Karagül-Yüceer, Y., Drake, M.A. ve Cadwallader, K.R. Aroma-Active Components of Nonfat Dry Milk, J. Agric. Food Chem., 49, 2948-2953 (2001).

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Aroma-Active Components of Nonfat Dry Milk

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Application of aroma extract dilution analysis (AEDA) on the volatile components of low-, medium-, and high-heat-treated nonfat dry milks (NDM) revealed aroma-active compounds in the $\log_3$ flavor dilution ($\log_3$ FD) factor range of 1 to 6. The following compounds contributed the highest $\log_3$ FD factors to overall NDM flavor: 2,5-dimethyl-4-hydroxy-3(2H)-furanone [(Furaneol), burnt sugar-like]; butanoic acid (rancid); 3-(methylthio)propanal [(methional), boiled potato-like]; *o*-aminoacetophenone (grape-like); *δ*-decalactone (sweet); (E)-4,5-epoxy-(E)-2-decenal (metallic); pentanoic acid (sweaty); 4,5-dimethyl-3-hydroxy-2(5H)-furanone [(sotolon), curry]; 3-methoxy-4-hydroxybenzaldehyde [(vanillin), vanilla]; 2-acetyl-1-pyrroline and 2-acetyl-2-thiazoline (popcorn-like); hexanoic acid (vinegar-like); phenylacetic acid (rose-like); octanoic acid (waxy); nonanal (fatty); and 1-octen-3-one (mushroom-like). The odor intensities of Furaneol, butanoic acid, methional, *o*-aminoacetophenone, sotolon, vanillin, (E)-4,5-epoxy-(E)-2-decenal, and phenylacetic acid were higher in high-heat-treated samples than others. However, the odor intensities of lactones, 2-acetyl-1-pyrroline, and 2-acetyl-2-thiazoline were not affected by heat treatment. Sensory evaluation results also revealed that heat-generated flavors have a major impact on the flavor profile of NDM.

Keywords: *Nonfat dry milk; AEDA; FD factor; gas chromatography−olfactometry; gas chromatography−mass spectrometry*

INTRODUCTION

The primary dry milk product manufactured in the U.S. is nonfat dry milk (NDM). It is mainly produced by spray drying of milk. The product does not have more than 5% moisture and 1.5% fat by weight. On the basis of heat treatment prior to spray drying, three types of NDM are produced: low heat (not over 71 °C for 2 min), medium heat (71−79 °C for 20 min), and high heat (88 °C for 30 min). The heat treatment affects the functional properties of the powder. These heat processes generate different degrees of protein denaturation distinguished by the level of soluble whey protein nitrogen. The product has a shelf life of 12−18 months (*1*).

Nonfat dry milk is widely used both as an ingredient and for direct consumption. Flavor quality is one of the most important factors to determine consumer acceptance or preference of dairy products. Processing and storage of milk may change the flavor properties of the final spray dried product. When used as an ingredient, flavor quality of NDM can also directly impact the final product quality.

Studies on flavor volatiles in NDM or skim milk powders have been conducted. Volatile flavor compounds in spray-dried skim milk were determined by Shiratsuchi et al. by simultaneous distillation−extraction (SDE) (*2*). They stated that free fatty acids and lactones were fundamental contributors to the flavor of skim milk powder. In addition, aldehydes, aromatic hydrocarbons, and some heterocyclic compounds affected the flavor indirectly. In other research, the contributors of sweet and fatty odors of skim milk powder were investigated (*3*). Nonanoic, decanoic, and dodecanoic acids were found to be responsible for this attribute. Sensory properties were not addressed in these studies. Researchers have studied sensory properties of NDM during storage (*4*). Time, storage temperature, and type of packaging were critical to providing desirable sensory qualities.

