Fatty acid, volatile and sensory profiles of milk and cheese from goats raised on native semiarid pasture or in confinement

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ABSTRACT

The fatty acid (FA), volatile and sensory profiles of cheese and milk, obtained from goats grazing native pastures (PS) of semiarid region of Brazil or kept under confinement (CS), were evaluated. Milk and cheese from native pasture-fed animals contained higher amounts of oleic acid, stearic acid, total polyunsaturated, *cis*-monounsaturated and *trans* FA, and lower amounts of medium chain FA, total saturated FA and rumenic acid compared with milk and cheese from confined goats. Two terpenes (α-terpineol and β-caryophyllene) were exclusively detected in PS milk and cheese. Milk from the PS group presented higher intensity for herbaceous flavour and lower butter aroma, butter flavour and residual persistence compared with CS milk. Both PS cheese and milk presented higher overall acceptability compared with CS counterparts.

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1. Introduction

The semiarid region in northeastern Brazil is characterised by arid soils and low rainfall, with the raising of animals based on native pastures plus supplements (Bomfim et al., 2011). The semi-arid native pastures of the Caatinga biome (i.e., the Brazilian xeric shrubland and thorn forest) comprises multiple plant species with high forage potential, and it constitutes a significant food source for sheep and goats in the region (Andrade, Costa, Santos, & Silva, 2010). The "coalho" cheese is a traditional Brazilian product with a medium to high moisture level produced from pasteurised cows' or goats' milk.

The plant composition of pastures also affects the compositions of lipids and volatile compounds of the animal feed, and thus, it can influence the quantity and quality of these compounds in ruminant-derived dairy products (Bugaud, Buchin, Hauwuy, & Coulon, 2001). Compared with conventional confinement feeding

systems, grazing diverse native pastures can influence the fatty acid (FA) and volatile compound contents in cheese and milk (Bonanno et al., 2013) and can affect the sensory attributes of these products. Some studies demonstrated that milk and cheese from pasture-fed ruminants display better nutritional and health promoting properties for consumers due to lower contents of saturated FAs (SFAs) and higher contents of monounsaturated FAs (MUFAs), polyunsaturated FAs (PUFAs), and terpenes, when compared with milk and cheese from intensive-fed ruminants (Chilliard et al., 2007; Coppa et al., 2011b; Morand-Fehr, Fedele, Decandia, & Frileux, 2007). Terpenes are of significance as some have been found to exhibit antibacterial, anticancer and antioxidant properties (Gonzalez-Burgos & Gomez-Serranillos, 2012). Moreover, dairy products from animals grazing native pastures, can be framed under the "terroir" concept, a key factor in defining typical and quality-labelled products (Coppa et al., 2011b). Also, pastures with a higher number of dicotyledon species led to cows' milk with higher contents of MUFAs and n-3 and n-6 PUFAs (Coppa et al., 2011a).

The effects of animal feed on the amount of volatile compounds as well as the FA and sensory profiles of cows' and sheep's milk and cheese have been previously demonstrated (Bonanno et al., 2013;

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Coppa et al., 2011c; Vasta, D'Alessandro, Priolo, Petrotos, & Martemucci, 2012). However, few studies focus on goats' milk and cheese in the context of the animal feeding system, and none is available for the Brazilian semiarid region, an area of unique climate and vegetation. Therefore, this study aimed to evaluate the influence of the dairy goat production system in Brazilian semiarid region on the FA, volatile and sensory profiles of milk and "coalho" cheese.

2. Materials and methods

2.1. Animals and diet

The animal experiment was conducted at the experimental station located in São João do Cariri (Paraíba state, Brazil). Twelve mixed-breed (Sannen × American Alpine) goats, weighing 51.35 ± 3.75 kg (mean ± SD), producing on average 1.3 L of milk per day and with approximately 30 days of lactation, were divided into the following two groups: native pasture-fed animals (pasture-fed system, PS) and animals fed in confinement (confinement system, CS). The animals were submitted to the food adaptation system for 40 days, so that the first sample of milk from each treatment was performed after 70 days of lactation. The next four days were used to collect milk samples. Goats were milked twice a day, at 07:00 and 16:00 h.

The PS goats had access to Caatinga native pastures between the two daily milkings, and then housed in individual pens where they received concentrate supplementation. The CS goats were kept permanently in individual pens, east-west oriented with feeders and drinkers. The CS diet consisted of elephant grass (Pennisetum purpureum) hay and concentrate supplementation at 1 kg per animal per day.

The concentrate supplementation for both systems was calculated according to the National Research Council (NRC, 2007) based on the minimum daily nutrient ingestion needed for the production of milk and weight maintenance. The diet composition of both production systems is shown in Table 1. The average chemical composition values for 100 g of milk (in g) from goats grazing Caatinga pasture (PS) were, respectively: moisture 88.04, fat 3.93, protein 3.71, lactose 4.45, ash 0.63, acidity 0.15 and pH 6.71, whereas the values for 100 g of milk from goats fed a confinement diet (CS) were (in g): moisture 88.87, fat 3.50, protein 3.68, lactose 4.39, ash 0.62, acidity 0.15 and pH 6.71 (Supplementary material Table S1).

