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Volatile Flavor Components of Stored Nonfat Dry Milk

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Nonfat dry milk (NDM) is widely used both as an ingredient in other preparations and for direct consumption. Flavor quality of NDM is a critical parameter because it can directly impact final product quality. Flavors can be formed in NDM during subsequent storage. Identification of compounds responsible for storage-induced flavors is necessary to correlate sensory quality with potential sources of the flavors. Six NDM samples were selected for volatile flavor analysis based on sensory analysis and storage time. Volatile components were extracted by direct solvent extraction/high vacuum distillation. Volatile extracts were separated into neutral/basic and acidic fractions and analyzed by gas chromatography−olfactometry (GCO) and aroma extract dilution analysis (AEDA). A variety of aldehydes, ketones, and free fatty acids were responsible for generation of flavors in stored NDM. The following compounds exhibited high aroma impact by AEDA: 3-(methylthio)propanal (boiled potato); *o*-aminoacetophenone (corn tortilla); 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone and 2-methyl-3-hydroxy-4*H*-pyran-4-one (burnt sugar); butanoic acid (cheesy); pentanoic acid (sweaty); acetic and hexanoic acids (sour/vinegar); octanoic, decanoic, and dodecanoic acids (waxy); *p*-cresol (cowy/barny); 3-methylindole (fecal); dimethyl trisulfide (cabbage); (*E*,*E*)-2,4-decadienal (fried/fatty); furfuryl alcohol (rubber/vitamin); phenylacetic acid (rose-like); and 1-octen-3-one (mushroom).

KEYWORDS: Nonfat dry milk; AEDA; flavor, gas chromatography−olfactometry; gas chromatography−mass spectrometry

INTRODUCTION

Skim milk powder is used for both direct consumption and as an ingredient in foods. As an ingredient, nonfat dry milk (NDM) enhances the body and texture and modifies the taste and flavor. Therefore, the quality of skim milk directly affects the quality of the final product. Flavor is one of the most important factors for consumer acceptance of a product. Because of consumer complaints, off-flavors are a major concern to the food industry. Off-flavors can originate from several sources such as oxidation of lipids, enzyme-catalyzed changes, microbial growth, or environmental sources. Development of off-flavors decreases the sensory quality and economic value of dairy products.

Specific off-flavors in milk powder have been studied. The role of Maillard reactions was investigated as an indicator of staling in nonfat dry milk (*1*). Constituents originating from nonenzymatic browning such as 2-furaldehyde, 2-furfuryl butyrate, alkylpyrazines, and *N*-ethyl-2-formylpyrrole may contribute to stale flavors. Early researchers (*2*) 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, methylpropanal, 3-methylbutanal, furfural, diacetyl, hexanal, and nonanal. *trans*-6-Nonenal has been identified as an off-flavor compound in fresh, foam spray-dried milks (*3*). The source of the compound originates from the ozonolysis of lipid components on the surface of the powder.

To our knowledge, no study has been published on the determination of volatile flavor compounds of stored NDM with both gas chromatography−olfactometry (GCO) and descriptive sensory analysis to date. The objective of the present study was to identify the chemical and sensory profiles of stored NDM.

MATERIALS AND METHODS

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 Tables 2 and 3 were provided from the following commercial sources: no. **1**−**6**, **10**, **12**−**19**, **22**−**24**, **27**, **28**, **31**, **32**, **35**, **36**, **38**−**43**, **45**, **46**, **48**, **49**, **51**, **53**, **54**, and **56** (Aldrich Chemical Co.); no. **7**, **20**, **47**, **50**, and **52** (Bedoukian Research Inc., Danbury, CT); no. **25**, **26**, **37**, and **44** (Sigma, St. Louis, MO); and no. **8** and 2-methylpentanoic acid (internal standard for acidic fractions) were purchased from Lancaster (Windham, NH). Compound **9** was obtained from Dr. R. Buttery (USDA, ARS, WRRC,

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

descriptor	reference	preparation
cooked/sulfurous	heated milk	heat pasteurized skim milk to 85 °C for 45 min
caramelized/ butterscotch/ burnt sugar	1. autoclaved milk 2. caramel syrup	1. autoclave whole milk at 121 °C for 30 min 2. dilute a tablespoon of caramel syrup in 400 mL of skim milk
sweet aromatic/cake mix	Pillsbury white cake mix	
cereal/grass-like	breakfast cereals (corn flakes, oats, and Wheaties)	soak 1 cup of cereal in 3 cups of milk for 30 min and filter to remove cereals
barny/animal-like	*p*-cresol	20 ppm in skim milk
brothy/potato-like	Kroger canned white potato slices	remove the sliced potatoes from the broth
animal/gelatin-like/wet dog	Knox unflavored gelatin	dissolve one bag of gelatin (28 g) in 2 cups of distilled water
fried fatty/painty	(*E*,*E*)-2,4-decadienal	2 ppb in skim milk
mushroom/metallic	fresh mushroom	slice fresh mushroom in skim milk for 30 min and filter to remove mushroom slices
papery/cardboard	cardboard paper	soak pieces of cardboard paper in skim milk overnight
burnt/charcoal	overtoasted bread slice	
vitamin/rubber	Enfamil polyvisol vitamin	
sweet taste	sucrose	5% sucrose solution
salty	NaCl	2% NaCl solution
sour	citric acid	1% citric acid solution
bitter	caffeine	0.5% caffeine solution
astringent	tea	soak six tea bags in water for 10 min

