calculated as μg/l milk, from the peak areas of the components and the added internal standard. Blanks were run between samples.

2.3. Sensory analysis

Milk was evaluated for overall flavour during the storage time. The score card used by each panellist (12 trained members) included an acceptability (hedonic) rating scale and a list of suggested flavour defects. At each session, both whole and skimmed milk stored samples were compared with a control sample (a fresh sample from the same dairy plant). Milk samples were coded and presented in random order to the panellists. Acceptability of the milk was recorded on a 6-point scale ranging from extremely unacceptable (1) to extremely acceptable (6). Samples were taken for analysis at 30, 60 and 90 days of storage (legal shelf life of the product).

3. Results and discussion

3.1. Evaluation of heat load

Heat load was evaluated in six batches of samples analysed within 20 days after processing. The levels of lactulose, furosine and undenatured β-lactoglobulin are presented in Table 1. Determination errors, measured as percentage RSD, were 1.6 for furosine, 6.8 for lactulose and 6.6 for α-lactoalbumin. The values of these indicators were within the ranges reported for direct UHT milks by other authors: lactulose 154–670 mg/l; furosine 15.7–50.5 mg/l and undenatured β-lactoglobulin 69-1387 mg/l (López-Fandiño, Corzo, Villamiel, Delgado, Olano & Ramos, 1993; Corzo, López-Fandiño, Delgado, Ramos & Olano, 1994). No differences in heat load were observed between whole and skimmed milk. The influence of fat content of milk on lactulose and

Table 1
Thermal indicators (lactulose, furosine and β-lactoglobulin) in control UHT-treated milks

Samples[a]	Lactulose (mg/l)	Furosine (mg/l)	β-Lactoglobulin (mg/l)
W1	272	35.9	580
W2	271	49.9	719
W3	226	24.0	701
S1	288	27.4	578
S2	321	23.7	799
S3	170	29.2	755

[a] W and S represent whole and skim milk, respectively; 1, 2 and 3 represent the brands.

furosine formation is still unclear: Geier and Klostermeyer (1983) and Andrews (1984) indicated that fat content of milk has no influence on lactulose formation, whereas De Koning, Badings, Van der Pol, Kaper and Vos-Klompmaker (1990) reported higher lactulose formation in whole milk than in semi-skimmed milk when both were submitted to the same heat treatment. On the other hand, Pellegrino (1994) found less lactulose and furosine and more undenatured β-lactoglobulin in whole milk than in its corresponding skimmed milk.

3.2. Proteolysis

NCN value increased during storage for both skimmed and whole milks, as shown in Fig. 1. Values were always higher (>99% significance level) for skimmed milks than for the corresponding whole milks. This fact could be attributable to a lower enzymatic activity in whole milk due to a possible protective effect of the fat against enzymatic attack of the protein, as was reported by López-Fandiño, Corzo et al. (1993). These authors found that proteolysis (estimated by SDS-PAGE) was faster in skimmed milk than whole milk. Similarly, García-Risco et al. (1999) observed, in skimmed milk, higher levels of denatured soluble whey proteins not attached to the micelle surface that could have less resistance to aggregation.

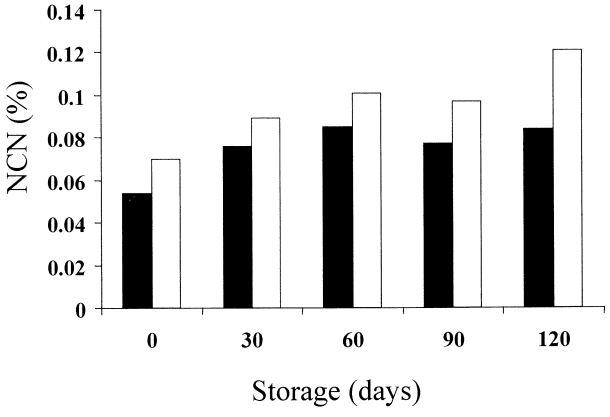

Fig. 1. Proteolysis (expressed as NCN) during storage of UHT whole (black bars) and skimmed (white bars) milk samples during storage.

