DAIRY FOODS

Formation of Volatile Free Fatty Acids During Ripening of Cheddar-like Hard Goat Cheese

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ABSTRACT

Concentrations of FFA in Cheddar-like hard goat cheeses were all above the threshold concentrations, except for pentanoic, heptanoic, and 10-undecenoic acids. The relative abundance of n-chain FFA in Cheddar-like hard goat cheeses, from greatest to least, were n-C_{10}, n-C_{12}, n-C_8, n-C_6, n-C_4, n-C_9, and n-C_{11}. Similarly, the relative abundance of branched-chain fatty acids in Cheddar-like hard goat cheeses, from greatest to least, was 4-methyloctanoic, methyldecanoic, 3-methylbutanoic, and 4-ethyloctanoic acids. Branched-chain fatty acids such as 4-ethyloctanoic and 4-methyloctanoic acids have intense aromas, and even minute quantities can affect the flavor of dairy products.

Ripening time significantly affected the concentrations of FFA; concentrations increased during the initial 12 wk of aging and remained relatively constant for the rest of the 24-wk ripening period. Therefore, the intensity and sharpness of flavor that originated from or was enhanced by the presence of these FFA did not change greatly after 12 wk of aging.

The percentage of NaCl or the ratios of salt to moisture, within the range used in hard goat cheeses, did not affect the concentrations of FFA or, apparently, lipolysis in this study.
(**Key words**: goat cheese, free fatty acids, salt to moisture ratio, ripening time)

Abbreviation key: **BCFA** = branched-chain FA, **FA** = fatty acids, **MSDE** = microsimultaneous distillation extraction, **S/M** = salt in moisture phase.

INTRODUCTION

Goat milk and goat milk products have a characteristic odor and flavor that have been the subject of several investigations. The effect of short n-chain FFA on the flavor of goat milk has been evaluated (4, 8). The general consensus among researchers is that mixtures of alkanoic acids with carbon chains from C_2 to C_{10} seem to have a major effect on the flavor of cheeses (7, 19, 20, 23, 29, 30). Although n-chain fatty acids (**FA**) occur in abundance, certain minor volatile branched-chain FA (**BCFA**) exhibited characteristic flavors at very low concentrations (11, 12, 13, 27, 28). Ha and Lindsay (16, 17) determined that BCFA, such as 4-ethyloctanoic and 4-methyloctanoic acids, contributed goat-like and mutton-like flavor notes to cheeses made from goat and sheep milk, respectively. 3-Methylbutanoic acid provides a sweat-like, fruity flavor note (1, 16).

Flavor is a major attribute that influences the selection and consumption of cheeses. With the increased consumption and popularity of cheeses made from goat milk, investigation and resolution of some of these problems have become economically more important.

The objectives of this investigation were 1) to quantify the volatile n-chain and BCFA with 12 or fewer carbon atoms in 1-d-old cheese and at 6-wk intervals during an aging period of 24 wk, 2) and to examine the relationship between varying percentages of salt in moisture (**S/M**) and the quantity of FFA in cheese.

MATERIALS AND METHODS

Reagents

The purity of all chemical reagents and FA standards that were used have been previously described (5).

Samples

Raw milk from French-Alpine goats at the International Dairy Goat Research Center at Prairie View A&M University was processed to Cheddar-like hard goat cheese according to the processing techniques described by Attaie et al. (6). The percentage of NaCl and moisture, S/M, and pH of the cheeses in this study were analyzed previously by Attaie et al. (6). Duplicate 5-g samples of each cheese were taken for analyses of short n-chain and BCFA on d 1 and at

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6-wk intervals for 24 wk. These cheeses were vacuum-packed (Multivac, Koch Supplies, Kansas City, MO) and stored at 4 to 5°C for sampling and aging.