Table 2. Neutral/Basic Aroma-Active Compounds (Log$_3$ FD Factor $\geq$ 3) of Stored Nonfat Dry Milks Detected during Aroma Extract Dilution Analysis

		RI[a]			log$_3$ FD factor[b]					
no.	compound[c]	DB-Wax	DB-5	odor[d]	I	II	III	IV	V	VI
1	3-methylbutanal^A	906	624	sweet, fruity	<3	<3	4	<3	nd	nd
2	2,3-butanedione^B	970	621	buttery	<3	<3	5	<3	<3	<3
3	hexanal^A	1060	794	green, grass	3	3	4	<3	<3	3
4	3-methylthiophene^B	1078	774	plastic	<3	<3	4	<3	nd	<3
5	1-hexen-3-one^B	1147	775	rubbery	3	3	<3	<3	<3	4
6	ethyl disulfide^A	1192	768	gasoline	3	<3	<3	nd	<3	4
7	(*Z*)-4-heptenal^B	1216	899	biscuit-like	<3	3	3	<3	<3	<3
8	1-octen-3-one^B	1279	973	mushroom	4	3	5	4	<3	<3
9	2-acetyl-1-pyrroline^B	1311	916	popcorn	5	7	3	7	5	3
10	dimethyl trisulfide^A	1360	963	cabbage	nd	5	<3	<3	nd	5
11	(*Z*)-1,5-octadien-3-one^B	1384	978	metallic	nd	3	4	nd	nd	nd
12	2-acetylthiazole^B	1404	1018	popcorn	<3	4	3	4	<3	4
13	(*E*)-2-octenal^A	1416	1060	fatty	6	3	3	<3	<3	<3
14	methional^A	1427	899	boiled potato	6	8	6	4	5	5
15	(*Z*)-2-nonenal^B	1478	1147	hay	3	<3	3	<3	<3	<3
16	(*E*)-2-nonenal^B	1509	1155	hay	5	3	<3	<3	<3	3
17	(*E*,*Z*)-2,6-nonadienal^B	1568	1148	cucumber	3	<3	<3	<3	<3	<3
18	phenylacetaldehyde^A	1622	1039	rose	3	4	<3	<3	<3	<3
19	furfuryl alcohol^A	1635	813	vitamin, rubber	<3	<3	nd	nd	nd	8
20	(*E*,*E*)-2,4-nonadienal^A	1681	1211	fatty, soapy	3	<3	3	<3	nd	<3
21	unknown	1710		hay, saffron	<3	4	4	<3	<3	<3
22	2-acetyl-2-thiazoline^A	1743	1103	popcorn	3	4	4	3	4	nd
23	(*E*,*E*)-2,4-decadienal^A	1793	1313	fried fatty	4	5	4	4	4	4
24	benzothiazole^A	1838	1269	rubber	4	6	4	4	3	5
25	2-phenylethanol^A	1905	1114	rose	4	4	4	3	3	6
26	β-ionone^A	1954	1482	hay	nd	3	<3	<3	<3	<3
27	(*E*)-2-undecenal^B	1976	1360	metallic	5	5	6	5	<3	3
28	*p*-cresol^A	2057	1070	cowy/barny	4	5	4	3	3	4
29	unknown	2090		minty	3	<3	4	<3	3	5
30	unknown	2153		animal	<3	3	<3	nd	4	<3
31	δ-decalactone^A	2190	1490	sweet, fatty	6	6	5	6	6	5
32	*o*-aminoacetophenone^A	2204	1308	foxy	6	7	7	7	6	10
33	unknown	2246		animal	3	5	3	<3	4	3
34	unknown	2293	1547	burnt protein	<3	6	3	<3	<3	5
35	δ-undecalactone^A	2356	1653	green, cilantro	<3	<3	4	<3	<3	<3
36	γ-dodecalactone^A	2384	1675	sweet, green	4	4	7	4	4	4
37	3-methylindole (skatole)^A	2468	1391	fecal	<3	3	3	<3	3	6

[a] Retention indices (RI) calculated from GCO results. [b] Average log$_3$ of flavor dilution factors on DB-Wax column. Roman numbers represent the samples analyzed: I, 3 months old; II, 25 years old; III, 2 years old; IV, 1 year old; V, 3 months old, international source; VI, 3 years old. nd, not determined. [c] Compounds designated with a superscript A were positively identified (RI, odor, MS); those designated with a superscript B were tentatively identified (RI, odor). [d] Odor description at the GC-sniffing port during GCO.

Albany, CA). Compound **11** was synthesized according to the method of Ullrich and Grosch (*4*). Sodium bicarbonate (99.7%) and hydrochloric acid (36.5%) were obtained from Fisher Scientific (Pittsburgh, PA).