3.3. Sensory analysis

Hedonic test results during the storage of whole and skimmed UHT milks are presented in Fig. 2. Although it is difficult to assign any statistical significance to the trends that appear in the figure, because the usual high dispersion of the results, a clear decrease in quality is observed during the shelf life. Sensory quality was in general better in whole milk batches than in the corresponding skimmed milks, in agreement with the NCN results (Fig. 1).

A slight stale flavour was detected by 60% of the panellists in batches W3 and S3 after three months of storage. Both batches showed gelation a month later but samples belonging to other batches remained without apparent alterations.

3.4. Volatile composition of processed milk

Fig. 3 shows a typical TIC chromatogram from both skimmed and whole milk UHT samples. About 77 peaks were identified or characterised in the freshly processed samples of the six batches; the more abundant components were selected for quantitative determination (41 and 54 in whole and skimmed milks, respectively). The results, calculated as the average values of duplicate packs from the three brands, appear in Tables 2 (whole milks) and 3 (skimmed milks). The main group of volatile compounds found in the former were methyl ketones with 3, 4, 5 and 7 carbon atoms. Whereas acetone and butanone are supposed to be derived from bovine

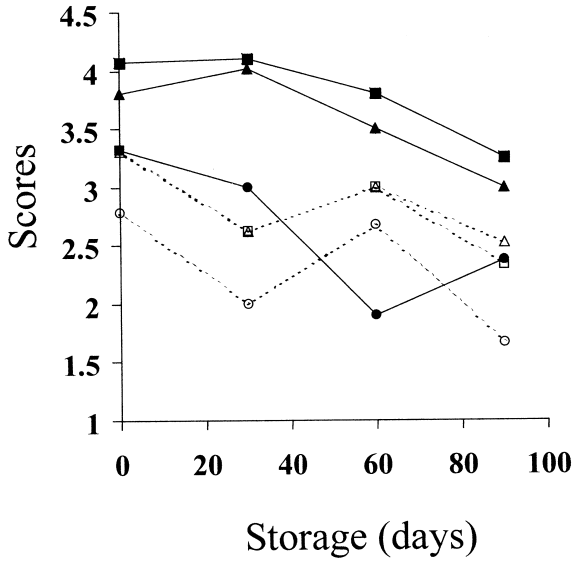

Fig. 2. Sensory scores during storage of UHT whole (black symbols) and skimmed (white symbols) milk samples during storage. Squares: brand 1; triangles: brand 2; circles: brand 3.

metabolism (Bassette, Turner & Ward 1966; Gordon & Morgan, 1972; Urbach & Milne, 1988), 2-pentanone and 2-heptanone are in part thermally-induced products, arising from β-ketoacid decarboxylation (Calvo & de la Hoz, 1992); they can also be formed by β-oxidation of fatty acids, followed by decarboxylation (Grosch, 1982). Dimethyl sulfide and dimethyl disulfide were also found; they probably derive from methionine (Dumont & Adda, 1979) and have a strong contribution (along with methyl ketones) to the aroma of UHT milk (Badings 1984); they have also been related to the intensity of thermal treatment (Bosset, Bühler-Moor, Eberhard, Gauch, Lavanchy & Sieber, 1994). Acetaldehyde, butanal, hexanal, 2-methyl butanal and 3-methyl butanal were the main aldehydes found, while others, such as furfural and benzaldehyde were present in smaller proportions.

