Original article

Composition and physico-chemical characteristics of goat milks containing the A or O α_{s1} casein variants

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Abstract — The composition of goat milks originating from three animals homozygous for α_{s1} casein, variant A, and from three others, homozygous O, was compared monthly over a lactation. Mean fat value was higher by 4.7 g kg⁻¹ in A milk, the difference between A and O reaching 9.8 g kg⁻¹ in the early lactation. Total nitrogen matter was higher by 6.8 g kg⁻¹ in A milk on the whole lactation. Total casein levels in A and O milks were respectively 21.2 and 17.8 g kg⁻¹. Caseins (CN) other than α_{s1} were at similar levels in the two groups of milks, α_{s1} CN was ~ 5.2 g kg⁻¹ in A milk and ~ 0.0 g kg⁻¹ in O milk. Mineral contents showed a high individual variability. Rennet coagulation tests led to higher firming rates and higher firmness in A milks, while coagulation time was not different between A and O milks. Total fatty acid proportions in milks were different: more short and medium length saturated fatty acids in A milk, balanced by a lower C16 level. Lipolysis was by far lower in A milk and the relative proportion of fatty acids in the free fatty acid fraction was different in A and O milks, meaning a difference in lipase level and/or in lipase specificity due to the enzyme itself or to its environment. In contrast, proteolysis of the plasmin type was higher in A milks. © Inra/Elsevier, Paris.

goat milk / casein/ L_{s1} variant / chemical composition / coagulation

Résumé — Composition et caractéristiques physico-chimiques des laits de chèvre contenant des caséines α_{s1} du variant A ou O. Les laits de trois chèvres homozygotes pour la caséine α_{s1} (α_{s1} CN), variant A, ayant une teneur en α_{s1} CN de ~ 5,2 g kg⁻¹ ont été comparés aux laits de trois chèvres O, dépourvus de caséine α_{s1} . L'analyse des laits durant la lactation a montré que les laits A étaient plus riches en matière grasse (MG) et en matière azotée totale (MAT). Les teneurs moyennes en MG étaient respectivement de 32,7 et 26,3 g kg⁻¹ pour les laits A et O, avec une dif-

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férence maximale de 9,8 g kg⁻¹ en début de lactation. Pour la MAT, les teneurs moyennes des laits A et O étaient de 33,7 et 26,9 g kg⁻¹, l'écart moyen sur l'ensemble de la lactation étant de 6,8 g kg⁻¹. Les teneurs en caséines individuelles autres que α_{s1} CN étaient peu différentes dans les deux types de laits. Les teneurs en minéraux (Ca, P, Na, K) ne présentaient pas de différence remarquable. L'aptitude à la coagulation par la présure du lait A était meilleure, tant pour la vitesse de raffermissement que pour la fermeté finale, sans doute du fait de sa plus haute teneur en caséine (21,2 et 17,8 g kg⁻¹). Les acides gras totaux de la MG présentaient des proportions un peu différentes d'un lait à l'autre, en ce qui concerne les acides gras saturés : le lait A contenait davantage d'acides gras à chaînes courtes et moyennes, compensés par moins de C16. La lipolyse était beaucoup plus faible dans les laits A et les proportions relatives des acides gras libérés étaient différentes des laits O, indiquant une différence entre les lipases des laits et/ou dans leur mode d'action. La protéolyse endogène de type plasminique était au contraire plus élevée dans les laits A au cours d'une incubation du lait à 37 °C. © Inra/Elsevier, Paris.

lait de chèvre / caséine / variant α_{s1} / composition / coagulation

1. INTRODUCTION

A high genetic variability of the casein (CN) constituents of goat milks has been demonstrated, principally concerning α_{s1} CN [1, 16]. Several α_{s1} CN variants have been identified (ABCDEF, O), and their protein sequences determined [11, 13]. This biochemical variability goes with quantitative aspects, as the α_{s1} CN secretion level in milk also varies from no secretion with the O variant, to 3.6 g kg⁻¹ by allele with the A variant.

Milks with α_{s1} CN variants producing high levels of proteins are of technological interest for cheese manufacture therefore genetic selection of breeds is in question. Indeed, cheese yields obtained from milk high in α_{s1} CN (variant A) were found significantly higher than those from milks with low level of α_{s1} CN (variant F), as demonstrated by Vassal et al. [20] and Delacroix-Buchet et al. [4].