2.2. Plant species composition and sampling

In the native pasture of the semiarid region studied, 71 plant species were found and classified according to family. Species belonging to the families *Asteraceae*, *Fabaceae* and *Poaceae* (11%

Table 1
Composition (%) of dietary components for the two production systems.[a]

Dietary components	System	
	Pasture (PS)	Confinement (CS)
Native "Caatinga" vegetation	ad libitum	—
Elephant grass (*Pennisetum purpureum*) hay	—	51
Soybean meal	30	12.5
Corn meal	69	36
Mineral supplement	1	0.5

[a] Data for PS are the percentage of the concentrate supplementation based on animals' weight (1.5%); data for CS are the percentage of the concentrate supplementation (based on 1 kg per animal per day).

each) were the most abundant, followed by species of *Malvaceae* (7%), *Euphorbiaceae* (6%), *Cactaceae* (4%) and *Apocynaceae* (2%).

The native plants most consumed by the animas in the PS were sampled using the "grazing simulation" technique, according to which a few goats were randomly selected, and their grazing patterns were observed (Carpino et al., 2004). Some goats were randomly selected for monitoring and observing their pasture regime. During the observation period, the selected plant types and parts of the plants consumed were recorded. Four plant species were detected as being the most consumed by the goats: *Aspidosperma pyrifolium* (family *Apocynaceae*), *Croton sonderianus* (family *Euphorbiaceae*), *Caesalpinia pyramidalis* (family *Fabaceae*) and *Sida* sp. (family *Malvaceae*). The species *Pennisetum purpureum* used in the CS treatment belongs to the family *Poaceae*.

2.3. Preparation of coalho cheese

Three Coalho cheeses of approximately 220 g each were prepared in the laboratory from the milk collected from each goat group, in 4 consecutive days. The cheeses were prepared from the total evening plus morning milk. For that, milk was heated at 65 °C for 30 min, then cooled to 37 °C, mixed with 50% calcium chloride at 0.5 mL L^{-1}, and finally mixed with commercial coagulant (Ha-la Christian Hansen®; Chr. Hansen, Hørsholm, Denmark) at 0.9 mL L^{-1}. The mixture was allowed to rest for 40 min for complete coagulation into a curd. After verifying that the desired consistency had been achieved, the curd was carefully cut horizontally and vertically, drained and salted (1% NaCl relative to the mass weight). The curd was distributed into perforated moulds of 250 g and pressed continuously for 4 h at room temperature. The pressed cheeses were vacuum-packed and stored for 12 days at 4 °C (±1) until analysis. The average chemical composition values for 100 g of cheese (in g) from goats grazing Caatinga pasture (PS) were, respectively: moisture 52.85, fat 21.66, protein 21.10, lactose 2.00, ash 2.81, acidity 0.01 and pH 7.21, whereas the values for 100 g of cheese from goats fed a confinement diet (CS) were (in g): moisture 52.09, fat 21.13, protein 21.03, lactose 1.99, ash 3.09, acidity 0.02 and pH 7.20 (Supplementary material Table S1).

2.4. Fatty acids analysis

For cheese and milk FA analysis, 50 mg of cheese or lyophilised milk was weighed, transferred to test tubes and mixed with 1 mL of n-hexane, 1 mL of internal standard (C19:0, 1 mg mL^{-1}) and 0.2 mL of KOH in methanol. The tubes were vortexed for 3 min, allowed to rest for 15 min and 1 mL of HCl in methanol was added. The tubes were vortexed for 10 s and transferred to a 50 °C water bath for 10 min. Tubes were let to cool down to room temperature, and 2 mL of ultrapure water plus 2 mL of n-hexane were added. Tubes were mixed for 10 s followed by centrifugation for 5 min. The supernatant was transferred to a clean tube containing 0.5 g of anhydrous sodium sulphate. Tubes were vortexed for 30 s and centrifuged for 5 min. Then, the n-hexane phase containing the FA methyl esters was transferred to a gas chromatography (GC) vial, capped and frozen until sample injection. Fatty acid methyl esters were analysed by GC with flame ionisation detection (GC-FID) using a Shimadzu QP2010-plus (Shimadzu, Kyoto, Japan) equipped with a fused silica capillary column (SP-2560, 100 m × 0.25 mm × 0.20 μm, Supelco, Bellefonte, PA, USA). The injector and detector were kept at 250 °C and 280 °C, respectively, during analysis. Helium was the carrier gas at 1 mL min^{-1} constant flow rate, and 1 μL of sample was injected. The temperature program was as follows: 50 °C for 1 min; ramp to 150 °C at 50 °C min^{-1}, held for 20 min; ramp to 190 °C at 1 °C min^{-1}, held for 1 min; and ramp to 220 °C at 2 °C min^{-1}, held for 30 min.

Identification of FA methyl esters was achieved by comparison of the retention times with those of commercial standards (FAME mix 37 components from Supelco Inc.). Additional identification of the FAs was achieved by electron impact mass spectrometry using a Shimadzu GC-MS QP2010 Plus (Shimadzu). The FA results were expressed as a percentage of the sum of detected FAs (g 100 g^{-1} of total FAs) and relevant partial sums of FA were computed. The FA atherogenic index computed according to Ulbricht and Southgate (1991).

2.5. Volatile compound analysis

Volatile compounds were extracted using the solid phase micro-extraction (SPME) technique. The volatile compounds in milk samples (20 g) were extracted according to the optimised procedure carried out by Sant'Ana et al. (2017). The volatile compounds in cheese samples (20 g) were extracted according to the optimised procedure carried out by Bezerra et al. (2016).