Extraction of FFA

Volatile BCFA and n-chain FFA were extracted and quantified according to the method of Ha and Lindsay (15) with the following modifications. Approximately 5 g of finely ground Cheddar-like hard goat cheese, 1 ml of double-distilled diethyl ether containing 10 μg of 2-ethylnonanoic acid (internal standard), 15 ml of double-distilled diethyl ether, and 0.5 ml of 5.5*N* H_2SO_4 were mixed into a screw-cap test tube (150 mm × 18 mm i.d). The mixture was blended using a biohomogenizer at high speed for 25 s. The mixture was cooled by immersion in crushed ice for 2 min. The cooled mixture was blended two more times for 25 s each at high speed. The biohomogenizer probe was rinsed twice with 10 ml of distilled hexane, and the rinse was added to the mixture. The mixture was mixed well and centrifuged in a Babcock centrifuge (Garver Manufacturing Co., Union City, IN) at 163 × *g* for 5 min; the precipitate was then discarded. The FFA extraction was carried out according to the referenced technique.

The sample was subjected to microsimultaneous distillation extraction (**MSDE**; configuration I; Chrompack, Inc., Raritan, NJ) for recovery of short-chain volatile FFA ($<C_{12}$). The joints of the MSDE apparatus were sealed with a dried solution of bondex clay (plaster of Paris). A mixture of crushed ice and water was used to maintain the water temperature at 2°C at the cold finger of the apparatus. The solvent flask of the unit was submerged in a beaker of water maintained at 65°C while the sample flask was heated to approximately 95 to 100°C by heating the MSDE mantle. The sample was distilled and extracted for 20 min.

Butyl esters of FFA were prepared by the addition of 0.5 ml of BF_3 in butanol (14%, wt/vol; Sigma Chemical Co., St. Louis, MO) and heating the screw-capped test tube in a boiling water bath for 10 min by the procedure of Ha and Lindsay (15). The 20 μl of concentrated extract of FFA were transferred to a small capillary tube, sealed, and stored at –50°C until gas chromatographic analysis.

Concentrations of 4-ethyloctanoic acid, compared with other FFA, were very low and could not be quantified by the same analyses. Therefore, separate analyses with the following modifications were performed: Two micrograms of 2-ethylnonanoic acid were employed for quantitative determination of this FFA in Cheddar-like hard goat cheese. Approximately 10 g of each sample were ground finely and accurately weighed. The rest of the extraction procedure was the same except that the final FFA extract was concentrated to approximately 3 μl and sealed in a small capillary tube until gas chromatographic analysis.

Gas Chromatographic Analysis

The FA esters were separated using a bonded polyethylene glycol fused silica capillary column (Supelcowax-10; 60 m × 0.32 mm i.d., 0.25-μm coating thickness; Supelco Inc., Bellefonte, PA) and quantified as described (5). Both the integrator attenuation and threshold were set at 2.

Gas chromatography-mass spectrometry of volatile FFA butyl esters was performed with a chromatography system (model 5988A; Hewlett-Packard, Avondale, PA) as described (5). The FFA were tentatively identified from comparison of coelution time with known FFA by gas chromatography and confirmed by mass spectral fragmentation patterns.

Statistical Analysis

The statistical design was a split-plot, 3 × 3 × 5 factorial, and data were analyzed by analysis of variance using the general linear models procedure of SAS (22). The following model was used:

$$Y = \mu + D_i + S_j + \delta_{ij} + T_k + (ST)_{jk} + \epsilon_{ijk}$$

where

Y = mean value of each FFA (the dependent variable),
μ = population mean,
D_i = days of cheese making (i = A, B, and C),
S_j = S/M in cheeses (j = 1, 2, and 3, where 1 = 4.41%, 2 = 3.73%, and 3 = 2.70%),
δ_{ij} = whole plot error, measured by interaction of D × S,
T_k = time the samples were taken for analyses (k = 1, 6, 12, 18, and 24 wk),
ST = interaction of salt and time, and
ϵ = split-plot error term (the random variable) assumed to be normally distributed with mean equal to zero and variance σ^2.