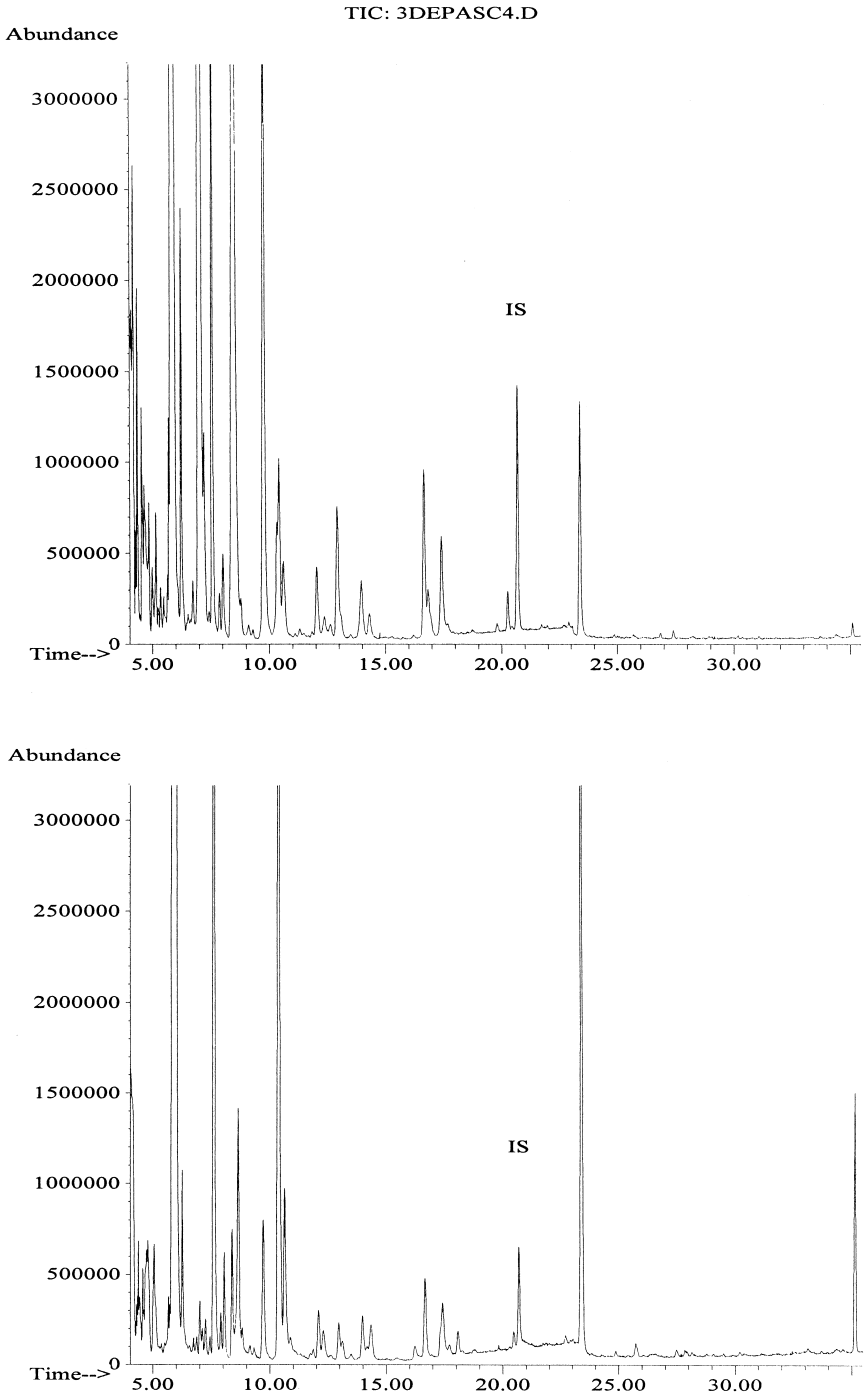

Fig. 3. Reconstructed chromatograms of the volatile fraction from a skimmed (top) and a whole (bottom) UHT milk sample after 30 days storage. IS: internal standard. Identification of other peaks as in Tables 2 and 3.

Table 2
Comparative volatile composition of whole UHT milk during storage. Average of three brands (μg/l)