These authors have also observed other different biochemical characteristics between the two milks, particularly concerning a very different milk lipase activity. Moreover, a comparative study of the sizes of casein micelles showed that milk with a high α_{s1} CN level, A variant, had a micel-

lar diameter lower by 30% compared to milks with no α_{s1} CN, O variant [15]. At last, differences in rennet coagulum properties have been reported [16, 17].

Some physicochemical properties of goat milks thus seemed to be related to the α_{s1} CN variants. Selection of animals on one character only would tend to modify some traditional properties of normal goat milk, so it seems useful to characterize the likely evolution of milk composition.

With this aim, we decided to study the composition and characteristics of milks with different α_{s1} CN levels. To magnify the differences due to α_{s1} CN, the comparison was made between milks from variants containing no α_{s1} CN (O milks) and variants with the highest α_{s1} CN levels (A milks).

2. MATERIALS AND METHODS

2.1. Milks

Goat milks, A and O, of selected composition for α_{s1} casein, were produced each by three animals. The animals originated from Inra (Unité Expérimentale de Bourges, Station d'Amélioration Génétique des Animaux,

31 Castanet-Tolosan, France). They had been genetically typed and characterized as homozygous at the α_{s1} CN loci, respectively A variant and O variant, at Inra Laboratoire de Génétique Biochimique (Jouy-en-Josas, France). The milk used in the experiments was fresh raw milk, either individual milk or mixed milks from three animals of the same specific genotype. Mixed samples were collected monthly for the determination of milk composition over the lactation. Other analyses were done on samples collected three times by the mid lactation, during June.

2.2. Proteins

Determination of total nitrogen matter (TNM) and of pH 4.2 soluble nitrogen matter (SN), extracted by the Rowland procedure [19] were made by Kjeldahl analysis ($N \times 6.38$). Casein (CN) yield was calculated as: $CN = TNM - SN$. The pH was chosen at 4.2 for the separation of SN, because it corresponded to the isoelectric pH of goat casein in milk, as determined in preliminary experiments.

High performance liquid chromatography (HPLC), performed on a Varian 5 000 equipment (Palo Alto, CA, USA) allowed the separation of individual components in total casein. Reverse phase separation on a C4 column (4.6 mm diameter, 150 mm length, Vydac Interchim, Montluçon, France) was achieved as already described [15]. Fraction x of casein corresponded to an hydrophobic component which eluted at a higher elution volume than the β CN peak. The content of the individual caseins in milk was calculated from the proportions obtained on the HPLC profiles, taking into account the specific absorptivities [15], combined with the total casein content of milk estimated by N analysis.

The proteolytic activity due to plasmin-like protease in milk was measured. To a sample of morning mixed milk (30 mL) were added NaN_3 , to a final content 200 μ g/mL, and penicillin, up to 10^3 U/mL, as bacterial inhibitors. Milks were incubated for 48 h at 37 °C, with 5 mL aliquots sampled at times 0, 24 and 48 h. The β CN level in the milk was determined using HPLC as previously described. The decrease in the native β CN level was kept as the proteolytic activity index.

Calcium, magnesium, sodium and potassium levels were determined by atomic absorption spectrophotometry (Spectra A 300, Varian, Palo Alto, CA, USA), phosphorus according to FIL-IDF no 33-B [7]. Total minerals were determined by analysis of the milks, and soluble minerals by analysis of the ultrafiltrates (CF 25 Centricon, Amicon, Paris, France).

The rennet coagulation time and the rheological characteristics of the curd, were determined using a Formagraph apparatus (Foss Electric, Nanterre). Measurements were at 30 °C with 50 μ g mL⁻¹ of chymosin in milk (Pure chymosin, Hansen, Copenhagen, Denmark). Coagulation parameters were: coagulation time (TC, min), firming time (K20, min) and maximum firmness (aR, cm).

Photon correlation spectroscopy (PCS) was used to determine the mean size of micelles in skimmed milks. Measurements were performed with a Coulter N4MD apparatus (Coultronics, Hialeah, FL, USA), with the experimental conditions as already described [15].