The least significant difference test on least squares means was used to determine significant differences between the treatment means at each sampling time (22). The three cheese replicates were made on three different days. The split plots that had mean S/M of 2.7, 3.7, and 4.4 constituted the three treatments. There were five sampling times during aging.

RESULTS AND DISCUSSION

Response factors for FFA were determined using a mixture of authentic compounds and 2-ethylnonanoic acid as the internal standard (10 μg of each FA in 1 ml of diethyl ether). The mixture was butylated and analyzed; the response factor for each FA was calculated as previously described (5). A representative chromatogram with corresponding peak numbers for the FFA of the cheese is shown in Figure 1.

n-Chain FFA

The mean FFA concentrations for butanoic acid, immediately after cheese manufacture and at 6-wk intervals during ripening, are shown in Table 1. Concentrations of butanoic acid increased ($P < 0.05$) during ripening of cheese. Butanoic acid, because it is soluble in water, might have been partially lost in the separation chamber between water and ether phases during MSDE. Hence, these data might reflect slightly lower amounts of butanoic acid than were actually present in the samples. Our results, however, agreed with butanoic acid values reported by Ha and Lindsay (16), who used the same method for analyzing semi-hard cheese made from goat milk.

The concentration of butanoic acid increased during the first 12 wk ($P < 0.05$) of aging and then remained constant. This lack of change after 12 wk could be caused by the lack of availability of substrate for conversion to FFA by lipolysis or by diminished enzymatic activity from prolonged storage and microenvironmental changes in cheese. The reported aroma threshold value for this FA is 1.11 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1), and the flavor threshold is 6.2 ppm in a solution of ethanol and water (24). However, the flavor threshold has been reported as 1.9 and 6.1 ppm in citrate-phosphate buffer at pH 4.5 and 6.0, respectively (10). The FFA concentrations in our study ranged from 19.7 to 41.8 ppm, which were considerably higher than the flavor thresholds. Therefore, butanoic acid is expected to influence the overall aroma and flavor of these cheeses.

Similarly, the concentrations of hexanoic, heptanoic, octanoic, 4-methyloctanoic, 4-ethyloctanoic, nonanoic, decanoic, a methyldecanoic, a second methyldecanoic, 9-decenoic, undecanoic, and dodecanoic acids (Tables 1, 2, and 3) increased and were significantly different ($P < 0.05$) among ripening times. The concentrations of nearly all of these FFA remained relatively unchanged from 12 to 24 wk