Milk Powders. Five nonfat dry milk samples (I, II, III, IV, VI) were obtained from domestic commercial sources. Sample V was an international sample. Samples were received by overnight shipment. Upon receipt, powders were stored at −20 °C in Qorpak clear standard

Table 3. Acidic Aroma-Active Compounds ($\log_3$ FD Factor ≥ 3) of Stored Nonfat Dry Milks Detected during Aroma Extract Dilution Analysis

		RI[a]			$\log_3$ FD factor[b]					
no.	compound[c]	DB-FFAP	DB-5	odor[d]	I	II	III	IV	V	VI
38	acetic acid[A]	1419	663	sour, vinegar	5	4	4	4	4	5
39	propionic acid[A]	1498	926	sweaty	<3	3	3	<3	<3	<3
40	isobutyric acid[A]	1520	937	sweaty	5	3	3	<3	4	4
41	butanoic acid[A]	1624	826	rancid cheese	6	8	6	6	6	6
42	2-/3-methylbutyric acid[A]	1661	872	sweaty	3	3	5	4	<3	5
43	pentanoic acid[A]	1720	921	Swiss cheese	5	5	6	7	4	4
44	hexanoic acid[A]	1830	1014	cheesy, sour	5	5	5	5	<3	5
45	maltol[A]	1943	1091	burnt sugar	4	4	5	6	6	<3
46	2,5-dimethyl-4-hydroxy 3(2*H*)-furanone (Furaneol)[A]	1991	1083	caramel	8	7	6	6	7	8
47	octanoic acid[A]	2030	1289	waxy, soapy	4	6	4	3	7	6
48	nonanoic acid[A]	2116	1762	waxy, rubbery	3	4	3	4	4	4
49	4,5-dimethyl-3-hydroxy-2(5*H*)-furanone (sotolon)[A]	2164	1111	curry	5	7	6	6	6	6
50	decanoic acid[A]	2250	2013	waxy	4	7	6	5	4	8
51	unknown	2332		sour, dishrag	5	3	4	<3	nd	<3
52	dodecanoic acid[A]	2438	2156	waxy	3	3	4	4	4	4
53	phenylacetic acid[A]	2519	1291	rose, styrene	5	5	6	5	5	4
54	vanillin (3-methoxy-4-hydroxy-benzaldehyde)[A]	2530	1406	vanilla	3	<3	6	7	4	6
55	unknown	2559		honey, floral	7	6	4	5	nd	<3
56	3-phenylpropionic acid[A]	2577	1363	rose	6	6	5	4	<3	4

[a] Retention indices (RI) calculated from GCO results. [b] Average $\log_3$ of flavor dilution factors on DB-FFAP column. Roman numbers represent the samples analyzed: I, 3 months old; II, 25 years old; III, 2 years old; IV, 1 year old; V, 3 months old, international source; VI, 3 years old. nd, not determined. [c] Compounds designated with a superscript A were positively identified (RI, odor, MS); those designated with a superscript B were tentatively identified (RI, odor). [d] Odor description at the GC-sniffing port during GCO.

wide-mouth bottles sealed with Teflon-lined closures (VMR Scientific Products, St. Louis, MO). Powders ranged in age from approximately 3 months to 25 years. Samples I and V were 3 months old. Sample II was stored in a nitrogen-flushed container (can) for 25 years. Samples III and IV were 2 and 1 years old, respectively. Sample VI was stored at room temperature and high humidity conditions for 3 years. Other samples were stored at ambient temperature and low humidity after production.

Preparation of Extracts for Aroma Extract Dilution Analysis (AEDA). To prepare the samples for AEDA, direct solvent extraction and high-vacuum distillation methods were used as described by Karagül-Yüceer and co-workers (*5*).

GCO. The GCO system consisted of an 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. The neutral/basic fraction of each extract (2 μL) was injected into a polar capillary column [DB-Wax, 30 m length × 0.25 mm i.d. × 0.25 μm film thickness (d_f); J&W Scientific, Folsom, CA] and a nonpolar column (DB-5ms, 30 m length × 0.32 mm i.d. × 0.25 μm d_f; J&W Scientific). For the acidic fraction, a DB-FFAP (30 m length × 0.25 mm i.d. × 0.25 μm d_f; J&W Scientific) was used as a polar capillary column. Column effluent was split 1:1 between the FID and sniffing port using deactivated fused silica capillaries (1 m length × 0.25 mm i.d.). The GC oven temperature was programmed from 35 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 maintained at a temperature of 250 °C. The sniffing port was supplied with humidified air at 30 mL/min. Two experienced panelists conducted AEDA, which is a semiquantitative GCO technique, to determine the intensity of aroma-active compounds in food extracts (*6*). 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 the flavor dilution (FD) factor (*6*).

Gas Chromatography−Mass Spectrometry (GC-MS). The system consisted of an HP5890 series II GC/HP 5972 mass selective detector (MSD, Hewlett-Packard Co.). Separations were performed on a fused silica capillary column (DB-FFAP, 30 m length × 0.25 mm i.d. × 0.25 μm d_f; J&W Scientific). Carrier gas was helium at a constant flow of 1 mL/min. Oven temperature was programmed from 35 to 225 °C at a rate of 4 °C/min with initial and final hold times of 5 and 30 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, 5 scans/s. Each extract (2 μL) was injected in the on-column mode. Duplicate analyses were performed on each sample.

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 comparison of the mass spectra of unknown compounds with those in the National Institute of Standards and Technology (NIST, 1992) mass spectral database or on RI values and odor properties of unknowns matched against those of authentic standards. Retention indices were calculated by using an *n*-alkane series (*7*).