The volatile compounds from the milk sample headspace were identified and quantified using a Varian Saturn 2000R 3800 gas chromatographer coupled to a Varian Saturn 2000R 2000 mass spectrometer and a VF-5MS (60 m × 0.25 mm × 0.25 μm, Agilent, Santa Clara, CA, USA) column. The temperature program was 40 °C for 10 min, followed by ramping to 240 °C at 5 °C min^{-1}, where it was held for 11 min. The total run time was 61 min. The injector temperature was kept at 250 °C, and helium was the carrier gas at a constant flow of 1.0 mL min^{-1}.

To identify the volatile compounds, a standard solution of ho-mologous n-alkanes (C7-C30) was analysed prior to the sample injection to obtain the linear retention index (LRI). In addition, the spectral library for gas chromatography mass spectrometry (GC/MS) from the National Institute of Standards and Technology (NIST)/Environmental Protection Agency (EPA)/National Institute of Health (NIH) mass spectral database (version 7.1) was used. The spectra and LRI values obtained for the volatile compounds from the goat cheeses were also compared with values found in the literature. Cheese volatile compounds identification was performed according to Bezerra et al. (2016).

2.6. Sensory analysis

The sensory attributes of the goats' milk and cheeses were evaluated using quantitative descriptive analysis (QDA) (Stone & Sidel, 1993). The proposal for this analysis was approved by the Research Ethics Committee of the Health Sciences Centre, Federal University of Paraíba under CAAE #02228812.7.0000.5188. Ten trained panellists aged from 20 to 30 years were selected based on their experience in discriminative sensorial analysis. Sessions were held to determine the descriptive terminology, to allow familiar-isation with reference materials and for training as well as final selection of the panel members. The milk was pasteurised (65 °C 30 min^{-1}) and stored for 2 d in the fridge, and the cheeses were stored for 12 d in the fridge prior to sensory evaluation by the panel. Sensory evaluation was performed in individual cubicles with white light and samples (20 g) served in disposable plastic cups labelled with random three-digit numbers.

Milk samples were characterised regarding aroma (goat milk, butter, and herbaceous), flavour (goat milk, butter, and herbaceous) and aftertaste (intensity and persistence). Cheese samples were characterised based on appearance (smooth, wet, whitish colour, and creamy colour), aroma (goat milk, butter, and herbaceous), flavour (goat milk, butter, herbaceous, acidic, and salty) and texture (softness and homogeneity). The perceived intensity of each attribute was scored using a non-structured scale ranging from 0 (weak) to 9 (strong). The panel members also evaluated their

general level of acceptability of the dairy products on a scale from 1 (strongly disliked) to 9 (strongly liked).

2.7. Statistical analysis

Data were analysed using the Proc GLM of SAS 9.0 software (SAS Institute Inc, Cary, NC, USA) considering the effect of the feeding systems as single fixed effect. The least square means and standard error of the means and the P values of the models were presented in the tables.

3. Results and discussion

3.1. Fatty acid profile

The FA profile of milk and cheese from both experimental groups is presented in Table 2. The most abundant FAs (above 1% of total FAs) present in both milk and cheese samples were in descending order, palmitic (16:0), oleic (18:1c9), stearic (18:0), myristic (14:0), capric (10:0), lauric (12:0), caprylic (8:0), caproic (6:0), butyric (C4:0) and linoleic (18:2n-6) acids, and all except the 4:0 were affected by the feeding system. Milk and cheese from PS group presented higher ($P < 0.01$) proportions of 16:0, 18:0, 18:1c9, and 18:2n-6 and lower ($P < 0.01$) proportion of 6:0, 8:0, 10:0, 12:0 and 14:0. In general, the differences between groups were larger in milk than in cheese. The proportion of 16:0 was 4 percent points higher in milk and 2 percent points higher in cheese from PS than from CS group. The proportion of 18:0 was also 2 percent points higher in PS than in CS milk and cheese, whereas the increase of 18:1c9 was circa 1 percent point in milk and only 0.5 percent point in cheese. The 18:2n-6 was also circa 0.6 percent points higher in both milk and cheese from PS than CS group. Conversely, the 14:0, 12:0, 10:0, 8:0 and 6:0 were, respectively, 3.6, 1.5, 2.4, 0.7 and 0.4 percent points higher in CS than in PS milk and only 1.2, 1.1, 1.1, 0.4, and 0.3 percent points higher in CS than in PS cheese. Other minor FAs also presented significant differences between groups and 16:1c9, 17:0, 17:1c9 and 18:3n-3 were higher in PS than in CS both in milk and cheese samples. Conversely, anteiso-15:0, 14:1c9, 15:0, and phytanic acid, were higher ($P < 0.01$) in CS than in PS milk and cheese samples.

Several trans-MUFAs that derived from ruminal bio-hydrogenation (Bessa, Santos-Silva, Ribeiro, & Portugal, 2000) were detected. The PS milk contained higher ($P < 0.01$) proportion of most trans-18:1 isomers than CS milk, with the notable exception of the vaccenic acid (18:1t11). The same pattern is observed in cheese besides the fact that 18:1t11 did not differ between feeding system. The concentration of rumenic acid (18:2c9t11), the main CLA iso-mer, was higher in both milk and cheese from the CS group compared with the PS group.

The activity of delta-9 desaturase (or stearoyl-CoA desaturase) was estimated using the proportions of FA products and substrate ratios (i.e., Product/(Product + Substrate)*100) and for all pro-duct:substrate pairs, except for the 17:1c9/17:0, the delta-9 desa-turase activity indexes were higher in the CS than in the PS group (Fig. 1).