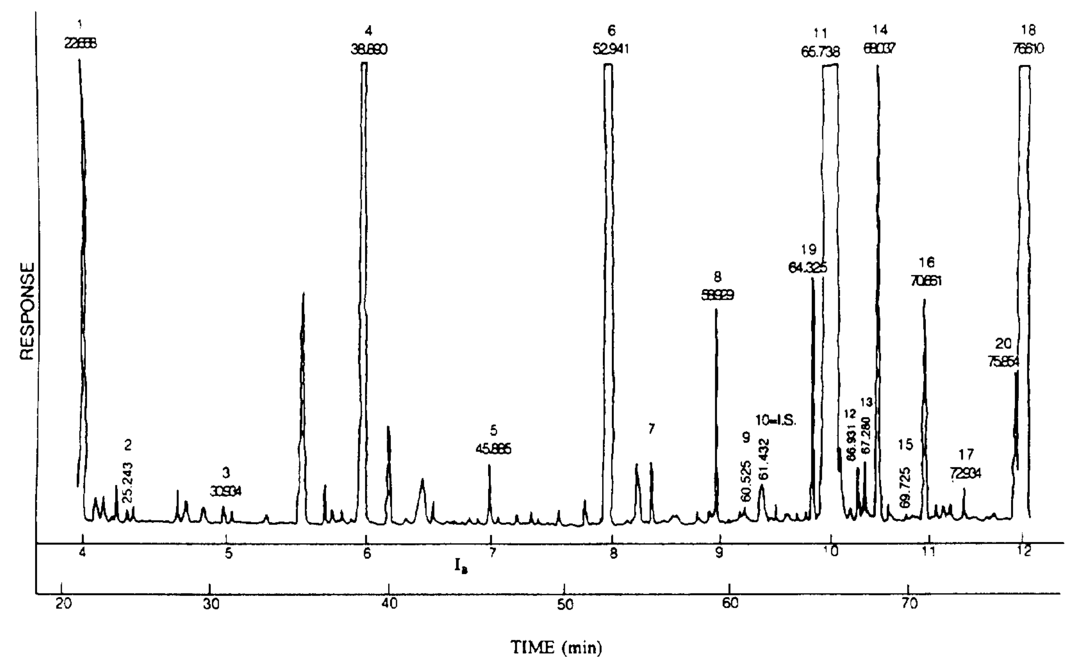

Figure 1. Gas chromatogram of butyl esters of volatile FFA isolated from Cheddar-like hard goat cheese. I.S. = Internal standard. I_B = index of butyl esters. Peaks: 1 = butyl butanoate, 2 = butyl 3-methyl butanoate, 3 = butyl pentanoate, 4 = butyl hexanoate, 5 = butyl heptanoate, 6 = butyl octanoate, 7 = butyl 4-methyloctanoate, 8 = butyl nonanoate, 9= butyl 4-ethyloctanoate, 10 = butyl 2-ethylnonanoate, 11 = butyl decanoate, 12 = butyl methyldecanoate, 13 = a butyl methyldecanoate, 14 = butyl 9-decenoate, 15 = butyl didecenoate, 16 = butyl undecanoate, 17 = butyl 10-undecenoate, 18 = butyl dodecanoate, 19 = 2-tridecanone, and 20 = 2-pentadecanone.

TABLE 1. Concentrations[1] of n-chain FFA with even-numbered carbons in Cheddar-like hard goat cheese.

FFA[2]	Ripening period					SEM[3]
	0 wk	6 wk	12 wk	18 wk	24 wk	
	(μg/g of cheese)					
C_4	19.7[b]	30.4[ab]	41.8[a]	34.9[a]	34.8[a]	4.0
C_6	38.6[b]	60.5[a]	80.4[a]	70.1[a]	81.0[a]	6.7
C_8	75.6[b]	106.9[ab]	135.7[a]	128.7[a]	127.5[a]	10.3
C_{10}	349.8[b]	432.7[b]	593.8[a]	528.6[a]	539.3[a]	31.9
C_{12}	180.1[c]	241.3[b]	299.3[a]	277.6[ab]	297.3[a]	14.7

[a,b,c]Means in rows without a common superscript differ ($P < 0.05$).

[1]Least squares means.

[2]C_4 = Butanoic acid, C_6 = hexanoic acid, C_8 = octanoic acid, C_{10} = decanoic acid, and C_{12} = dodecanoic acid.

[3]Degrees of freedom = 12.

of aging, indicating that lipolytic activity occurred mainly during the initial 12 wk.

Concentrations of hexanoic acid (Table 1) increased between 1 d and 6 wk of aging ($P < 0.05$). The flavor threshold for this FFA was reported as 8.6 ppm in citrate-phosphate buffer at pH 4.5 (9) and 15 ppm in a dilute solution of ethanol and water (24). The aroma threshold for this compound is 9.2 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1). The concentrations of hexanoic acid ranged from 39 to 81 ppm, which were considerably higher than the thresholds for flavor and aroma indicated for hexanoic acid; hence, hexanoic acid is likely to contribute to the overall flavor of hard goat cheeses.