Specific off-flavors in milk powders have also been studied. The role of Maillard reaction was investigated as an indicator of staling in nonfat dry milk (*5*). Constituents such as 2-furaldehyde, 2-furfuryl butyrate, alkylpyrazines, and *N*-ethyl-2-formylpyrrole originating from nonenzymatic browning may contribute to the stale flavor. Early researchers (*6*) isolated carbonyl compounds responsible for the cereal-type flavor from instant and noninstant types of NDM. The compounds identified from instant NDM were formaldehyde, acetaldehyde, acetone, butanone, methyl propanal, 3-methylbutanal, furfural, diacetyl, hexanal, and nonanal.

Many researches have focused on isolation of heat treatment induced volatile compounds in fluid whole milk (*7*−*11*). The effect of heat treatment on flavor characteristics of NDM has not been systematically studied. This study provides information on the chemical nature of predominant aroma components of low-heat, medium-heat, and high-heat NDM. The results will aid in establishing baseline data so that flavor defects in NDM caused by processing and storage may be more clearly detected and characterized. The purposes of the present study were to identify and compare the chemical nature of aroma-active compounds of low-,

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10.1021/jf0009854 CCC: $20.00
Published on Web 05/11/2001

medium-, and high-heat-treated NDM and to compare them with descriptive sensory analysis results.

EXPERIMENTAL PROCEDURES

Chemicals. Diethyl ether (anhydrous, 99.8%), sodium chloride (99%), sodium sulfate (99%), and 2-methyl-3-heptanone (internal standard for neutral/basic fractions) were obtained from Aldrich Chemical Co. (St. Louis, MO). Aroma compounds listed in Table 3 were provided from the following commercial sources: nos. 1−5, 8−10, 13, 15, 17−21, 24, 26, 27, 32, 33, 36, 37 (Aldrich Chemical Co.); nos. 14, 31, 38 (Bedoukian Research Inc., Danbury, CT); nos. 12, 34, and 35 (Sigma, St. Louis, MO) and no. 16 and 2-methylpentanoic acid (internal standard for acidic fractions) were purchased from Lancaster (Windham, NH). Compound no. 7 was synthesized according to the method of Schieberle and Grosch (*12*). Compound no. 11 was obtained from Dr. R. Buttery (USDA, ARS, WRRC, Albany, CA). Compound no. 28 was obtained from Firmenich Inc. (Plainsboro, NJ). Sodium bicarbonate (99.7%) and hydrochloric acid (36.5%) were obtained from Fisher Scientific (Pittsburgh, PA).

Milk Powders. Nonfat dry milks (18) of varying heat treatments (low, medium, high) were obtained from domestic commercial sources. Samples were received by overnight shipment. Upon receipt, powders were stored in Qorpak clear standard wide-mouth bottles sealed with Teflon-lined closures (VMR Scientific Products, St. Louis, MO). Powders ranged in age from 3 months to approximately one year. Six expert dairy judges screened the milk powders for specific flavor defects and overall quality. These individuals each had more than 80 h of experience judging the flavor quality of fluid and dried milks using the American Dairy Science Association Scorecard, USDA Grading, and descriptive analysis. Panelists were between the ages of 21 and 59; three were female, and three were male. A list of common milk powder characteristics and defects (*13*−*16*) was used to allow the panelists an opportunity to comment on the flavor quality of each sample. A 10-point scale was used to measure overall flavor quality where 1 = poor quality to 10 = excellent quality. Bland defect-free milk powders (two from each heat treatment) were selected for chemical flavor analysis and quantitative descriptive analysis.

Preparation of Extracts for AEDA. *Direct Solvent Extraction.* Milk powders (100 g) were hydrated with 500 mL of odor-free water (prepared by boiling 4 L of distilled water until its volume was decreased by one-third) and blended with an electric hand-held mixer. The pH values of reconstituted milks ranged between 6.3 and 6.4. 2-Methyl-3-heptanone (5.44 μg/μL) and 2-methylpentanoic acid (6.18 μg/μL) in methanol were added as internal standards (10 μL) for neutral/basic and acidic fractions, respectively. Each sample was extracted with diethyl ether (3 × 300 mL) in 250-mL Teflon bottles with Tefzel closures (Nalgene, Rochester, NY). Solid NaCl (180 g) was added to the milk to break the emulsion during extraction. Each sample was agitated on a Roto Mix (Thermolyne, type 50800; Dubuque, IA) for 30 min at the highest speed, and then centrifuged at 3500 rpm for 30 min. After centrifugation, each sample was slowly stirred to break the emulsion.