Overall, the differences observed in individual FAs are reflected on higher ($P < 0.001$) MUFAs, PUFAs and trans-FAs proportion and lower SFAs proportion on PS than CS milk and cheese.

Goat milk is characterised by a very high content of medium chain SFAs (i.e., 6:0 to 14:0) which could play a major role in the occurrence of the characteristic goat flavour (Sanz Sampelayo, Chilliard, Schmidely, & Boza, 2007). The milk and cheese pro-duced from goats with access to native pasture had lower propor-tion of these medium chain FAs. The medium chain FAs are exclusively de novo synthesised by the mammary gland (Chilliard,

Table 2
Fatty acid composition (% of total fatty acids) of milk and cheese from goats grazing Caatinga pasture (PS) or fed a confinement diet (CS).[a]

Fatty acids	Milk				Cheese			
	PS	CS	SEM	P-value	PS	CS	SEM	P-value
4:0	1.55	1.74	0.209	0.535	1.91	2.14	0.103	0.171
6:0	1.84	2.23	0.031	<0.001	1.95	2.27	0.008	0.008
8:0	1.79	2.46	0.042	<0.001	2.02	2.39	0.001	<0.001
10:0	6.52	8.95	0.040	<0.001	7.18	8.28	0.001	<0.001
12:0	2.12	3.58	0.008	<0.001	2.59	3.26	0.021	<0.001
iso-14:0	0.11	0.12	0.004	0.090	0.10	0.15	0.002	<0.001
14:0	8.16	11.73	0.055	<0.001	9.05	10.86	0.014	<0.001
iso-15:0	0.23	0.24	0.006	0.460	0.20	0.26	0.008	0.002
anteiso-15:0	0.33	0.40	0.008	<0.001	0.34	0.42	0.005	<0.001
14:1c9	0.08	0.15	0.003	<0.001	0.11	0.14	0.006	0.007
15:0	0.75	0.83	0.006	<0.001	0.73	0.86	0.015	<0.001
iso-16:0	0.37	0.27	0.005	<0.001	0.30	0.34	0.013	0.049
16:0	37.61	33.49	0.132	<0.001	33.60	31.68	0.123	<0.001
iso-17:0	0.40	0.38	0.004	0.005	0.36	0.40	0.013	0.097
16:1c7	0.41	0.25	0.005	<0.001	0.41	0.31	0.016	0.005
16:1c9	0.99	0.94	0.004	<0.001	0.59	0.56	0.009	0.056
3,7,11,15 Me-16:0	0.10	0.18	0.002	<0.001	0.14	0.18	0.003	<0.001
17:0	0.67	0.51	0.004	<0.001	0.60	0.53	0.005	<0.001
iso-18:0	0.06	0.07	0.006	0.704	0.05	0.10	0.003	<0.001
17:1c9	0.27	0.20	0.006	<0.001	0.25	0.23	0.004	0.007
18:0	10.76	8.10	0.034	<0.001	10.25	8.82	0.069	<0.001
18:1t6/t7/t8	0.16	0.12	0.008	0.011	0.16	0.13	0.005	0.003
18:1t9	0.14	0.12	0.002	0.001	0.16	0.13	0.004	0.008
18:1t10	0.17	0.11	0.007	0.001	0.16	0.11	0.004	<0.001
18:1t11	0.46	0.50	0.005	0.002	0.51	0.50	0.006	0.302
18:1t12	0.21	0.15	0.011	0.009	0.23	0.17	0.004	<0.001
18:1c9	20.17	19.24	0.094	<0.001	21.66	21.21	0.092	0.014
18:1t15	0.07	0.04	0.006	0.012	0.08	0.05	0.005	0.008
18:1c11	0.37	0.33	0.006	0.002	0.38	0.31	0.008	0.002
18:1c12	0.13	0.05	0.021	0.037	0.14	0.08	0.003	<0.001
18:1t16 + c14	0.13	0.07	0.012	0.011	0.15	0.11	0.002	<0.001
18:2n-6	1.63	1.31	0.006	<0.001	1.94	1.38	0.017	<0.001
20:0	0.29	0.23	0.010	0.006	0.28	0.27	0.003	0.090
18:3n-3	0.19	0.07	0.004	<0.001	0.23	0.10	0.005	<0.001
20:1	0.03	0.04	0.003	0.024	0.05	0.04	0.005	0.164
18:2c9t11 (CLA)	0.26	0.36	0.008	<0.001	0.33	0.38	0.004	<0.001
22:0	0.09	0.07	0.005	0.070	0.08	0.08	0.004	0.714
20:4n-6	0.17	0.18	0.004	0.129	0.18	0.16	0.006	0.134
24:0	0.06	0.06	0.002	0.981	0.04	0.05	0.003	0.040
22:5n-3	0.05	0.05	0.002	0.313	0.05	0.04	0.002	0.004
Sums								
SFAs	73.89	75.71	0.114	<0.001	71.89	73.48	0.112	<0.001
cis-MUFAs	22.45	21.20	0.104	<0.001	23.57	22.88	0.092	0.002
trans-MUFAs	1.35	1.11	0.034	0.003	1.45	1.18	0.018	<0.001
PUFAs	2.31	1.97	0.017	<0.001	2.74	2.06	0.017	<0.001
Ratios								
PUFA/SFA	0.03	0.02	0.001	<0.001	0.04	0.03	0.001	0.027
AI	2.95	3.68	0.012	<0.001	2.79	3.19	0.010	<0.001
n-6/n-3	7.41	12.47	0.977	<0.001	7.43	11.14	0.307	<0.001

[a] Abbreviations are: SEM, standard error of means; CLA, conjugated linoleic acid; SFAs, saturated fatty acids; cis-MUFAs, cis-monounsaturated fatty acids; trans-MUFAs, trans-monounsaturated fatty acids; PUFAs, polyunsaturated fatty acids; AI, atherogenic index ($[(12:0 + (4 \times 14:0) + 16:0)]/(cis\text{-}MUFA + n\text{-}6\ PUFA + n\text{-}3\ PUFA)$), n-6/n-3: ratio between n-6 PUFA and n-3 PUFA.