Concentrations of octanoic acid (Table 1) increased only from d 1 until 12 wk of aging ($P < 0.05$). Octanoic acid, although once considered to be the main goaty compound in dairy products (3, 11, 25), is now recognized as a partial contributor and exhibits a waxy, heavy goaty aroma at concentrations of about 50 ppm. However, octanoic acid lacks the highly characteristic goatiness found in goat milk cheese (16). The reported flavor thresholds of octanoic acid were 5.83 ppm in dilute solution of ethanol and water (24) and 8.7 ppm in citrate-phosphate buffer at pH 4.5 (9). The aroma threshold for octanoic acid was 19 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1). In our study, octanoic acid concentrations of all cheeses ranged from 75.6 ppm for 1-d-old cheeses to 135.7 ppm for 24-wk-old cheeses, which exceeded the reported flavor thresholds for this compound in cheese medium. Thus, octanoic acid is likely to contribute to the flavor of hard goat cheeses.

The concentration of decanoic acid (Table 1) increased from d 1 until 12 wk of aging. The flavor thresholds reported for this FA were 2.2 and 14.8 ppm

TABLE 2. Concentrations[1] of branched-chain FFA in Cheddar-like hard goat cheese.

FFA[2]	Ripening period					SEM[3]
	0 wk	6 wk	12 wk	18 wk	24 wk	
	(μg/g of cheese)					
$3MC_4$	0.44	0.43	0.50	0.48	0.48	0.08
$4MC_8$	0.96[c]	1.42[b]	1.99[a]	1.96[a]	1.81[a]	0.14
$4EC_8$[4]	37.14[b]	ND[5]	ND	ND	83.05[a]	6.48
A_1MC_{10}	0.81[c]	1.07[b]	1.47[a]	1.38[a]	1.30[a]	0.08
A_2MC_{10}	1.06[c]	1.32[b]	1.60[a]	1.52[ab]	1.39[ab]	0.08

[a,b,c]Means in rows without a common superscript differ ($P < 0.05$).

[1]Least squares means.

[2]$3MC_4$ = 3-Methylbutanoic acid, $4MC_8$ = 4-methyloctanoic acid, $4EC_8$ = 4-ethyloctanoic acid, A_1MC_{10} = a methyldecanoic acid, and A_2MC_{10} = a second methyldecanoic acid.

[3]Degrees of freedom = 12.

[4]Parts per billion.

[5]Not determined.

TABLE 3. Concentrations[1] of odd-numbered carbons and unsaturated FFA in Cheddar-like hard goat cheese.

FFA[2]	Ripening period 0 wk	6 wk	12 wk	18 wk	24 wk	SEM[3]
	(μg/g of cheese)					
C_5	0.46	0.60	0.67	0.62	0.65	0.06
C_7	1.31[b]	1.81[b]	2.35[a]	2.06[a]	2.17[a]	0.18
C_9	12.35[c]	13.91[bc]	18.43[a]	17.31[a]	16.66[ab]	1.28
$9C_{10}$	8.24[b]	8.43[b]	10.49[a]	11.31[a]	11.07[a]	0.70
DC_{10}	0.26	0.27	0.34	0.34	0.35	0.08
C_{11}	6.18[c]	7.77[bc]	10.38[a]	9.36[ab]	9.84[ab]	0.77
$10C_{11}$	0.42	0.44	0.41	0.33	0.39	0.02

[a,b,c]Means in rows without a common superscript differ ($P < 0.05$).

[1]Least squares means.

[2]C_5 = Pentanoic acid, C_7 = heptanoic acid, C_9 = nonanoic acid, $9C_{10}$ = 9-decenoic acid, DC_{10} = didecenoic acid, C_{11} = undecanoic acid, and $10C_{11}$ = 10-undecenoic acid.

[3]Degrees of freedom = 12.

in citrate-phosphate buffer solutions at pH 4.5 and 6.0, respectively (9). The aroma threshold for this compound has been reported as 2.19 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1). Woo et al. (29) and Woo and Lindsay (30) reported that higher concentrations of decanoic acid in cheese caused soapy flavor. The FFA concentrations in the cheese ranged from 350 to 594 ppm, which were much higher than the threshold values reported for this compound. Decanoic acid undoubtedly influences the flavor of hard goat cheeses.