Identification				Storage time (days)								
Retention time (min)	GC	MS	Compound	0	15	30	45	60	75	90	105	120
4.731	+	+	Acetaldehyde	1.51	1.61	1.57	1.51	1.50	1.72	1.52	1.82	1.70
4.785	+	+	Heptane	0.842	0.785	0.705	0.356	0.412	0.362	0.425	0.384	0.412
5.040		+	Dimethyl sulfide	1.83	1.76	1.70	1.24	1.34	1.25	1.46	1.52	1.77
5.335		+	C_7H_{14}	0.089	0.065	0.056	0.044	0.058	0.089	0.065	0.052	0.087
5.854	+	+	Acetone	47.8	45.2	39.7	31.1	35.1	42.1	48.2	49.5	55.3
6.198		+	3-Methylenheptane	1.78	1.52	1.45	1.29	1.21	1.30	1.25	1.30	1.36
6.685		+	3-Methylheptane	0.217	0.301	0.251	0.215	0.186	0.157	0.201	0.102	0.089
6.788		+	Methylfuran	0.180	0.152	0.139	0.121	0.098	0.087	0.102	0.215	0.779
6.924	+	+	Butanal	0.535	0.486	0.471	0.521	0.489	0.621	0.529	0.721	1.06
7.024		+	2-Butenal	0.262	0.198	0.201	0.235	0.198	0.201	0.175	0.213	0.425
7.155	+	+	Ethyl acetate	0.707	0.582	0.542	0.686	0.523	0.578	0.452	0.562	0.785
7.495	+	+	2-Butanone	12.9	12.0	12.5	10.8	10.8	11.0	10.8	13.3	17.6
7.797	+	+	2-Methylbutanal	0.326	0.298	0.312	0.258	0.231	0.185	0.241	0.421	0.776
7.937	+	+	3-Methylbutanal	0.640	0.598	0.625	0.565	0.621	0.584	0.498	0.985	1.82
8.359	+	+	2-Propanol	1.34	1.24	1.22	0.93	1.02	0.96	1.11	0.923	0.838
8.398	+	+	Dichlorometane	7.78	4.24	4.85	3,92	2.99	4.24	3.87	2.15	2.87
8.558	+	+	Ethanol	9.22	8.24	7.5243	5.3642	4.98	3.94	5.12	4.24	6.02
8.625	+	+	Benzene	0.243	0.213	0.198	0.282	0.197	0.158	0.201	0.124	0.195
8.689		+	3-Buten-2-ol	0.136	0.124	0.129	0.112	0.087	0.097	0.101	0.097	0.059
9.588		+	2,2,4,6,6-Pentamethyl- heptane	5.63	4.02	4.11	4.13	3.85	3.99	4.01	4.52	5.11
10.181	+	+	2-Pentanone	10.8	10.5	10.5	10.5	10.9	11.0	10.3	12.3	23.5
10.409	+	+	Diacetyl	1.63	1.02	0.99	0.78	0.52	0.63	0.55	1.24	2.11
10.635		+	4-Methyl-2-pentanone	0.154	0.125	0.142	0.169	0.098	0.085	0.075	0.085	0.074
11.827	+	+	Acetonitrile	0.652	0.568	0.452	0.371	0.249	0.301	0.408	0.325	0.286
12.658	+	+	Trichloromethane	2.38	0.895	0.914	0.969	1.13	1.05	1.25	1.54	1.16
12.874	+	+	2-Butanol	0.419	0.235	0.325	0.123	0.087	0.095	0.114	0.115	0.142
13.676	+	+	Toluene	1.94	1.25	0.987	0.925	1.02	0.854	1.17	1.23	1.53
14.035		+	3-Methyl-2-buten-3-ol	0.371	0.120	0.142	0.112	0.098	0.071	0.124	0.741	1.02
15.887		+	2,3-Pentanedione	0.229	0.124	0.110	0.098	0.074	0.105	0.067	0.082	0.124
16.364	+	+	Dimethyl disulfide	3.24	3.13	3.86	2.90	2.25	3.52	2.99	2.85	1.93
17.141	+	+	Hexanal	1.24	0.96	0.88	0.77	1.23	1.42	1.33	1.58	2.01
17.124	+	+	2-Hexanone	0.198	0.125	0.096	0.069	0.099	1.02	0.095	1.12	1.10
18.590	+	+	2-Methyl-1-propanol	0.284	0.125	0.254	0.105	0.042	0.021	0.087	0.210	0.321
19.592		+	C_8H_{10}	0.067	0.075	0.052	0.065	0.021	0.042	0.051	0.021	0.077
22.544	+	+	1-Butanol	0.356	0.021	0.012	0.025	0.058	0.047	0.077	0.087	0.141
22.852	+	+	Limonene	0.062	0.075	0.045	0.124	0.021	0.054	0.038	0.041	0.031
23.236	+	+	2-Heptanone	12.3	11.5	12.1	11.6	11.9	12.3	18.7	28.3	36.3
25.794	+	+	3-Methylbutanol	0.116	0.089	0.084	0.128	0.214	0.087	0.074	0.104	0.161
27.533	+	+	1-Pentanol	0.209	0.084	0.025	0.073	0.124	0.187	0.154	0.198	0.232
35.143	+	+	Furfural	0.161	0.012	0.021	0.093	0.074	0.114	0.087	0.245	0.503
36.865	+	+	Benzaldehyde	0.118	0.125	0.102	0.084	0.124	0.241	0.287	0.715	0.964