Quantification of Selected Compounds. Reconstituted milk, after deodorization by high-vacuum distillation, or water was used as a matrix to prepare standard solutions. Calibration was accomplished by the addition of 0 (blank), 2, 5, 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 119.2 μg of **3**, 46.4 μg of **6**, 142.2 μg of **10**, 71.6 μg of **13**, 11.6 mg of **14**, 44.6 μg of **18**, 3.36 mg of **19**, 22.2 μg of **20**, 46 μg of **22**, 51 μg of **23**, 34.6 μg of **24**, 56.6 μg of **26**, 134.6 μg of **28**, 1.22 mg of **31**, 48.4 μg of **32**, 70.6 μg of **35**, 58.4 μg of **36**, 4.5 mg of **38**, 2.66 mg of **39**, 3.74 mg of **40**, 15.48 mg of **41**, 4.32 mg of **42**, 1.6 mg of **43**, 12.68 mg of **44**, 2.34 mg of **45**, 54.6 μg of **46**, 12.94 mg of **47**, 3.9 mg of **48**, 88 μg of **49**, 10.84 mg of **50**, 110.6 μg of **52**, 2.84 μg of **53**, 56 μg of **54**, and 66 μg of **56** per milliliter of methanol. For quantification of these compounds, a DB-FFAP column was used.

To identify and quantify methional by GC-MS, selected ion monitoring (SIM) mode was used. The selected ions for methional were *m*/*z* 104 and 76 and for 2-methyl-3-heptanone were *m*/*z* 85 and 57.

Sensory Evaluation and Statistical Analysis. Five expert dairy judges evaluated 20 reconstituted samples based on USDA grading for NDM. The six samples selected for instrumental analysis were scored as low quality by expert dairy judges (*8*). The procedure by Karagül-Yüceer et al. (*5*) was followed to prepare and evaluate the samples for descriptive sensory analysis. Powders were evaluated four times in a

Table 4. Flavor Attributes of Stored Nonfat Dry Milks[a]

attribute	sample I	II	III	IV	V	VI
cooked/sulfurous	2.3^{ab}	2.4^{ab}	2.5^{a}	2.3^{ab}	2.4^{ab}	2.1^{b}
caramelized/burnt sugar	0.1^{bc}	1^{a}	0^{c}	0.1^{bc}	0^{c}	0.3^{b}
sweet aromatic/cake mix	1.4^{ab}	0.8^{c}	0.95^{c}	1.8^{a}	1.1^{bc}	0.2^{d}
cereal	0.8^{bc}	1.4^{a}	0.8^{bc}	1.2^{ab}	0.6^{c}	0.2^{d}
animal/gelatin-like/wet dog	0.8^{b}	0.4^{bc}	1.3^{a}	0.6^{bc}	0.7^{bc}	0.3^{c}
brothy/potato-like	1.5^{bc}	2.1^{a}	1.9^{ab}	1.3^{c}	1.4^{c}	0.2^{d}
papery/cardboard	1.5^{a}	0.7^{b}	1.4^{a}	1.4^{a}	1^{b}	0.6^{b}
burnt/charcoal	0^{b}	0^{b}	0^{b}	0^{b}	0^{b}	0.5^{a}
fried fatty/painty	0	0	0	0	0	0
barny/animal-like	0^{b}	0.8^{a}	0.3^{ab}	0^{b}	1.5^{a}	0^{b}
vitamin/rubber	0^{b}	0^{b}	0^{b}	0^{b}	0^{b}	4.4^{a}
sweet taste	1.6^{a}	1.3^{b}	1.6^{a}	1.7^{a}	1.5^{ab}	0.6^{c}
salty	0^{b}	1.3^{a}	0^{b}	0^{b}	0^{b}	0^{b}
sour	0^{b}	1.9^{a}	0^{b}	0^{b}	0^{b}	0^{b}
bitter	0^{b}	0^{b}	0^{b}	0^{b}	0^{b}	0.5^{a}
astringent	1.1^{b}	1.3^{ab}	1.1^{b}	1.3^{ab}	1^{b}	1.7^{a}

[a] Means within a row without a common superscript differ ($p < 0.05$). Roman numbers represent the samples analyzed: I, 3 months old; II, 25 years old; III, 2 years old; IV, 1 year old; V, 3 months old, international source; VI, 3 years old.

randomized balanced block design. Differences among treatments were evaluated by analysis of variance (ANOVA) with means separation. Correlation analysis (PROC CORR) was conducted to determine the relationships between individual descriptive terms and concentrations of certain chemicals in NDM. All analyses were performed using SAS version 7 (*9*).

RESULTS AND DISCUSSION

Average odor intensities of each compound given by two sniffers are shown in Tables 2 and 3 for the six samples including both neutral/basic and acidic phases. The FD factors listed in these tables for each chemical compound provide a measure of the odor intensity of each aroma compound. Sensory evaluation results of each sample are presented in Table 4.

On the basis of the results of AEDA, several groups of aroma-active compounds contributed to the development of some undesirable flavors in NDM such as aldehydes, ketones, free fatty acids, lactones, and alcohols. These flavors can be transmitted from feed, packaging materials, or the environment or generated by chemical reactions including nonenzymatic browning and lipid and light oxidations.

Volatile compounds of NDM were also studied by Shiratsuchi and co-workers (*10*). They isolated volatiles by simultaneous steam distillation−extraction under reduced pressure using diethyl ether. Major compounds determined were hydrocarbons, aldehydes, ketones, alcohols, fatty acids, esters, furans, and phenolic compounds. These volatiles originated from the breakdown of the major components of milk, volatile chemicals or their secondary reactions, or transfer from the forage. They concluded from quantitation results that free fatty acids were the major volatiles in NDM. These findings agreed with our quantitation results.