High Vacuum Distillation. Prior to use all glassware was baked at 160 °C for at least 2 h. The solvent extract was dried over anhydrous sodium sulfate (Na_2SO_4), and then concentrated to 100 mL at 38 °C using a Vigreux column (150 × 15 mm; VMR Scientific Products, St. Louis, MO). Separation of volatile material from nonvolatile residue by high-vacuum distillation was as follows: sample was placed in a 1-L round-bottom flask and immersed in a Dewar flask containing liquid nitrogen until the sample was frozen. The flask was connected to a rough pump/diffusion pump vacuum source and fitted with a receiving tube and waste tube. The unit was similar to the apparatus described by Sen and co-workers (*17*). The receiving and waste tubes were immersed in Dewar flasks containing liquid nitrogen throughout the distillation period. Vacuum was applied (ca. 10^{-5} Torr) to the system for 4 h. The sample flask was kept at room temperature for the first 2 h then the temperature was increased to 60 °C (in a water bath) and the process was continued for a further 2 h. After distillation, volatile extract was recovered from the first receiving tube and concentrated to 20 mL under a gentle nitrogen gas stream. After that it was washed with sodium bicarbonate ($NaHCO_3$; 0.5 M; 2 × 15 mL) and a saturated solution of sodium chloride in water (3 × 5 mL). The upper (ether) phase containing the neutral/basic volatiles was dried over anhydrous Na_2SO_4 and concentrated to 0.5 mL under a gentle stream of nitrogen gas. The pooled aqueous phase (bottom layer) was acidified with hydrochloric acid (18% v/v) to pH 1.5−2 and the acidic volatiles were extracted with diethyl ether three times, dried over anhydrous Na_2SO_4, and concentrated to 0.5 mL under a nitrogen stream.

Gas Chromatography−Olfactometry (GCO). The GCO system consisted of a HP5890 series II GC (Hewlett-Packard Co., Palo Alto, CA) equipped with a flame ionization detector (FID), a sniffing port, and an on-column injector. Each extract (2 μL) was injected into a capillary column (DB-WAX 30 m length × 0.25 mm i.d. × 0.25 μm film thickness (d_f) or DB-5ms 30 m length × 0.32 mm i.d. × 0.25 μm d_f; J & W Scientific, Folsom, CA). Column eluate was split 1:1 between FID and sniffing port using deactivated fused silica capillaries (1 m length × 0.25 mm i.d.). GC oven temperature was programmed from 35 °C to 200 °C at a rate of 10 °C/min, with initial and final hold times of 5 and 30 min, respectively. The FID and sniffing port were each maintained at a temperature of 250 °C. The sniffing port was supplied with humidified air at 30 mL/min. Two experienced panelists conducted GCO. The extracts containing the neutral/basic and acidic volatiles were diluted stepwise with diethyl ether at a ratio of 1:3 (v/v). The dilution procedure was performed until no odorants were detected by GCO. The highest dilution was defined as flavor dilution (FD) factor (*18*).

Gas Chromatography−Mass Spectrometry (GC−MS). The system consisted of an HP5890 Series II GC/ 5972 mass selective detector (MSD, Hewlett-Packard, Co.). Separations were performed on fused silica capillary columns (DB-WAX or DB5ms, 60 m length × 0.25 mm i.d. × 0.25 μm d_f, J & W Scientific). Carrier gas was helium, and it was maintained at a constant flow of 0.96 mL/min. Oven temperature was programmed from 35 °C to 200 °C at a rate of 3 °C/min with initial and final hold times of 5 and 45 min, respectively. MSD conditions were as follows: capillary direct interface temperature, 280 °C; ionization energy, 70 eV; mass range, 33−350 amu; EM voltage (Atune + 200 V); scan rate, 2.2 scans/s. Each extract (2 μL) was injected in the on-column mode.