The concentrations of dodecanoic acid (Table 1) increased up to 12 wk of aging ($P < 0.05$) and ranged from 180 to 299 ppm. Higher concentrations of this FFA in cheeses have been reported (2, 29, 30) to cause soapy flavor. These concentrations may be sufficient to affect the overall flavor of hard goat cheeses.

Branched-Chain FFA

The concentrations of 3-methylbutanoic acid (Table 2) did not change during ripening ($P > 0.05$). This FFA was not found in goat milk fat (unpublished data). Apparently, 3-methylbutanoic acid may have principally originated from bacterial metabolism during cheesemaking, which is in agreement with observations of Ha and Lindsay (15, 16). Isovaleric acid or 3-methylbutanoic could be produced by leucine degradation (14, 21). Biede et al. (10) showed that isovaleric acid was produced by *Propionibacterium shermanii* in Swiss cheese. Although the flavor threshold for 3-methylbutanoic acid has not been indicated, Ha and Lindsay (16, 17) claimed that, at higher concentrations, this BCFA contributed sharp, sweat-like, sweet, and fruity flavors to cheeses. The aroma threshold for 3-methylbutanoic acid was reported as 0.13 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1) and 0.07 ppm in dilute citric acid solution at pH 2.0 (12). Concentrations of 3-methylbutanoic acid in our experiment ranged from 0.43 to 0.50 ppm, which were considerably higher than the aroma threshold values indicated for this compound. Therefore, this BCFA is likely to influence the overall aroma and flavor of these cheeses.

Concentrations of 4-methyloctanoic acid increased ($P < 0.05$) between d 1 and 12 wk of aging (Table 2). 4-Methyloctanoic acid has been reported (12, 13, 17) to be a flavorful FA that exhibits a goaty-muttony aroma and has a threshold value of 0.6 ppm in cheeses. Wong et al. (27, 28) demonstrated that the flavor of 4-methyloctanoic acid was evident at concentrations of 0.5 ppm or higher in cooked meats. Goat meat samples contained the highest concentration of this FA, which was responsible for a common flavor note in cooked mutton and goat meats. The goat milk cheeses had concentrations of 4-methyloctanoic acid ranging from 0.96 to 1.99 ppm, which were higher than the threshold of 0.6 ppm. The latter value is comparable to concentrations of this compound found in Roquefort cheeses that had undergone extensive lipolysis (16). According to Ha and Lindsay (16), when 4-methyloctanoic acid was evaluated at concentrations below 100 ppb, it exhibited a mutton-like aroma; however, 4-methyloctanoic acid blended easily with the goaty aroma of 4-ethyloctanoic acid to produce distinctive goatiness.

The aroma threshold for 4-ethyloctanoic acid, a potent goaty compound, has been reported as 1.8 ppb

(11) and 6.0 ppb (12) in dilute citric acid solution at pH 2.0. In our experiment, the concentration of this compound increased during ripening from 37.14 ppb for 1-d-old cheeses to 83.05 ppb for 24-wk-old cheeses (Table 2). Because low concentrations of this FFA existed in Cheddar-like hard goat cheeses, only the concentrations at the extremes of the ripening period were determined.

The concentrations of 4-ethyloctanoic acid found in cheeses were higher than the threshold limits. This compound likely contributed a characteristic goaty flavor to the Cheddar-like hard goat cheeses. Ha and Lindsay (16, 17) systematically assessed aromas of individual FA and found that 4-ethyloctanoic acid was the main compound responsible for characterizing goaty-type aroma in goat milk cheeses. Sugiyama et al. (26) reported that, among the odoriferous substances from secretions of sebaceous glands of the mature male goat, 4-ethyloctanoic acid had a strong, goaty odor at very low concentrations.