Methional was identified as an off-flavor compound in NDM. Log_3 FD factors of methional in the samples analyzed varied between 4 and 8 in neutral/basic fractions of extracts (Table 2). The aroma was described as boiled potato-like. Sensory analysis also detected potato/brothy flavors in NDM. All samples exhibited this flavor by both instrumental and sensory analyses. The highest intensity of potato-like flavor by both GCO (Table 2) and sensory evaluation (Table 4) was observed in sample II. Concentration results (Table 5) agreed with these results as the highest concentration of methional was found in sample II. Methional is the first product of Strecker degradation of methionine (*11*, *12*). It can also be formed from methionine when milk is exposed to light (*13*). It has been reported as the key flavor compound of Cheddar cheese (*14*) and an off-flavor of wine (*15*). A meaty−brothy odor was identified in low-fat Cheddar cheese. The higher retronasal odor activity values (OAV) of homofuraneol, methional, and Furaneol were related to the meaty−brothy odor in low-fat Cheddar cheese (*14*). A cooked vegetable-like off-flavor in wine that had undergone spontaneous oxidation was attributed to methional (*15*). On the basis of statistical evaluation, methional was correlated with brothy/potato-like flavor ($r = 0.74$, $p < 0.1$).

Some thermally induced aroma-active compounds, including Furaneol, maltol, and sotolon, were also identified at high odor intensities in acidic fractions. The same compounds were also presented as key aroma-active compounds of low-, medium-, and high-heat-treated NDM (*5*); however, the odor intensities of these compounds were higher in stored samples. The GCO data showed that these furanones have caramel/burnt sugar-like or butterscotch-like odors. It is possible that they are the contributors of the caramel/burnt sugar-like and sweet aromatic flavors described by sensory analysis (Table 4). Schnermann and Schieberle (*16*) identified these furanones as key odorants of milk chocolate. Furaneol (*17*) and sotolon (*18*) were indicated as causing an off-flavor in stored citrus juices. Powder samples II and VI had higher concentrations of maltol and sotolon than other samples (Table 5). The reason might be that they were stored longer than other samples at ambient temperatures. Maillard reactions can predominate in dried foods (*19*).

Heat-generated aroma compounds of milk were investigated (*20*). The following volatiles were identified as heat-induced: methyl ketones, δ-lactones, benzaldehyde, furfural, phenylacetaldehyde, vanillin, 1-octen-3-ol, *n*-heptanol, 2-butoxyethanol, maltol, acetophenone, benzonitrile, benzothiazole, and 2,3-butanedione (diacetyl). The amount of diacetyl in raw milk was 5 ppb and was 38 ppb in the heated milk.

Phenylacetaldehyde and phenylacetic acid, which are Strecker degradation products of the amino acid phenylalanine (*21*), were associated with a rose-like aroma. 2-Phenylethanol was also identified as a rose-like odor in the neutal/basic fraction of samples. Floral aromas were not detected by sensory analysis because the sensory threshold might be too high.

Other thermally generated, aroma-active compounds were 2-acetyl-1-pyrroline, 2-acetyl-2-thiazoline, and 2-acetylthiazole. These odorants were identified as a popcorn-like aroma in neutral/basic fractions. The intensities of 2-acetyl-1-pyrroline were much higher in samples II and IV than others (Table 2). Sensory analysis indicated that these samples had higher intensities of cereal/grassy flavors. In other words, pyrrolines, thiazolines, and thiazoles may contribute to cereal flavors in NDM. Bassette and Keeney (*2*) isolated some carbonyl compounds responsible for the cereal-type flavor from instant and noninstant NDMs. The compounds identified from instant NDM were formaldehyde, acetaldehyde, acetone, butanone, methylpropanal, 3-methylbutanal, furfural, diacetyl, hexanal, and nonanal; however, they did not address the sensory evaluation of these samples in that study. We also identified 3-methylbutanal, diacetyl, and hexanal in samples II and III. On the basis of sensory analysis, these samples also had cereal/grassy flavor. In addition, the odor intensities of 2-acetyl-1-pyrroline and 2-acetyl-2- thiazoline were high.

Furfuryl alcohol and some sulfur-containing compounds such as benzothiazole, dimethyl trisulfide (DMTS), and ethyl disulfide were also identified. High intensities of furfuryl alcohol with a

Table 5. Mean Concentrations of Selected Aroma Compounds in Stored Nonfat Dry Milks