Ferlay, Rouel, & Lamberet, 2003) and thus their increased concentration in milk from CS goats might reflect a higher metabolisable energy availability to support milk production compared with PS goats. Consistently, the increased proportions of 18:0 and 18:1c9 in PS milk compared with CS milk also suggest that PS goats had less energy available to support the lactation, as when the energy balance of lactating goats decrease, more 18:0 and 18:1c9 are mobilised from adipose tissue reserves and incorporated in milk (Palma et al., 2017). In fact, it has been reported that the variation of energy balance in goats explains about 59% of the 18:0 plus 18:1c9 proportions in milk (Chilliard et al., 2003). Higher energy availability allowed by CS feeding was also reflected in the apparent increased delta-9 desaturase activity, which is consistent with increased mammary gland lipogenesis.

The effect of PS feeding system on the milk FA profile is also very clear on the increased concentrations of 18:3n-3, 18:2n-6 and most of biohydrogenation intermediates, with the exception of 18:1t11 and 18:2c9t11, when compared with CS feeding system. These results suggest a higher PUFA intake in grazing animals compared with CS animals, which is very well established for 18:3n-3 (Dewhurst, Shingfield, Lee, & Scollan, 2006) but not so often for 18:2n-6. The increased concentration of most of biohydrogenation intermediates is easily explained by the probable increased intake of dietary PUFAs but the modulatory effects of Caatinga plants tannins on biohydrogenation pathways might play a role on increasing biohydrogenation intermediates (Vasta & Bessa, 2012). The lower content of 18:1t11, and thus of 18:2c9t11, in PS milk when compared with CS milk is surprising as grazing ruminants usually
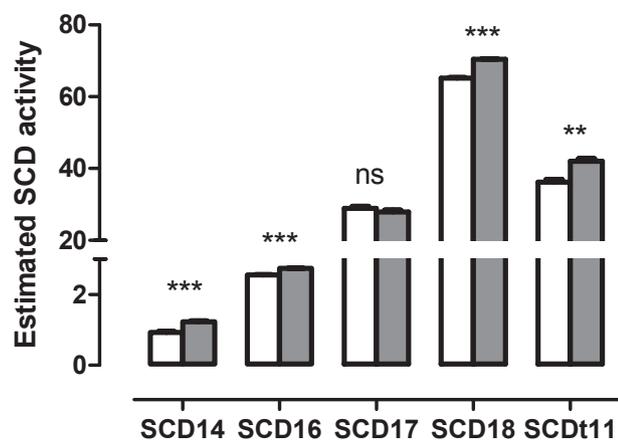
Fig. 1. Estimated stearoyl-CoA desaturase activity indices (SCD) computed from product/substrate ratios computed with the fatty acids in milk (feeding systems: □, pasture; ■, confinement). SCD14, (14:1c9/(14:1c9 + 14:0) × 100); SCD16, (16:1c9/(16:1c9 + 16:0) × 100); SCD17, (17:1c9/(17:1c9 + 17:0) × 100); SCD18, (18:1c9/(18:1c9 + 18:0) × 100); SCDt11, (18:2c9t11/(18:2c9t11 + 18:1t11) × 100). Column pairs with asterisks differ significantly: ***$P < 0.001$; **$P < 0.01$; ns, not significantly different ($P > 0.05$).

produce milk enriched with 18:1t11 when compared with confined ruminants (Chilliard et al., 2007) and because it does not follow the pattern observed for all the other trans-18:1.

The FA composition of cheese follows closely the milk FA composition although the differences between feeding systems are slightly mitigated. Cheese and milk PS presented slight higher PUFAs/SFAs and a clear lower atherogenic index and n-6/n-3 ratios, which is favourable consider the potential health impact on consumers. The decrease in SFA observed in PS is mostly due to the decrease of medium chain FA and not from 16:0, the main hypercholesteraemic FA. Nevertheless, both 12:0 and 14:0 are considered hypercholesteraemic FA and thus its reduction in milk is favourable and explain the clear decrease in atherogenic index. However, one of the major nutritional advantages of goat milk, as reviewed by Sanz Sampelayo et al. (2007), is its richness in shorter chain saturated FAs like 6:0, 8:0 and 10:0. These FA present several health promoting effects and its reduction in PS milk and cheese is not positive. The differences in trans-FAs, including 18:1t11 and 18:2c9t11, and of 18:3n-3 although significant are very small and probably had a negligible effect on the nutritive value of cheese.