2.3. Lipids

2.3.1. Extraction

An aliquot of each milk sample (10 mL) was saturated with NaCl (4 g) to reduce acidic lipids solubility in the water phase according to Folch et al. [8] and then mixed with 15 mL of a mixture hexane/isopropanol (2/1; v/v). After decantation, the upper phase was collected and filtered through a disposable microporous inorganic membrane (Whatman Anodisc; 0.22 μ m) using a glass syringe.

2.3.2. Preparation of isopropyl esters

2.3.2.1. Total fatty acids (TFA)

25 μ L of the clear hexane solution and 100 μ g of heptadecanoic acid (C17) as internal standard were transferred into a teflon lined screw capping tube and isopropylated according to Wolff and Fabien [21]. The fatty acid isopropyl esters (FAIPE) were extracted by 2 mL of hexane and analyzed by gas chromatography.

2.3.2.2. Free fatty acids (FFA)

5 mL of lipid extract were transferred in a 100 mL round bottom flask diluted in 30 mL of

a mixture acetone/methanol (2/1, v/v) according to Gandemer et al. [10], 100 μg C17 were added as internal standard, then free fatty acids were fixed on an ion exchange resin Amberlyst 26 according to Needs et al. [14]. The resin was then collected by filtration and the fatty acids were isopropylated directly on the resin as described previously. The Needs method is the more accurate to extract free fatty acids but fatty acids isopropyl esters are more convenient for subsequent gas chromatography analysis so combination of the two methods give better results than Needs method alone.

2.3.3. Gas chromatography

Quantitative analyses of FAIPE were carried out on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionisation detector heated at 250 °C and a cold on column injector. The column used was a JW DB 225 (30 m $\times$ 0.32 mm; 0.25 μm film) with hydrogen (2 mL/min) as carrier gas. The oven chromatograph was maintained at 50 °C for 3 min then programmed from 50 to 180 °C at 10 °C/min and held at 180 °C for 5 min. As all the FAIPE have the same response coefficient, the relative concentration of each fatty acid was expressed as surface percent of the corresponding peak in the chromatogram. Lipolysis was calculated as the ratio between free fatty acid and total fatty acid concentrations in the lipid extract determined using the C17 internal standard: $\text{FFA} \times 100/\text{TFA}$.

2.4. Volatile fraction

The volatile organic fraction of milks was extracted from a one liter sample of milk in acidic (pH 2) or in neutral conditions (pH 7), according to Etievant and Bayonove [6], and then concentrated [5, 9]. Their constituents were separated and chemical identification obtained from analysis by gas chromatography-mass spectrometry (Hewlett-Packard Model 58%, serie II; Nermag R10-10 quadrupole).

3. RESULTS AND DISCUSSION

3.1. Gross composition

3.1.1. Lactation course

Mixed milks from the three animals of a same group were analyzed monthly over the lactation. A milk showed higher TNM and fat levels than O milk (*figure 1*). The maximum difference between fat levels, 9.8 g kg^{-1} , was in the early lactation, and it slowly decreased to reach a similar level in the late milks. Mean values for fat over the lactation were 32.7 and 26.3 g kg^{-1} , respectively for A and O milks. TNM showed a lesser variation during lactation. Mean values were 33.7 and 26.9 g kg^{-1}

Figure 1. Fat (a) and TNM (b) contents of A (—■—) and O (---□---) milks during the course of lactation. Mixed milk of three animals of each genotype, A and O.

Figure 1. Teneur en matière grasse (a) et en matière azotée totale (b) des laits A (—■—) et O (---□---) au cours de la lactation. Lait de mélange de trois animaux pour chaque groupe, A et O.

for A and O milks, the mean difference on the whole lactation being 6.8 g kg^{-1} . The whole difference in TNM could be explained by the α_s1 CN secretion level in A milks, which can reach, according to Grosclaude et al. [11] 3.6 g kg^{-1} milk for one allele, i.e. 7.2 g kg^{-1} for an homozygous goat.