Identification of Odorants. Positive identifications were made by comparing retention indices (RI), mass spectra, and odor properties of unknowns with those of authentic standard compounds analyzed under identical conditions. Tentative identifications were based on comparing mass spectra of unknown compounds with those in the Wiley 138 mass spectral database (John Wiley & Sons, Inc., 1990) and a database generated from authentic standards in the Department of Food Science and Technology Flavor Laboratory (Mississippi State University, Mississippi State, MS) or on matching the RI values and odor properties of unknowns against those of authentic standards. Retention indices were calculated by using an *n*-alkane series (*19*).

Quantification of Selected Compounds. Reconstituted milk, after deodorization by high-vacuum distillation, was used as a matrix to prepare standard solutions. Calibration was accomplished by addition of 0 (blank), 2 μL, 5 μL, or 20 μL from a stock solution. Each mixture was also spiked with 10 μL of internal standard solution. The same procedure for preparation of extracts from samples was followed to prepare the standard solutions. The standard stock solution contained 54.6 μg of no. 1, 15.48 mg of no. 2, 48.4 μg of no. 4, 1.22 mg of no. 5, 1.6 mg of no. 8, 56 μg of no. 10, 12.68 mg of no. 12, 2.84 mg of no. 13, 12.94 mg of no. 14, 47 μg of no. 15, 46 μg of no. 17, 58.4 μg of no. 18, 51 μg of no. 21, 66 μg of no. 24, 2.34 mg of no. 26, 3.74 mg of no. 27, 22.2 μg of no. 31, 4.5 mg of no. 37, and 10.84 mg of no. 38 per ml in methanol.

Table 1. Preparation of Reference Materials for Descriptive Sensory Evaluation of Nonfat Dry Milk

descriptor	reference	preparation
cooked/sulfurous	heated milk	heat pasteurized skim milk to 85 °C for 30 min
caramelized/	1. autoclaved milk	1. autoclave whole milk at 121 °C for 30 min.
butterscotch/	2. caramel syrup	2. dilute small amount of caramel syrup in skim milk
burnt sugar	3. butterscotch candy	
sweet aromatic/	vanillin crystals	dilute small amount of vanillin in skim milk
cake mix	(3-methoxy-4-hydroxybenzaldehyde)	
fried fatty	(E,E)-2,4-decadienal	400 ppb (E,E)-2,4-decadienal in skim milk
mushroom/	1. 1-octen-3-one	1. 10 ppb 1-octen-3-one in skim milk
metallic	2. mushroom	2. sliced fresh mushroom in skim milk
papery	cardboard paper	soak cardboard paper in skim milk overnight
sweet taste	5% sucrose solution	
astringent	tea bags	soak 6 tea bags in water for 10 min

Table 2. Flavor Attributes of Nonfat Dry Milks

attributes	low	medium	high
cooked/sulfurous	3^{c}	3.61^{b}	4.25^{a}
caramelized	0.75^{c}	1.42^{b}	2.25^{a}
sweet aromatic/cake mix	1.05^{a}	0.5^{b}	0.16^{b}
fried fatty	0	0	0
mushroom	0	0	0
papery	0	0	0
sweet	1.45^{a}	1.46^{a}	1.05^{b}
astringent	0.5^{b}	0.65^{b}	1.26^{a}

^{a,b,c} Means within a row without a common superscript differ ($P < 0.05$).

Sensory Evaluation and Statistical Analysis. *Sample Preparation.* For flavor evaluation, 10 g of NDM was suspended in 100 mL of odor free water at 40 °C and mixed by electric mixer (Biospec Products, Inc.; Bartlesville, OK) at the lowest speed for 2 min. Samples were evaluated at 20 ± 2 °C. Liquid samples for flavor evaluation were served in Styrofoam cups equipped with plastic lids and straws to prevent the appearance of the milk from influencing the panelist's decision and to prevent formation of light-induced flavors.