neutral/basic compound	RI on DB-FFAP column[a]	concn ± SD[b] (μg/100 g)					
		I	II	III	IV	V	VI
hexanal	<1100	5940 ± 27	1500 ± 450	5060 ± 1400	664 ± 374	159 ± 195	595 ± 842
ethyl disulfide	1192	217 ± 15	86 ± 53	294 ± 91	242 ± 65	193 ± 19	124 ± 176
dimethyl trisulfide	1352	nd	4 ± 1	nd	nd	nd	733 ± 1040
(*E*)-2-octenal	1410	50 ± 26	173 ± 244	68 ± 35	nd	nd	69 ± 97
methional	1443	56 ± 5	158 ± 43	110 ± 55	26 ± 2	37 ± 12	14 ± 20
phenylacetaldehyde	1627	266 ± 62	3510 ± 1820	100 ± 8	142 ± 30	127 ± 46	32 ± 45
furfuryl alcohol	1652	1450 ± 170	4340 ± 1560	79 ± 1	715 ± 218	1010 ± 342	42300 ± 59800
(*E*,*E*)-2,4-nonadienal	1683	50 ± 11	10 ± 14	44 ± 8	375 ± 257	5 ± 7	442 ± 625
2-acetyl-2-thiazoline	1736	0.5 ± 0.7	nd	nd	nd	3 ± 0.6	nd
(*E*,*E*)-2,4-decadienal	1749	33 ± 31	20 ± 7	14 ± 8	80 ± 19	13 ± 2	6 ± 9
β-ionone	1926	nd	6 ± 5	1 ± 1	3 ± 2	1 ± 0.1	67 ± 95
benzothiazole	1932	5 ± 7	177 ± 222	24 ± 1	26 ± 4	46 ± 11	22 ± 31
p-cresol	2069	271 ± 319	1030 ± 400	761 ± 201	40 ± 2	287 ± 103	1231 ± 1741
δ-decalactone	2173	374 ± 406	1231 ± 52	782 ± 876	1060 ± 500	1710 ± 530	93 ± 132
γ-dodecalactone	2353	55 ± 9	91 ± 8	925 ± 1070	1010 ± 990	171 ± 91	112 ± 158
δ-undecalactone	2402	60 ± 62	231 ± 90	244 ± 290	327 ± 226	287 ± 156	152 ± 215
o-aminoacetophenone	>2600	5 ± 4	35 ± 49	13 ± 10	7 ± 7	8 ± 4	14 ± 20

acidic compound	RI on DB-FFAP column[a]	concn ± SD[b] (mg/100 g)					
		I	II	III	IV	V	VI
acetic acid	1434	140 ± 9	179 ± 12	114 ± 19	78 ± 1	268 ± 89	80 ± 113
propionic acid	1520	8 ± 8	6 ± 0.8	7 ± 0.5	7 ± 0.3	5 ± 1	2 ± 2
isobutyric acid	1547	79 ± 3	28 ± 1	22 ± 15	9 ± 2	40 ± 9	36 ± 50
butanoic acid	1604	1080 ± 420	2380 ± 1330	1320 ± 35	905 ± 46	2410 ± 310	633 ± 896
2-/3-methylbutyric acid	1649	426 ± 118	137 ± 10	233 ± 22	31 ± 39	302 ± 41	20 ± 29
pentanoic acid	1719	5 ± 0.7	8 ± 0.7	4 ± 0.03	2 ± 0.2	4 ± 0.7	3 ± 4
hexanoic acid	1829	299 ± 106	504 ± 300	464 ± 7	362 ± 64	675 ± 41	211 ± 299
maltol	1949	8 ± 4	16 ± 5	0.4 ± 0.1	12 ± 16	0.2 ± 0.2	131 ± 186
Furaneol	2016	0.5 ± 0.2	0.6 ± 0.7	0.04 ± 0.03	1 ± 2	0.01 ± 0.005	0.4 ± 0.6
octanoic acid	2044	154 ± 29	233 ± 122	252 ± 0.2	183 ± 38	288 ± 49	141 ± 199
nonanoic acid	2149	6 ± 2	8 ± 0.2	10 ± 1	4 ± 0.2	5 ± 2	9 ± 12
sotolon	2181	nd	0.6 ± 0.01	nd	nd	nd	1 ± 1
decanoic acid	2261	147 ± 46	200 ± 95	286 ± 37	210 ± 69	229 ± 132	176 ± 248
dodecanoic acid	2471	0.2 ± 0.1	0.2 ± 0.01	0.7 ± 0.6	0.3 ± 0.1	0.1 ± 0.2	0.5 ± 0.7
phenylacetic acid	2540	8 ± 9	15 ± 4	3 ± 0.2	nd	27 ± 28	16 ± 22
vanillin	2551	0.2 ± 0.3	0.005 ± 0.001	0.07 ± 0.005	0.03 ± 0.009	0.01 ± 0.001	8 ± 11
3-phenylpropionic acid	>2600	0.2 ± 0.2	0.2 ± 0.02	0.09 ± 0.08	0.03 ± 0.03	0.03 ± 0.05	0.1 ± 0.1

[a] Retention indices (RI) calculated from mass spectrometry (MS) results. [b] Roman numbers represent the samples analyzed: I, 3 months old; II, 25 years old; III, 2 years old; IV, 1 year old; V, 3 months old, international source; VI, 3 years old. nd, not determined.

rubber-like note were identified in sample VI (Tables 2 and 5). Sensory analysis indicated that sample VI (Table 4) had an intense vitamin/rubber-like note. Furfuryl alcohol was also identified as a contributor of barrel-aged wine flavor (*22*). Furfuryl alcohol is the degradation product of furfural. The intensities of DMTS were higher in samples II and VI with a cabbage-like aroma note. DMTS was found to be an important contributor to milk chocolate flavor (*16*). It was speculated that the application of high temperatures during conching of the chocolate might generate this flavor. In the present study, furfuryl alcohol ($r = 0.99$, $p < 0.01$), *p*-cresol ($r = 0.93$, $p < 0.01$), β-ionone ($r = 0.99$, $p < 0.01$), and dimethyl trisulfide ($r = 0.99$, $p < 0.01$) were highly correlated with vitamin-like/rubber attributes. One or a mixture of these compounds might cause a vitamin/rubber-like sensory flavor in NDM.