3.1.2. Individual milks

The individual variability within a same group was studied through the analysis of three successive samplings of individual milks during June. Values corresponding to individual milks (average values of three determinations), as well as mean values of the whole A and whole O groups are reported on *table I*. For TNM, the variation between successive samples of the same animal was low, while large differences were found from one to another animal. For fat, the differences affected as well successive samples from the same animal as milks from different animals, so the resulting mean variation of fat in the group was higher. Constituents highly varied from one milk to the other leading

to large standard deviations for the average values.

The maximum TNM value obtained for an individual milk was 32.7 g kg^{-1} in A milks, and 27.9 g kg^{-1} in O milks. For fat, the maximum were respectively 29.5 and 29.3 g kg^{-1} .

It is noticeable that A milks had a lower pH value, by 0.08 pH unit . This is presumably in relation with the difference in TNM.

3.2. Minerals

Total and ultrafiltrable mineral levels were determined on individual milks. The mean values corresponding to the three milks of each group are reported in *table II*. For most of the constituents, the mean values for A and O milks were close, however in some cases standard deviations were high, showing a high individual variability. The only difference concerned ultrafiltrable calcium, however the high standard deviation reduced its signification.

Table I. Gross composition of individual A and O milks. Mean values of three samples collected on mid lactation, during June, g kg^{-1} milk (standard deviation).

Tableau I. Composition des laits individuels de variants A et O. Valeurs moyennes de trois échantillons collectés en milieu de lactation (mois de juin) ; g kg^{-1} lait (écart type).

	Goat	TS	Lactose	Fat	TNM	pH
A	a	112.9 (3)	44.3 (0.4)	29.5 (2)	32.7 (1.5)	6.57 (0.03)
	b	90.3 (4)	42.2 (0.5)	15.8 (4)	27.1 (0.5)	6.59 (0.06)
	c	112.7 (3)	44.9 (1)	29.3 (3)	32.5 (0.5)	6.46 (0.09)
Average A		105.3 (12)	43.8 (1)	24.9 (3)	30.8 (3)	6.54 (0.07)
O	1	86.0 (3)	45.4 (0.6)	14.3 (4)	22.0 (0.9)	6.61 (0.05)
	2	105.1 (5)	44.2 (1)	29.3 (3)	26.7 (1)	6.60 (0.08)
	3	101.7 (1)	45.6 (0.3)	23.0 (2)	27.9 (0.6)	6.64 (0.07)
Average O		97.6 (10)	45.1 (0.7)	22.2 (7.5)	25.5 (3)	6.62 (0.02)

Table II. Total and soluble minerals (mmol kg^{-1}) in A and O milks. Mean values of the three individual milks of a same group (standard deviation).

Tableau II. Minéraux totaux et solubles (mmol kg^{-1}) dans les laits A et O. Valeurs moyennes des trois laits individuels du même groupe (écart type).

		Ca	P	Mg	Na	K
Total	A	27.5 (2.3)	29.2 (2.8)	5.1 (0.0)	14.0 (1.4)	50.2 (5.0)
	O	26.9 (1.0)	28.0 (5.3)	4.5 (0.5)	14.3 (0.7)	49.1 (3.7)
Soluble	A	7.9 (0.2)	13.0 (1.7)	3.2 (0.2)	14.1 (1.8)	48.2 (4.7)
	O	10.9 (3.5)	12.6 (2.7)	3.1 (0.0)	14.0 (0.4)	47.3 (3.9)

3.3. Micellar casein

The total casein contents were 21.8 g kg^{-1} in A milk and 17.4 g kg^{-1} in O milk, as a mean of the three individual milk determinations. The difference between the two was 4.4 g kg^{-1} . The ratio CN/TNM was found 0.70 in A milk and 0.66 in O milk. The colloidal calcium related to casein was respectively 36 and 37 mg Ca g^{-1} casein in A and O milks.

Levels of the different caseins in individual milks are reported in *table III*. The α_{s1} CN was present only in A milks. Its average level in the milk calculated from the data was 4.8 g kg^{-1} . It explained the difference observed between the total casein levels of A and O milks. Nevertheless, this amount did not correspond to the total genetic potentiality of the A variant ($3.6 \times 2 \text{ g}$) as already discussed. Milks were analyzed in June, which roughly corresponded to the 15th week of lactation. Brown et al. [3] have noticed that this lactation stage corresponded to the lowest α_{s1} CN level observed in goat milk during all the lactation.