Quantitative Descriptive Analysis (QDA). Fourteen panelists were selected based on interest, time available, and liking for dairy foods. Descriptive analysis of flavor was conducted on NDM samples (*20*). Panelists were presented with an array of rehydrated NDM samples including, but not limited to, the samples analyzed in this study, and were asked to identify and define flavor terms. Terms identified and selected by the panelists are listed in Table 1. Panelists marked their responses on a 10-point numerical intensity scale anchored on the left with "none" and on the right with "extreme". Panelists received approximately 30 h of training during which they refined terms and decreased group standard deviation. Powders were evaluated in duplicate in a randomized balanced block design. Differences among treatments were evaluated by analysis of variance with means separation (ANOVA). All analyses were performed using SAS Version 7 (*21*).

RESULTS AND DISCUSSION

Quantitative descriptive analysis results showed that intensity levels of all aroma descriptors ranged between 0 and 4.25 (Table 2). Skim milk powders have delicate mild flavors, and intensities would be expected to be low. Cooked/sulfurous, caramelized flavors, and sweet taste were the most intense attributes for all powders. The intensities of sweet aromatic/cake mix and astringency were low. In other words, heat generated flavors were the most intense attributes. High-heat-treated powders exhibited more intense cooked/sulfurous and caramelized flavors than low- or medium-heat-treated powders (Table 2). Lipid oxidation flavors (fried fatty, mushroom/metallic, and papery), although identified in some milk powders during sensory language development, were not detected in the powders analyzed in this study. These samples were pre-screened and were selected for analysis based on their bland, defect-free flavor.

The results of AEDA of the neutral/basic and acidic fractions in NDM are summarized in Table 3. Aroma profiles (FD chromatograms) of low-, medium-, and high-heat-treated NDM samples were similar, and only a few components differed markedly in $\log_3$ FD factors between the samples. These results concur with quantification results in which the concentration of compounds did not differ between samples (Table 4). The principal flavor of NDM originates from the native volatile compounds in milk, and chemical degradations during processing and storage of the product. As shown (Table 4) the number and abundance of volatile free fatty acids, lactones, and maltol in all heat treatment levels were high. Other thermally induced volatiles in skim milk powder included Furaneol, methional, 2-acetyl-1-pyrroline, 2-acetyl-2-thiazoline and 2-actylthiazole. Aroma components of high-heat-treated NDM powders had $\log_3$ FD factors higher than those of medium- and low-heat-treated NDM powders, indicating higher aroma intensities of some thermally induced compounds (Table 3). Schieberle (*22*) isolated Furaneol in popcorn and bread, and stated that thermal treatment of sugars generated this compound from fructose-1, 6-biphosphate via acetylformoine as the intermediate. Other related compounds, 2-methyl-3-hydroxy-4H-pyran-4-one (maltol) and 4,5-dimethyl-3-hydroxy-2 (5H)-furanone (sotolon) also were detected in acidic fractions. Methional was described as having a boiled potato-like aroma. It was reported that Strecker degradation of methionine might cause the formation of this compound (*23*). It can also be formed from methionine when milk is exposed to light (*24*).

Other groups of thermally induced aroma-active compounds such as 2-acetyl-1-pyrroline (no. 11), 2-acetyl-2-thiazoline (no. 17), and 2-acetylthiazole (no. 32) have popcorn-like notes. Proline is the most important precursor of popcorn odor by 2-acetyl-1-pyrroline. The reaction between the amino acids proline or ornithine and the reactive sugar-degradation product 2-oxopropanal generates 2-acetyl-1-pyrroline (*25*). Thiazolines and thiazoles are breakdown products of cysteine by heat treatment (*26*, *27*).