Acetaldehyde has been reported in heated milk (Jaddou, Pavey & Manning, 1978). 3-methylbutanal and hexanal contribute moderately to the UHT flavour (Badings, 1984). It is noteworthy that the levels found in the present paper for acetaldehyde, acetone, butanone, 3-methylbutanal, dimethyl disufide, pentanone, heptanone and hexanal are close to those reported by Contarini et al. (1997) in direct UHT milk.

Skimmed samples displayed a different pattern: hydrocarbons (aliphatic, alicyclic, terpenic and aromatic) represented an important part of the detected compounds. Aromatic and terpenic hydrocarbons have been reported in UHT milk (Contarini et al., 1997; Jeon et al., 1978; Moio, Etievant, Langlois, Dekimpe & Addeo, 1994). Some of the branched hydrocarbons also have a characteristic odour (Chung & Cadwallader, 1993) and have been reported in polyethylene-packed mineral water (Linssen, Janssens, Roozen & Posthumus, 1993), vacuum-packed crabmeat (Chung & Cadwallader, 1993), fish sauce (Shimoda, Peralta & Osajima, 1996) and dry-cured ham (Buscailhon, Berdagué & Monin, 1993). Other differences found between whole and skimmed milk were higher methyl ketones and lower diacetyl concentrations in whole milks.

3.5. Evolution upon storage

Evolution of volatiles was different in whole and skimmed milks submitted to the direct UHT processing. Several qualitative and quantitative changes were

observed in skimmed milks during storage (Table 3). New components began to appear after 60 days: furan derivatives (especially hydrocarbons), styrene, alcohols (pentanol and hexanol), 2-octanone, octanal, 1H-pyrrole and traces of free acids (acetic and butyric). Other compounds, such as furfural, 2-heptanone, 3-methylbutanol and benzaldehyde clearly started to increase at different times. The concentrations of hydrocarbons (including

Table 3
Comparative volatile composition of skimmed UHT milk during storage. Average of three brands (μg/l)