o-Aminoacetophenone (*o*-AAP) was identified in all samples and described as a foxy note. It was reported that *o*-AAP was the key aroma compound of muscadine grape juice (*23*) and identified as the cause of a stale flavor in dairy products (*24*, *25*). *o*-AAP was also determined as the cause of aging off-flavor in wines (*26*). Dollmann and coworkers (*26*) analyzed 22 off-flavored wines with amounts of *o*-AAP ranging from 0.7 to 12.8 μg/L. It was stated that *o*-AAP is produced by degradation of L-tryptophan, which is naturally found in wine. Nonenzymatic browning may cause off-flavors, such as staleness, in milk powders. Benzothiazole and *o*-AAP are the major contributors of staleness (*24*). *o*-AAP was also addressed as the contributor of glue-like flavor in old casein (*27*). It was also identified as an off-flavor compound in micromilled and stored (12 months) milk powder (MMP) (*28*). The odor property of MMP was described as musty and wet popcorn by GCO. *o*-AAP was identified as one of the character impact odorants of NDM (*5*). The intensity of *o*-AAP was higher in stored samples. The intensity of *o*-AAP was highest in sample VI ($\log_3$ FD factor $= 10$) (Table 2). In addition, panelists described an animal/wet-dog-like off-flavor in all samples. There was no correlation between this attribute and *o*-AAP, but the mix effects of more than one chemical may generate it.

Both GCO and sensory evaluation data indicated that milk powders have animal-like, cowy, or fecal flavors. *p*-Cresol and skatole may be the contributors of this undesirable flavor in milk (Table 2). The intensities of these compounds with animal-like/fecal odor notes were much higher in older samples. Some compounds released from the forage by the cow's metabolism may induce the development of off-flavors in milk. For example, certain types of weeds (Crucifera), lucerne, or *Brassica* sp. may increase the concentration of indole, skatole, mercaptans, sulfides, nitriles, and thiocyanates (*29*). Loss of the alanine moiety from tyrosine and tryptophan causes the formation of phenol and indole, respectively. Their homologues, *p*-cresol and skatole, contribute to the flavor of soft cheeses (*30*). *p*-Cresol was found to be mainly responsible for a cowy–barny note in

British Farmhouse Cheddar cheese (*31*). Shiratsuchi and co-workers (*32*) demonstrated the sources of cowhouse-like off-flavor in skim milk powders. They indicated that β-ionone, benzothiazole, and tetradecanal were much higher than in normal powders. We also identified β-ionone with a hay-like aroma note in sample II and benzothiazole with rubber-like note in samples II and VI (Table 2). Fortification of skim milk or reduced-fat milk with vitamin A often causes hay-like off-flavors (*33*). β-Ionone and dihydroactinidiolide have a mild, typical hay-like odor and are the main oxidation products of vitamin A. The sensory panel detected that sample V had a barny/animal-like flavor (Table 4). We determined both benzothiazole and β-ionone in this sample by GCO (Table 2). *p*-Cresol, 3-methylindole (skatole), and unknown compounds (no. **30** and **33**) with cowy, fecal or animal-like odors might be the contributors of this aroma (Table 2). Statistical analysis indicated that benzothiazole ($r = 0.63$, $p = 0.18$), acetic acid ($r = 0.73$, $p < 0.1$), butyric acid ($r = 0.95$, $p < 0.01$), and hexanoic acid ($r = 0.86$, $p = 0.02$) were correlated with barny/animal-like attributes.

Large amounts of free fatty acids were identified in all samples (Table 3). Octanoic, nonanoic, decanoic, and dodecanoic acids were described as soapy/waxy/rubbery. Specifically, octanoic and decanoic acids had very high $\log_3$ FD factors in all samples (Table 3). Shiratsuchi and co-workers (*34*) also identified the same compounds as responsible for a sweet, fatty, and butter-like odor in skim milk powder. It was stated that soapy flavors were characteristics of decanoic and dodecanoic (lauric) acids produced by bacterial enzyme activities (*35*). Specifically $C_{10}-C_{12}$ caused a soapy flavor in cheese (*36*). Hydrolysis of plant acyglycerols and animal depot fats is the source of soapy-tasting fatty acids (*37*). Sensory evaluation results indicated that sample II was the only sample that exhibited sour and salty tastes (Table 4). The pH of the reconstituted sample was 6.4. Sour taste was correlated with pentanoic acid ($r = 0.79$, $p < 0.1$). In addition, the highest amount of pentanoic acid was determined in sample II (Table 5).

Other free fatty acids, which have cheesy notes, are butanoic and hexanoic acids. These acids were reported as the major free fatty acids of skim milk powders (*1*). Propionic, isobutyric, 2-/3-methylbutyric, and pentanoic acids with sweaty or Swiss cheese-like aroma notes were positively identified in acidic fractions of samples (Table 3).

Sensory evaluation data indicated that sweet odor and taste also contributed to the flavor of NDM. Sniffing results showed that δ-decalactone and γ-dodecalactone gave sweet odor properties to the milk powder. Sweet and milky odor properties were characterized by lactones including γ-undecalactone, γ-dodecalactone, δ-decalactone, and δ-undecalactone (*34*). Vanillin was also identified at high odor intensity. It was described as a sweet aromatic/vanilla cake mix-like aroma. Vanillin may also contribute to sweet aroma in milk powders.