The other major compounds that contributed to NDM flavor were free fatty acids liberated by hydrolysis from naturally occurring fats. Milkfat is an important source of volatile flavor compounds in dairy foods. The short-chain fatty acids (C_4−C_{12}) are main flavor contributors of cheese and other dairy products (*28*). Butanoic (no. 2) and pentanoic (no. 8) acids with cheesy notes were detected at high odor intensities in the acidic fraction

Table 3. Aroma-Active Compounds (Log_3 FD Factor ≥ 2) of Low (L), Medium (M), and High (H) Heat-Treated Nonfat Dry Milks Detected during Aroma Extract Dilution Analysis

			RI [b]			Log_3 FD Factor [d] by heat treatment		
no.	compound	fraction[a]	DB-WAX	DB-5	odor[c]	L	M	H
1	2,5-dimethyl-4-hydroxy 3(2H)-furanone (Furaneol)[A]	A	2027	1057	caramelized, burnt sugar	5	5	6
2	butanoic acid[A]	A	1606	802	rancid, cheesy	5	5	6
3	methional[A]	N/B, A	1443	904	boiled potato	5	5	6
4	*o*-aminoacetophenone[A]	N/B	2218	1308	grape, foxy	5	5	6
5	δ-decalactone[A]	N/B	2183	1502	burnt, sweet, fatty	5	6	5
6	unknown	N/B	2202	1560	cilantro	5	6	5
7	(E)-4,5-epoxy-(E)-2-decenal [B]	N/B	2000	1392	metallic, green	3	5	6
8	pentanoic acid[A]	A	1756	902	cheesy, sweaty	4	3	5
9	4,5-dimethyl 3-hydroxy-2(5H)-furanone (sotolon) [B]	A	2204	1118	curry, butterscotch	3	4	5
10	vanillin (3-methoxy-4-hydroxy-benzaldehyde)[A]	A	2540	1401	vanilla, waffle, pudding	4	5	5
11	2-acetyl-1-pyrroline[B]	N/B	1331	919	popcorn	4	5	4
12	hexanoic acid[A]	A	1834	1008	sour, vinegar, cheesy	4	4	4
13	phenylacetic acid[A]	A	2568	1265	rosy	3	4	5
14	octanoic acid[A]	A	2048	1289	waxy, soapy, sweaty	5	3	4
15	nonanal[A]	N/B	1384	1099	fatty, stale, soapy	4	3	5
16	1-octen-3-one[B]	N/B	1294	977	mushroom	3	3	5
17	2-acetyl-2-thiazoline[A]	N/B	1762	1107	popcorn	4	5	3
18	γ-dodecalactone[A]	N/B	2398	1656	cilantro, sweet	4	4	4
19	(*E*)-2-nonenal[A]	N/B	1532	1162	hay, cucumber	4	3	4
20	(*E*)-2-undecenal[B]	N/B	1722	1367	waxy, green	4	4	3
21	(*E*,*E*)-2,4-decadienal[A]	N/B	1807	1320	fried fatty	3	4	3
22	unknown	N/B	2130	1582	fresh fishy	3	3	4
23	unknown	N/B	1361	981	fresh air, milky	4	3	3
24	3-phenylpropionic acid [A]	A	> 2600	1356	sour, rose-like	3	4	4
25	unknown	N/B	2108	1345	mint, green	2	4	4
26	maltol[A]	A	1978	1088	cotton candy	3	3	4
27	isobutyric acid[A]	A	1556	959	bug, Swiss cheese	3	2	3
28	β-damascenone [B]	N	1822	1370	apple sauce	1	2	1
29	unknown	A		1199	metallic, waxy	3	3	1
30	unknown	N/B		1146	fatty, waxy	3	1	2
31	(*E*,*E*)-2,4-nonadienal[A]	N/B	1701	1218	stale, fatty, soapy	2	< 1	4
32	2-acetylthiazole[B]	N/B	1416	1025	popcorn	2	3	1
33	2-isopropyl-3-methoxy pyrazine[B]	N/B	1420	1091	earthy	1	2	3
34	β-ionone[B]	N/B	1945	1488	stale, hay	2	< 1	4
35	3-methylindole (skatole)[A]	N/B	2477	1395	mothball, skatole	1	2	1
36	(*E*,*Z*)-2,6-nonadienal[A]	N/B	1583	1153	cucumber	1	1	2
37	acetic acid[A]	A	1431	< 700	sour, vinegar	2	3	1
38	decanoic acid[A]	A	2262	1404	fatty, soapy	1	1	2