3.2. Volatile compounds in cheese

Thirty three different volatile compounds distributed by nine chemical classes were detected in milk and cheese from goats from PS and CS groups (Table 3). In milk and cheese from PS goats, the number of total volatile compounds was greater (17 and 27, respectively) than in milk and cheese from CS-fed animals (12 and 14, respectively). The larger diversity of volatile compounds in PS samples compared with CS samples is fully consistent with previous reports on cows' milk and cheese (Carpino et al., 2004).

Milk and cheese from PS exhibited higher amounts of total volatile carboxylic acids (fatty acids), particularly octanoic (caprilic, 8:0) and decanoic (capric, 10:0) acids. In milk, most of 8:0 and 10:0 are esterified in triacylglycerols and would be detected in headspace volatile analysis. It is interesting to note that the amount of non-esterified 8:0 and 10:0 do present the opposite pattern than the total 8:0 and 10:0 in milk and cheese, suggesting that a more extensive lipolysis occurs in PS than CS samples.

Three alcohols (1-butanol, 1-hexanol and maltol) were observed in PS milk whereas in CS milk only maltol was observed. Povolo, Contarini, Mele, and Secchiari (2007) reported that ewes fed pastures with great botanic diversity presented higher amount of alcohols in milk than those containing more specific plants and our results follow the same pattern. Regarding the cheeses, the primary alcohols 1-pentanol and 1-octanol were detected only in cheese from CS-fed animals and ethanol and maltol were detected only in cheese from PS-fed animals; and 1-butanol and 1-hexanol were detected in both cheeses. The presence of higher amounts of alcohols in the cheese when compared with the milk can be explained by the biochemical reactions that occur during cheese manufacturing process and storage. Primary alcohols are produced primarily by the reduction of the corresponding aldehydes and methyl-ketones and ethanol is derived from lactose fermentation or amino acid catabolism (Kalač, 2011; McSweeney, 2004) and is the most common alcohol involved in this reaction and thus is the limiting reagent in ester production (McSweeney, 2004). Thus, it is possible that the presence of both esters (ethyl acetate) and ethanol in PS cheese are related.

One ketone, the 2-pentadecanone, was detected only in the cheese samples from the pasture-fed system suggesting that is formed during the cheese-making process as intermediate products of FA or keto-acids degradation (McSweeney & Sousa, 2000). Some hydrocarbons were found only in cheese from pasture-fed animals (pentane, 2,3,4-trimethyl, heptane,2,2-dimethyl, octene, 2-octene and nonane), while octane, heptane and 3-octene were detected at the same concentrations ($P > 0.05$) in cheese from both groups.

Differences in the amounts of pyranes and furanones were not significant between the milk and cheese in this study. These compounds are unlikely to be directly related to the feeding system, once they are typical products of the Maillard reaction, as a result of the thermic degradation of hexoses in the presence of amines during the heating of milk (Nursten, 2005).

Four terpenes (α-pinene, limonene, α-terpineol and β-caryophyllene) were detected in PS milk and cheese samples and only 2 (α-pinene and limonene) in CS milk and cheese samples. The limonene concentration in milk or cheese did not differ between feeding systems ($P > 0.05$). Limonene is a monoterpene commonly present in many types of plants, and thus might not be a very sensitive tracer of feeding system. The α-pinene presented higher ($P < 0.05$) concentration in PS compared with CS milk and cheese. The α-terpineol and β-caryophyllene were detected exclusively in PS milk and cheese samples. α-Terpineol is a monoterpene derived from limonene via epoxidation of the double bond located at the isoprenial unit (Marosta Júnior & Pastore, 2007) and β-caryophyllene is an sesquiterpene often detected in milk and dairy products (Agabriel et al., 2007). Moreover, β-caryophyllene has been identified as potential dietary markers of pasture-fed cows (Engel et al., 2007). The presence of larger diversity of terpenes in PS samples than CS is surely linked to botanical diversity of Caatinga native pasture. Caatinga pastures are rich in dicotyledons, particularly Apiaceae, Asteraceae and Lamiaceae, that contain a higher quantity and variability of terpenes relative to pastures dominated by grasses (as Poaceae, fed to CS goats), which only have the most common types of terpenes (Bugaud et al., 2001; Mariaca et al., 1997).

However, for other volatile compounds, a direct link between its presence in diet and milk or cheese is not obvious, as most of them can be formed during milk storage and processing and cheese maturation due to degradative metabolism of the main milk components (McSweeney & Sousa, 2000). In contrast, terpenes present in the milk and cheese are strongly related to the animals' diet, given that these compounds can pass from the

Table 3
Volatile compounds identified in the milk and cheese from goats grazing Caatinga pasture (PS) or fed a confinement diet (CS).[a]