Light exposure may develop off-flavors in food products. Grosch and co-workers (*38*) investigated the effect of light exposure of butter oil on flavor changes. After light exposure, samples tasted green, strawy, and fatty. The following compounds contributed to the off-flavor: 3-methylnonane-2,4-dione, *trans*-4,5-epoxy-(*E*)-decanal, (*E*)-2-nonenal, and (*E*,*E*)-2,4-decadienal. We also detected (*E*)-2-nonenal (hay-like) and (*E*,*E*)-2,4-decadienal (fried fatty) at high odor intensities. Cadwallader and Howard (*39*) identified the following compounds as contributors of light-activated flavors in milk at high intensity: pentanal (sour/cut-grass), 1-hexen-3-one (plastic/water-bottle), hexanal (green/cut-grass), and 1-octen-3-one (mushroom). The mushroom note in NDM was contributed by 1-octen-3-one. The intensity of odor was higher in sample III (Table 2) than other samples. Mushroom flavors can develop in dairy foods under certain oxidation conditions. Stark and Forss (*40*) identified this compound in skim milk and butterfat as responsible for mushroom flavor.

The contributors of oxidized flavor in dairy foods are not well-known. 1-Octen-3-one was reported to be a responsible for the metallic off-flavor in butterfat (*41*) and milk (*42*). Ho and Chen (*43*) described the flavor as cardboard or oxidized when it was added to skim milk; however, some other researchers believed that the combined effect of some carbonyl compounds possibly resulted in oxidized flavor. Hammond and Hill (*44*) indicated that the reaction between 1-octen-3-one and an aldehyde such as 2-heptanal, octanal, or 2,4-heptadienal caused the oxidized flavor in milk. The other off-flavor that we determined was a cardboard- or paper-like flavor. Grosch and co-workers (*38*) analyzed the off-flavor compounds of butter oil. They demonstrated that a mixture of (*E*)-2-nonenal and (*Z*)-2-nonenal contributed to development of the cardboard-like off-flavor in butter oil after a long storage period at room temperature. The sniffing data in this study agreed with these results. Both compounds were identified as exhibiting a hay-like flavor in neutral/basic fractions.

Hexanal is known to be a prominent secondary oxidation product of linoleic acid (*45*). A headspace gas chromatographic method was applied to monitor oxidative deterioration of whole milk powder (WMP) under different storage conditions. Freshly produced WMP, analyzed within 24 h, contained less hexanal than WMPs stored at 30 °C in dark and at room temperature in normal daylight. Also, concentrations of both pentanal and hexanal were related to the development of a stale off-flavor in stored UHT milk (*46*). Lipid oxidation in the cream powder was followed by measuring aldehyde formation and oxygen consumption in the headspace (*47*−*49*). Hexanal content was directly related to the initial oxygen content at certain levels (*47*). Hexanal development was seen in the samples after 7 weeks of storage. The same researchers (*48*) also stated that exposure to light affected the rate of hexanal production and oxygen consumption in cream powder. After 5 weeks of storage, the sample stored in light and air showed a higher amount of hexanal than the same sample stored in darkness. The effect of oxygen concentration on the flavor and chemical stability of cream powder was investigated (*49*). Most of the samples stored with reduced oxygen content were significantly different from the air-packed samples after 25 and 45 weeks of storage in terms of hexanal concentration and sensory analysis. Correlation factors between the mean values of “cardboard” or “chemical” odor or flavor and the means of hexanal concentration ranged from 0.69 to 0.8. In the present study, the correlation between hexanal and the cardboard-like attribute was 0.64 ($p = 0.17$).

Sensory evaluation demonstrated that all milk powders had an astringent taste. Astringency is a common problem in high-heat-treated or UHT-sterilized milk (*50*) and NDM (*51*). Josephson and co-workers (*52*) stated that astringency in high-heat-treated milk was attributed to the interaction product involving whey proteins, calcium phosphate, and caseins. It was also linked to the production of γ-caseins from β-casein by cleavage of the peptide bound between residues 28 and 29, 105 and 106, and 107 and 108 (*53*).

The six NDM samples differed in their flavor profiles by sensory evaluation and instrumental analysis. The results presented here showed that the duration and condition of storage affects the flavor of NDM. The major differences in the flavor profiles of the samples are mainly caused by concentration/intensity differences of these flavors. For example, sample I had the highest intensity of papery/cardboardy flavor by sensory analysis (Table 4). In addition, this sample had the highest hexanal concentration (Table 5). The intensities of caramelized/burnt sugar, cereal, brothy/potato-like flavors, salty, and sour tastes in NDM II were higher than in other samples (Table 4). Characteristic flavor attributes for samples V and VI were barny/animal-like and vitamin/rubber-like, respectively (Table 4).

In conclusion, on the basis of comparative GCO and quantification results, a variety of aldehydes, ketones, alcohols, and free fatty acids were found to be responsible for the development of undesirable flavors in NDM. Mainly, Furaneol, maltol, and sotolon were the sources of burnt-sugar-like or curry-like flavors. Methional and *o*-aminoacetophenone had high odor intensities in NDM. Other major compounds were free fatty acids including butanoic and hexanoic acids with cheesey notes and octanoic, nonanoic, decanoic, and dodecanoic acids with a waxy note. Some descriptive terms were correlated with certain chemicals. However, the joint effects of several chemicals may generate other attributes.

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