[A]Compound positively identified (RI, odor, MS). [B] Compound tentatively identified (RI, odor). [a] N/B, neutral/basic fraction; A, acidic fraction. [b] Retention indices (RI) calculated from GCO results. [c] Odor description at the GC-sniffing port during GCO. [d] Average log_3 of flavor dilution factors on DB-5MS column, except for nos. 1, 2, 6−8, 10, 12−14, 17, 29, 37, 38.

of NDM. Butanoic and hexanoic acids were reported as the major free fatty acids of skim milk powders (*5*). These results agree with our findings. We also determined octanoic acid (no. 14) at high odor intensity, but the odor perceived with this acid was waxy or soapy. Hydrolysis of plant acyglycerols and animal depot fats is the potential source of soapy-tasting fatty acids (*28*).

Lactones are also important contributors to the flavor of NDM. They are formed from δ- and γ-hydroxy acids or triglycerides by heating (*26*), and provide desirable flavor notes to baked foods. Lactones that we detected contributed to sweet and fatty flavors in milk powder. The odor intensity (Table 3) and concentration (Table 4) of δ-decalactone (no. 5) were higher than those of γ-dodecalactone (no. 18). δ-decalactone has been identified as a key contributor to the flavor of butter (*29*). The lactones detected in our study were also reported by Shiratsuchi and co-workers (*2*).

o-Aminoacetophenone (no. 4), with a grape-like or foxy note, was detected in the neutral/basic fraction at high intensity. This compound was identified as a prominent odorant in tortilla-type corn products (*30*). The possible source of the flavor was alkali degradation of tryptophan. *o*-Aminoacetophenone is an important compound formed in stale dry milk (*31*) and in stale flavor fractions of sterilized concentrated milk (*32*). Vanillin (no. 10) was detected in acidic fractions at high odor intensity. This compound probably originates from plant lignin. Microorganisms in cow rumen may break down feed lignins to coniferyl alcohol, which passes into milk and may subsequently be oxidized to vanillin during heat treatment of milk (*33*). Phenylacetic acid (no. 13), which possesses a high odor intensity and a lingering rose-like aroma, is a metabolic product derived from phenylalanine (*34*) by Strecker-type reaction (*35*). This Strecker acid is formed by an oxidation of phenylacetaldehyde during the thermal treatment. 3-Methylindole (skatole) was perceived at low intensity in all powders. It might be the metabolite of the amino acid tryptophan or come from animal feeds such as peppercress (*36*).

Lipid oxidation of milk leads to flavors termed oxidized, cardboard, metallic, fatty (oily), painty, and fishy. The alkanals and alkenals with more than six carbon atoms, and ketones, are the typical volatiles generated

Table 4. Mean Concentrations (mg/100g) of Selected Key Odor-Active Compounds in Nonfat Dry Milks with Low, Medium and High Heat Treatments