Identification				Storage time (days)								
Retention time (min)	GC	MS	Compound	0	15	30	45	60	75	90	105	120
4.706	+	+	Acetaldehyde	3.99	1.77	0.867	1.72	1.62	0.525	0.358	0.220	0.218
4.799	+	+	Heptane	1.02	0.96	0.652	0.889	0.623	0.724	0.801	0.754	0.598
5.086		+	Dimethylsulfide	0.95	1.00	0.758	0.858	0.698	0.742	0.687	0.926	0.887
5.198		+	3-Ethylhexane	0.19	0.21	0.185	0.569	0.352	0.297	0.251	0.152	0.301
5.322		+	C_7H_{14}	0.29	0.23	0.300	0.235	0.174	0.135	0.258	0.214	0.174
5.556		+	Furan	0.58	0.60	0.541	1.04	1.00	1.124	0.987	1.25	1.46
5.840	+	+	Acetone	34.7	32.4	29.5	27.4	31.3	35.2	33.7	32.9	36.5
6.190		+	3-Methylenheptane	2.05	1.82	2.21	2.56	3.21	3.65	4.01	2.99	3.52
6.493			Unknown	0.27	0.10	0.213	0.190	0.201	0.098	0.124	0.214	0.198
6.673			Unknown	0.22	0.34	0.185	0.330	0.185	0.198	0.214	0.258	0.321
6.773		+	3-Ethylheptane	0.098	0.025	0.125	0.253	0.102	0.087	0.185	0.214	0.198
6.791		+	Methylfuran	0.00	0.00	0.00	0.020	0.058	0.082	0.102	0.092	0.128
6.929	+	+	Butanal	1.22	1.46	1.22	0.960	0.725	0.698	0.821	0.795	1.05
7.021		+	2-Butenal	0.079	0.16	0.097	0.123	0.087	0.092	0.105	0.112	0.095
7.161	+	+	Ethyl acetate	3.99	1.77	0.867	1.72	1.62	0.525	0.358	0.220	0.218
7.474		+	Methylfuran	0.00	0.00	0.125	0.321	0.128	0.214	0.195	0.098	0.254
7.499	+	+	Butanone	13.4	16.1	14.5	13.8	14.4	15.2	14.5	15.8	16.4
7.798	+	+	2-Methylbutanal	0.53	0.41	0.189	0.343	0.772	0.421	0.312	0.328	0.395
7.942	+	+	3-Methylbutanal	0.96	0.34	0.745	0.544	0.524	0.602	0.712	0.785	0.984
8.268	+	+	2-Propanol	1.75	1.95	2.01	2.05	1.39	2.01	1.99	1.75	1.99
8.302	+	+	Dichlorometane	9.28	6.23	8.13	7.63	7.78	7.24	7.11	8.03	8.25
8.409	+	+	Ethanol	7.01	8.33	5.26	5.56	7.52	5.20	6.25	7.15	5.99
8.689	+	+	Benzene	0.40	0.233	0.124	0.163	0.213	0.204	0.187	0.125	0.201
9.001		+	3-Buten-2-one	0.28	0.239	0.212	0.186	0.124	0.092	0.087	0.078	0.087
9.175		+	Dimethylfuran	0.19	0.229	0.258	0.106	0.125	0.201	0.384	0.287	0.486
9.630		+	2,2,4,6,6-Pentamethyl- heptane	10.6	12.1	10.8	9.43	13.3	15.3	16.5	17.9	19.5
10.272	+	+	2-Pentanone	3.71	3.40	3.52	1.94	5.32	3.94	3.92	4.46	4.50
10.430	+	+	Diacetyl	3.36	2.06	2.67	1.15	4.21	3.26	2.67	2.78	4.77
12.036		+	2,5,.9-Trimethyl-decane	0.81	0.715	1.26	1.22	1.19	1.25	1.05	1.59	1.29
12.691	+	+	Trichoromethane	1.22	1.02	0.669	0.607	0.895	0.915	1.45	1.17	1.05
13.524		+	3-Methyl-2-nonene	1.12	0.085	0.079	0.098	1.08	1.16	1.28	2.01	0.098
13.696	+	+	Toluene	1.76	1.56	1.70	1.16	1.25	1.36	1.43	0.985	1.05
13.854		+	2-Methyl-3-buten-2-ol	0.20	0.164	0.128	0.158	0.095	0.184	0.058	0.148	0.214
16.361	+	+	Dimethyl disulfide	3.29	7.07	2.91	1.26	1.58	1.43	1.84	1.23	1.11
17.119	+	+	Hexanal	1.86	0.597	0.461	0.318	0.634	0.758	0.937	1.08	0.524
19.534		+	C_8H_{10}	0.11	0.073	0.084	0.077	0.072	0.074	0.045	0.095	0.067
20.193		+	C_8H_{10}	0.085	0.030	0.025	0.155	0.052	0.088	0.052	0.045	0.063
23.107	+	+	2-Heptanone	2.62	2.11	1.93	2.14	4.24	3.82	5.95	5.77	4.57
24.230		+	Methyldihydrofuran	0.000	0.000	0.000	0.000	0.000	0.045	0.084	0.068	0.097
25.023		+	C_9H_{12}	0.058	0.062	0.050	0.078	0.054	0.084	0.097	0.087	0.075
25.523		+	Furan hydrocarbon	0.000	0.000	0.000	0.000	0.000	0.042	0.068	0.074	0.087
26.034	+	+	3-Methylbutanol	0.000	0.037	0.050	0.000	0.000	0.045	0.000	0.840	0.640
26.917		+	Styrene	0.000	0.000	0.000	0.057	0.540	0.000	0.670	0.000	0.080
27.274	+	+	1-Pentanol	0.000	0.000	0.000	0.058	0.097	0.041	0.039	0.098	0.084
27.637		+	C_9H_{12}	0.084	0.052	0.062	0.021	0.097	0.041	0.039	0.098	0.084
28.324	+	+	2-Octanone	0.000	0.000	0.000	0.065	0.054	0.087	0.074	0.087	0.95
28.563	+	+	Octanal	0.000	0.000	0.000	0.092	0.124	0.074	0.102	0.154	0.15
30.540		+	6-Methyl-5-hepten-2-one	0.000	0.000	0.000	0.054	0.084	0.084	0.041	0.075	0.185
30.918	+	+	1-Hexanol	0.000	0.000	0.000	0.098	0.087	0.012	0.073	0.087	0.105
32.001	+	+	Acetic acid	0.000	0.000	0.000	0.000	0.000	0.000	0.000	tr	tr
34.906	+	+	Furfural	0.000	0.125	0.084	0.158	0.050	0.104	0.098	0.125	0.284
36.100		+	1H-Pyrrole	0.000	0.000	0.000	0.041	0.000	0.085	0.074	0.850	0.093
36.628	+	+	Benzaldehyde	0.080	0.071	0.054	0.050	0.084	0.074	0.097	0.210	0.31
37.012	+	+	Butanoic acid	0.000	0.000	0.000	0.000	0.000	0.000	0.000	tr	tr