Class and compound	LRI		Milk				Cheese			
	Milk	Cheese	PS	CS	SEM	P value	PS	CS	SE	P value
Carboxylic acids			359[a]	116[b]	59.9	0.013	248[a]	30[b]	55.8	0.011
Acetic acid	<600	<600	2.26	2.23	0.405	0.972	0.31	nd	0.014	–
Pentanoic acid	999		23.7	nd	6.34	–	nd	nd	–	–
Heptanoic acid		1021	nd	nd	–	–	8.0	nd	0.36	–
Octanoic acid	1190	1216	64.8[a]	23.5[b]	10.10	0.011	44.3[a]	6.4[b]	9.29	<0.001
Decanoic acid	1387	1434	233[a]	67[b]	42.9	0.026	180[a]	24[b]	40.6	0.019
Dodecanoic acid	1578	1644	31.1	22.7	4.33	0.387	17.4	nd	8.56	–
Tetradecanoic acid	1824		2.06	nd	0.611	–	nd	nd	–	–
Alcohols			18.7	14.6	2.88	0.795	13.9	12.4	2.01	0.724
Ethanol		<600	nd	nd	–	–	4.36	nd	1.073	–
1-Butanol		<600	2.09	nd	0.603	–	1.61	1.46	0.220	0.772
1-Pentanol		754	nd	nd	–	–	nd	4.49	0.548	–
1-Hexanol		778	1.94	nd	0.341	–	1.53	0.65	0.296	0.150
1-Octanol		798	nd	nd	–	–	nd	5.76	1.140	–
Maltol	1141	1175	14.7	14.6	2.54	0.997	6.4	nd	4.15	–
Aldehydes			nd	9.3	2.30	–	6.90[a]	1.62[b]	1.374	0.017
3-Hydroxy-butanal	738		nd	1.51	0.	–	nd	nd	–	–
Undecanal	1113	1142	nd	7.76	2.426	–	6.90[a]	1.62[b]	1.374	0.017
Ketones			nd	nd	–	–	3.00	nd	0.625	–
2-Pentadecanone		1789	nd	nd	–	–	3.00	nd	0.625	–
Esters			2.96	nd	0.518	–	1.10	nd	0.119	–
Ethyl acetate		<600	nd	nd	–	–	1.10	nd	0.119	–
Nonanol acetate	1166		2.96	nd	0.518	–	nd	nd	–	–
Hydrocarbons			nd	nd	–	–	44.7	10.6	10.44	0.065
Pentane 2,3,4-trimethyl		755	nd	nd	–	–	1.70	nd	0.634	–
Heptane		762	nd	nd	–	–	2.84	0.76	0.684	0.137
Heptane 2,2-dimethyl		786	nd	nd	–	–	1.55	nd	0.661	–
Octane		798	nd	nd	–	–	11.6	7.5	1.71	0.274
Octene		806	nd	nd	–	–	17.7	4.57		–
2-Octene		814	nd	nd	–	–	4.0	nd	1.32	–
3-Octene		817	nd	nd	–	–	3.13	2.37	0.55	0.552
Nonane		899	nd	nd	–	–	2.16	nd	2.164	–
Furans			28.7	26.4	3.55	0.335	23.2	1.10	7.319	0.164
2-Furanmethanol	882	884	5.15	4.38	0.524	0.527	0.92	nd	0.269	–
2,4-Dihydroxy-2,5-dimethyl-3(2H)-furan-3-one	997	1017	23.5	22.0	4.32	0.215	22.9	1.10	7.262	0.167
Pyrans			37.2	25.3	6.63	0.432	14.0	3.39	2.285	0.423
4H-Pyran-4-one, 2,3-dihydro-3,5-dihydroxy-6-methyl-	1173	1199	37.2	25.3	6.63	0.432	14.0	3.39	2.285	0.423
Terpenes			4.56[a]	0.78[b]	0.847	0.042	7.78[a]	0.84[b]	1.989	0.035
α-Pinene	945	956	0.97[a]	0.18[b]	0.181	0.033	1.10[a]	0.20[b]	0.241	0.029
Limonene	1057	1062	0.76	0.60	0.058	0.491	0.82	0.64	0.110	0.511
α-Terpineol	1101	1107	1.68	nd	0.172	–	3.75	nd	0.522	–
β-Caryophyllene	1506	1511	1.15	nd	0.140	–	4.30	nd	1.448	–

[a] Abundance of volatile compounds is expressed as average area counts of their mass spectra base peak divided by 10^5; values with different superscript letters within a row and within a sample type (milk or cheese) are significantly different. LRI, linear retention index; SEM, standard error of means; nd, not detected.

plants to milk and dairy products with little to no metabolic alterations (Agabriel et al., 2007). These compounds are widely distributed in nature as secondary metabolites synthesised by plants and they are not synthesised by animals. Thus, terpenes in dairy products can be used as animal feeding system biomarkers and greatly contribute to define unique product characteristics associated to well defined geographic allowing the use of "terroir" as a relevant concept in defining typical and speciality products (such as those of protected denomination and from a specific geographic origin) (Coppa et al., 2011b; Kalac, 2011). In addition, terpenes are of significance as some have been found to exhibit antibacterial, anticancer and antioxidant properties (Gonzalez-Burgos & Gomez-Serranillos, 2012).

3.3. Sensory profile of milk and cheeses

In the sensory analysis of the milk samples, the judging panel described milk from CS as higher ($P < 0.05$) in butter aroma, higher in butter flavour and longer aftertaste persistence, while the milk from PS was described as having a stronger herbaceous flavour ($P < 0.01$). This herbaceous flavour can be explained by the presence of 1-butanol and 1-hexanol compounds in PS milk, once these molecules were already described as responsible for fruit and herbaceous notes during sensory analysis (Abilleira, Schlichtherle-Cerny, Virto, Renobales, & Barron, 2010).