compound	mean concentration (mg/100g)		
	low	medium	high
2,5-dimethyl-4-hydroxy 3(2H)-furanone	0.2[a]	0.4[a]	0.4 [a]
butanoic acid	1150[a]	1479[a]	1857[a]
o-aminoacetophenone	0.05[a]	0.02[a]	0.03[a]
δ-decalactone	2.3[a]	1.6[a]	0.7[a]
pentanoic acid	2.6[a]	4.3[a]	3.6[a]
vanillin	0.02[a]	0.004[a]	0.018[a]
hexanoic acid	501[a]	510[a]	677[a]
phenylacetic acid	3.9[a]	7.5[a]	7.3[a]
octanoic acid	228[a]	245[a]	379[a]
nonanal	0.3[a]	0.3[a]	0.06[a]
2-acetyl 2-thiazoline	0.001[a]	0.002[a]	0.002[a]
γ-dodecalactone	0.5[a]	0.3[a]	0.2[a]
(*E*,*E*)-2,4-decadienal	0.5[a]	0.04[a]	0.09[a]
3-phenylpropionic acid	0.05[a]	0.05[a]	0.04[a]
maltol	2.8[a]	8[a]	10.4[a]
isobutyric acid	12.7[a]	7.3[a]	9.1[a]
(*E*,*E*)-2,4-nonadienal	0.15[a]	0.011[a]	0.1[a]
acetic acid	24[a]	18[a]	28[a]
decanoic acid	241[a]	201[a]	314[a]

[a] Means within a row without a common superscript differ ($P < 0.05$).

by lipid oxidation (*2*, *26*). (E)-4,5-Epoxy-(E)-2-decenal was identified as an aroma-active compound with a metallic, green note in NDM in the present study. This compound was also identified as a character-impact odorant in other dairy products including butter (*29*) and regular-fat and low-fat Cheddar cheeses (*37*). 1-Octen-3-one (mushroom-like) has been described as having a metallic odor in some sources (*26*, *38*). It is formed by oxidation of arachidonic acid. 2,4-Decadienal, a product of linoleic acid oxidation (*26*), imparted a fried fatty odor in NDM. 1-Octen-3-one and (E,E)-2,4-decadienal previously were identified as primary odorants of milk products (*29*). Some other lipid oxidation products detected by GCO were nonanal, (E)-2-nonenal, (E,E)-2,4-nonadienal, and (E,Z)-2,6-nonadienal with fatty, hay-like, stale, and cucumber-like odor notes, respectively. Most of these compounds have been used to indicate oxidized flavor in reduced-fat Cheddar cheese containing lecithin (*39*). These "oxidized" flavors were not detected by sensory analysis of powders and were likely to have been below sensory threshold in the milks.

Sweet and astringent tastes in powders were also detected by sensory evaluation. Sweet and fatty odors of NDM were related to nonanoic, decanoic, and dodecanoic acids (*3*). In addition, the contributors of sweet and milky odors were γ-undecalactone, γ-dodecalactone, γ-lactone, δ-decalactone, and δ-undecalactone (*3*). Astringency is common in highly heated and UHT-sterilized milks (*40*) and NDM (*41*). Astringency in high-heat-treated milk was attributed to the interaction product involving whey proteins, calcium phosphate, and caseins (*42*).

CONCLUSIONS

This study has revealed the character-impact odorants for nonfat dry milks. The odor intensities of some compounds were affected by heat treatment. Similarly, differences in flavor intensities due to heat treatment were noted by sensory panelists. Thermally induced compounds were perceived at higher intensities in high-heat-treated skim milk powders. Furaneol, maltol, sotolon, vanillin, and butanoic acid were perceived at higher intensities in the acidic fractions of high-heat-treated NDM. Similarly, *o*-aminoacetophenone, (E)-4,5-epoxy-(E)-2-decenal, nonanal, and 1-octen-3-one were higher in the neutral/basic fraction of high-heat-treated NDM. Free fatty acids, lactones and browning/Maillard reaction products including maltol, Furaneol, and aldehydes were the primary contributors to the aroma of NDM. Moreover, ketones and skatole also participated in the flavor.

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Received for review August 8, 2000. Revised manuscript received March 20, 2001. Accepted March 22, 2001.Funding for this research was provided by the California Dairy Research Foundation (CDRF) and the Mississippi Agriculture and Forestry Experiment Station (MAFES). Ms. Karagül-Yüceer was supported by a Turkish Government fellowship. Approved as journal article no. 9739 of MAFES.

JF0009854