branched, furanic and aromatic) already present in freshly processed milk increased markedly. Loney, Bassette and Claydon (1968) observed that furan, methyl furan and some methyl ketones increased during storage at 21 and 37°C. Acetaldehyde seemed to decrease after two months storage. Diacetyl level did not show a clear trend but it was always sligthly higher in skimmed milks than in the whole samples.

Composition of whole milks varied less during storage as shown in Table 2; some quantitative changes become evident after three months storage. The main variation was the methyl ketones increase, their level during storage being clearly higher in whole milk than in skimmed milk. This could be caused by the presence of a higher amount of fat in the former (Grosch, 1982). Aldehydes (2-methylbutanal, 3-methylbutanal, benzaldehyde and furfural, but not acetaldehyde) also increased slightly. Reports on the behaviour of aldehydes during storage are contradictory. Jeon et al. (1978) and Rerkrai et al. (1987) attributed a general increase of aldehydes, particularly hexanal, during storage to oxygen availability and storage temperature; Contarini et al. (1997) found a small decrease in hexanal and heptanal content of whole UHT milks stored at room temperature for 90 days. Nevertheless, the above-mentioned aldehydes in milk originated from different reactions: hexanal is generated by oxidation of unsaturated fatty acids; furfural comes from lactose through the Maillard reaction; 2-methylbutanal and 3-methylbutanal probably originated from isoleucine and leucine by the action of enzymes, whereas benzaldehyde could be generated from phenylalanine (Nursten, 1997). Alcohols could be formed by reduction from the corresponding aldehydes (Nursten, 1997)

4. Discussion and conclusions

The variations observed in volatile composition during storage of whole milks may explain the higher scores obtained in these samples by sensory analysis; the increase in methyl ketone level during storage could decrease their sensory scores as compared to freshly processed samples. Skimmed milks seemed to undergo other reactions: the formation of furanic compounds and octanal indicate Maillard reaction and lipid oxidation, respectively. An explanation for the last reaction could be the physical distribution of lipids: in whole milk they are probably protected inside the globule fat, whereas in skim milk they may be available to oxygen or enzymes. The higher proteolytic activity found in skimmed milk, possibly from enzymes derived from psycrotrophic bacteria, might increase the number of free amino groups (López-Fandiño, Olano et al., 1993) which can participate with the reducing sugars in Maillard reactions. Acetic and butyric acids could be generated by lipolysis, proteolytic reactions or both. The occurrence of new volatile compounds, together with a higher proteolysis in the case of skimmed milk, is consistent with a lower sensory acceptability than whole milk.

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