Contrasting with what was observed with milk sensory evaluation, the production system did not affect ($P > 0.05$) the majority of the sensory attributes evaluated for the cheeses (Fig. 2). However, regarding general acceptability, both milk and cheese from PS goats were better accepted ($P < 0.05$) by the panel. The detection by sensory panels of feeding system effects on cheeses with short maturation times can be more difficult than when longer maturation times are used (Coppa et al., 2011c) although Claps, Fedele, Pizillo, Rubino, and Calandrelli (2003) observed sensorial differences in milk and cheeses identified by test panel members. Typically, coalho cheeses are marketed 10 d after production, and they must be consumed while still fresh (Oliveira, Garcia, Queiroga, & Souza, 2012). Given that milk is pasteurised and no cultures are added during the cheese production process, low levels of lipolysis are expected to occur (McSweeney & Sousa, 2000). Moreover, the
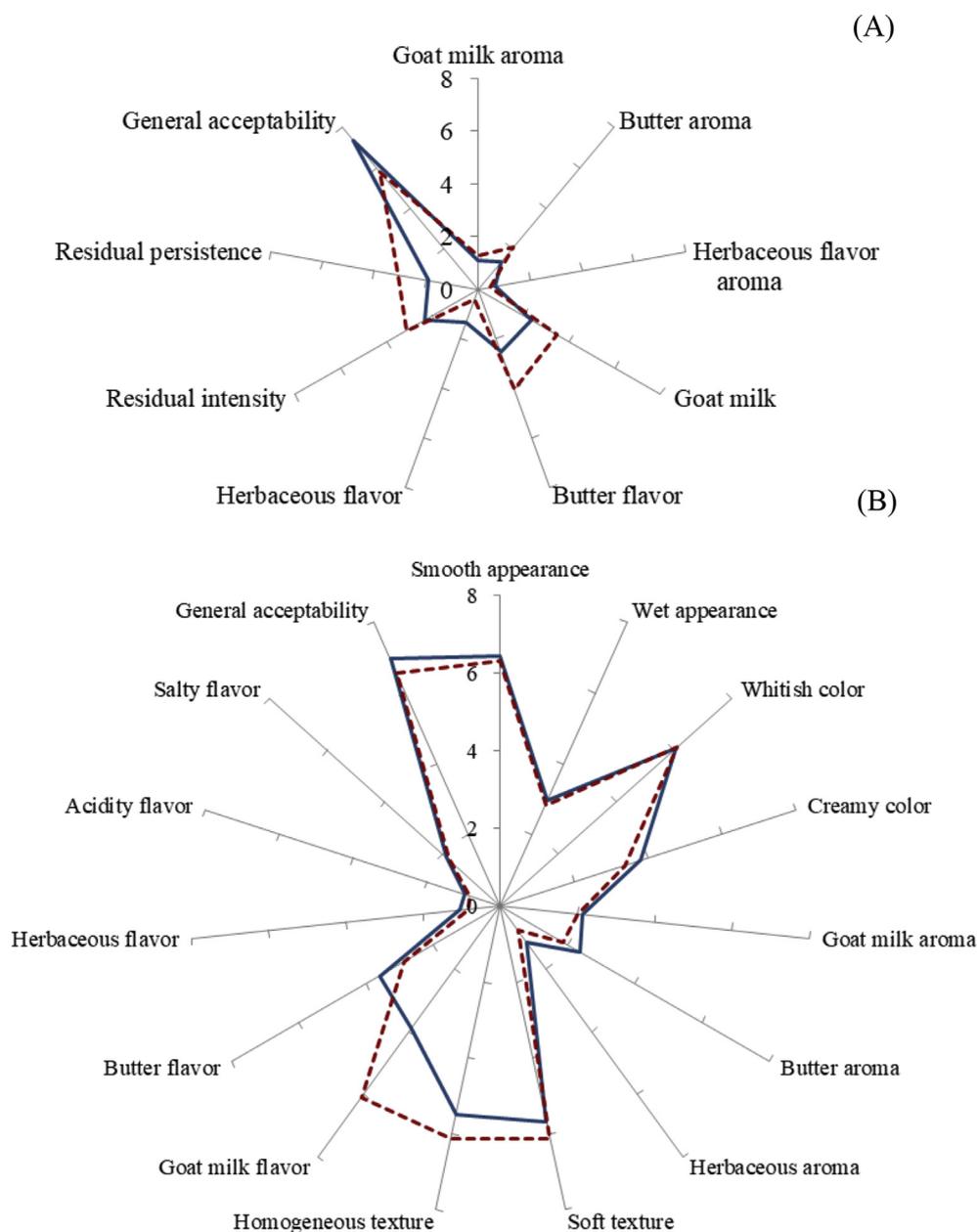
Fig. 2. Graphical representation of the sensory evaluation by quantitative descriptive analysis (QDA) of milk (A) and coalho cheese (B) from goats from pasture (PS) (———) and confinement (CS) (- - - -) feeding systems.

short coalho cheese storage time prior to sensory analysis might also contribute to the absence of detectable sensory traits associated with feeding systems.

4. Conclusion

The production system in the Brazilian semiarid region influences the FA and volatile profiles of goats' milk and cheese. These profiles can be useful in discriminating and indicating the origin of these products according to the type of food and farming characteristics. Moreover, the two feeding systems resulted in distinct FA profile of milk and cheese, with milk and cheese produced from goat with access to pasture presenting a higher PUFAs and MUFAs and lower SFAs, resulting in a clear reduction of its atherogenic index, thus presumably more beneficial for human health. The differences in the production systems were sufficient to promote a few notable differences in the sensory attributes of milk, but not of cheese. However, both milk and cheese from the grazing system are better accepted by the tasters. The results presented here can increase the value of raising dairy goats on the natural pasture (Caatinga) of the Brazilian semiarid region so that goat milk producers and processing plants in the region can improve their production system to obtain unique products with added value.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.idairyj.2018.09.008.

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