The concentrations of a methyldecanoic acid (Table 2) increased up to 12 wk of aging ($P < 0.05$) and ranged from 0.81 to 1.47 ppm in all cheeses. The aroma and flavor thresholds for this compound have not been reported in the literature. Therefore, it is not clear whether this compound contributes to the overall aroma and flavor of the cheeses. Results were nearly the same for a second methyldecanoic acid (Table 2); hence, the same conclusions apply to both FA.

Odd-Numbered Carbon and Unsaturated FFA

Similarly, the concentrations for pentanoic, didecenoic, and 10-undecenoic acids in Cheddar-like hard goat cheeses were not different ($P < 0.05$) during aging (Table 3). Relatively minute quantities of pentanoic acid exist in fresh goat milk as well as in goat cheeses. The aroma threshold for pentanoic acid was reported to be 1.37 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1). Brennand et al. (12) indicated an aroma threshold of 1.1 and 6.5 ppm in dilute citric acid solutions at pH 2.0 and 5.2, respectively. The description of the aroma for this FFA at 5 ppm was nutty and cheese-like. The concentrations of pentanoic acid ranged from 0.46 to 0.67 ppm during ripening. These concentrations were lower than the aroma thresholds; hence, pentanoic acid probably did not have a role in the flavor of these cheeses.

Concentrations of heptanoic acid differed between 6 and 12 wk ($P < 0.05$) but not before or after (Table 3). The aroma threshold for this FFA is 10.4 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1) and 0.28 ppm in dilute citric acid solution at pH 2.0 (12). The aroma of this FFA at 1 ppm was described as soapy, fatty, and acid-like. The concentrations of heptanoic acid in our cheeses ranged from 1.31 to 2.35 ppm. Because the flavor threshold of this compound is not known, whether heptanoic acid contributes to the flavor of the cheeses is also unknown.

The concentrations of nonanoic acid (Table 3) differed between 6 and 12 wk ($P < 0.05$) but not before or after. Aroma threshold values reported for this compound were 8.8 ppm in potassium-hydrogen-phthalate buffer at pH 4.8 (1) and 2.4 ppm in dilute citric acid solution at pH 2.0 (12). The aroma of this FA at 10 ppm has been described as fatty and soapy. The concentration of nonanoic acid in the cheeses ranged between 12.4 and 18.4 ppm. Although the flavor threshold for this FA is not clear, the concentrations in the experimental cheeses were large enough to have possibly contributed to the overall flavor of the hard goat cheeses.

The concentrations of 9-decenoic acid (Table 3) increased between 6 and 12 wk of aging but not before or after; the range was 8.24 to 11.31 ppm in all cheeses. The aroma of 9-decenoic acid at 5 ppm was described as sweet and fatty. The aroma threshold for this FA was 4.3 ppm in dilute citric acid solution at pH 2.0 (12). This concentration of 9-decenoic acid would be sufficient to affect the flavor of this type of cheese. However, this FFA might have been formed during sample preparation at MSDE, which is performed under acidic conditions at the boiling point of water, for 20 min. The longer chain unsaturated FA, such as oleic or linoleic acid, could split between C_{10} and C_{11} adjacent to the double bond and give rise to this uncommon FA. If this process actually occurs as described, 9-decenoic acid would have no influence on the flavor of the cheese.

The aroma or flavor thresholds for didecenoic acid have not been reported. Didecenoic acid might have been formed because of heat during the MSDE step of sample preparation from longer chain unsaturated FA containing two double bonds, such as 6, 9-octadecadienoic acid or eicosatrienoic acid. If eicosatrienoic acid splits between C_{10} and C_{11}, then a molecule would result with 10 carbon atoms and two double bonds between carbons number 5 and 6 and between 8 and 9. If didecenoic acid is formed by such a mechanism during sample preparation, then didecenoic acid does not exist in cheese and has no bearing on overall flavor.

The concentrations of undecanoic acid (Table 3) in cheeses increased during the first 12 wk. The aroma of undecanoic acid at 5 ppm was described as soapy and waxy. The aroma threshold reported for this compound is 0.1 ppm in dilute citric acid solution at pH 2.0 (12). The concentrations of undecanoic acid in the cheeses ranged from 6.2 to 10.4 ppm, were considerably larger than the aroma threshold, and might contribute to the soapy and waxy flavor of hard goat cheeses.

The mean concentrations of 10-undecenoic acid for 1-d-old and 24-wk-old cheeses were 0.42 and 0.39 ppm, respectively (Table 3). The description of the aroma of 10-undecenoic acid at 5 ppm is soapy and sweet. The aroma threshold of this FFA was reported as 2.3 ppm in dilute citric acid solution at pH 2.0 (12). These concentrations of 10-undecenoic acid in the cheeses were significantly lower than the threshold and, hence, probably not important to the flavor of hard goat cheeses. This FFA was also speculated to have been formed during the MSDE step of sample preparation. The longer chain unsaturated FA, such as linoleic acid, can split to give rise to this FFA. Carbon number 11 between the two double bonds of this unsaturated FA is most reactive, and the split was likely to have occurred there.

Carboxylic acids are weak acids that only partially ionize in aqueous solutions. Although the free, nonionized acid is volatile, the ionized salt is nonvolatile and odorless. As the pH of a solution is lowered, the threshold concentrations for FFA decrease until all the molecules are converted to the protonated form (9). Hence, the pH of the food or medium is critical and affects the concentration of FFA molecules that are volatile and odoriferous. Because most of the aroma and flavor thresholds for carboxylic acids reported in the literature were performed in buffer solutions, it is not clear how these acids affect the overall flavor of a nonaqueous food system. In a complex food matrix, such as that of cheese, which involves proteins, fats, minerals, and residual carbohydrates, the flavor effect of carboxylic acids from interactions with other substances is not known and warrants further research.

S/M

Statistical analyses showed that S/M generally had no influence on lipolysis, nor was the interaction of S/M and aging significant ($P > 0.05$). The exception was the concentration of methyldecanoic acid, which was higher at higher S/M ($P < 0.05$).

CONCLUSIONS

The concentrations of all FFA except pentanoic, heptanoic, and 10-undecenoic acid found in Cheddar-like hard goat cheeses were above the threshold limits of those FFA for which they are known. The relative abundance of n-chain FFA in Cheddar-like hard goat cheeses was, from greatest to least, n-C_{10}, n-C_{12}, n-C_8, n-C_6, and n-C_4, which is in proportion to the concentration of FA in lacteal secretions from goats (5, 16, 18). The concentrations of n-chain FFA with odd-numbered carbons also increased during the initial 12 wk of the ripening period, but only nonanoic and undecanoic acids were present at concentrations higher than threshold and might have contributed to the flavor of the cheeses.

Similarly, the concentrations of all BCFA increased during the first part of the ripening period and were considerably larger than the known limits of aroma or flavor thresholds. Branched-chain fatty acids, such as 4-ethyloctanoic, 4-methyloctanoic, and 3-methylbutanoic acids, have low threshold concentrations. These BCFA, especially the first two compounds, have intense aromas, and minute quantities can affect the flavor of dairy products. In Cheddar-like hard goat cheeses, unlike Cheddar from milk of cows, the contribution of FFA to overall cheese flavor is dominant and more pronounced.

Aging time significantly influenced the concentrations of FFA during the first 12 wk. The FFA concentrations remained relatively unchanged for the rest of the ripening period. Hence, the intensity and sharpness of flavor that were contributed by or originated from the presence of these FFA would not be affected after 12 wk of aging.

The percentage of NaCl or the S/M in hard goat cheeses did not affect the concentrations of FFA. The NaCl concentrations in this study were common for this type of cheese, which indicates that, within such a range, the percentage of NaCl or the S/M had no effect on lipolysis.

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