The hydrolytic activity of native plasmin-like proteases was tested in milks. A decrease in native β CN occurred (*figure 2*). After a 48 h incubation, 5.1 g kg^{-1} of native β CN disappeared in A milk, and 2.2 g kg^{-1} in O milk. This showed a higher plasmin-like proteolysis in A milk. If the substrate was in excess in the conditions of the test, it might be concluded that the plasmin-like protease level in A milk should be approximately two-fold the one in O milk. This higher plasmin-like activity seems to be associated in goat milks with the high secretion level α_{s1} CN variants: Brown et al. [3] have previously reported that γ caseins (which results from the hydrolysis of β CN by plasmin) were at higher levels in AB milks than in EE milks. Moreover, Delacroix-Buchet et al. [4] noticed that cheeses made from A milk (stirred curd type cheeses, pH 5.2) had a higher content of large peptides than cheeses from F milks. These peptides might originate from a higher endogenous proteolysis in A milk.

The size of casein micelles was also determined in the milk. The average diameter value obtained for A milk, 179

Figure 2. Residual native β casein in A (■) and O (□) milks under storage. (37 °C; NaN_3 20 $\mu\text{g mL}^{-1}$ and penicillin 10³ U mL⁻¹).

Figure 2. Teneur en caséine β native résiduelle dans les laits A (■) et O (□) après conservation (37 °C ; NaN_3 20 $\mu\text{g mL}^{-1}$ et pénicilline 10³ U mL⁻¹).

Table III. Mean concentration of total casein (CN) in the A and O milks ($n = 3$) and casein composition determined on a mixed milk from each type (standard deviation).

Tableau III. Teneur moyenne en caséine (CN) dans les laits A et O ($n = 3$) et composition de la caséine déterminée sur le mélange des laits d'un même type (écart type).

	TNM ----- (g kg ⁻¹)	CN (g kg ⁻¹)	CN/TNM ----- (0.03)	Casein composition (%)				
				κ CN	α_{s2} CN	α_{s1} CN	β CN	x
A	31.2 (3.8)	21.8 (2.2)	0.70 (0.03)	15	10	22	47	6
O	26.2 (2.9)	17.4 (3.0)	0.66 (0.05)	20	14	0	57	9

(S.D. = 7) nm, was lower than that of O milk, 253 (S.D. = 5) nm, which confirmed the results of a previous study [15].

3.4. Fatty acids

The total fatty acids (TFA) of A and O milks were similarly distributed between the different classes of fatty acids (table IV). Contrarily the free fatty acids (FFA) in A milk contained significantly

less unsaturated FFA than in O milk, and even less than in the own TFA of A milk.

Individual fatty acids were also quantified in the TFA and FFA of milks. Proportions of the main fatty acids (FA) are reported on figure 3.

3.4.1. TFA

In A milk, more short and medium chain length saturated TFA (C4 to C14) were contained, as well as more C18 and

less C16 than O milk. Such a difference was previously reported by Delacroix-Buchet et al. [4] comparing A and F milks, and seemed thus related to the A variant.

No difference in the unsaturated TFA was observed between A and O milks.

3.4.2. FFA

In both A and O milks, FFA contained significantly more saturated short or medium chain length (C4-C12) fatty acids than the corresponding TFA (*figure 3*). Furthermore, the proportions of the short chain FFA (C4, C6, C8) in O milk were higher than in A milk. In contrast, A milk had more long chain saturated FFA (C14, C16, C18) than O milk. Concerning unsaturated FFA, the only difference observed concerned C18:1 in A milk which was lower than in O milk FFA, and even than in its own TFA.

From these results, it appeared that the lipases in A and O milks could have slightly different specificity. O milk lipase seemed to have a high preferential acti-

vity on saturated short chain FA, while A milk lipase hydrolyzed the saturated FA more rapidly than the unsaturated ones.

The extent of lipolysis (FFA / TFA%) in A milk was notably lower than in O milk (*table IV*). Lipase in O milk could thus be more abundant and/or more active, as also noticed for F milks compared to A milks [4].

Combining results concerning the lipolysis level and the specific activity of the lipase, it can be calculated that the short chain FFA contents ($\mu\text{mol kg}^{-1}$ milk) were by 3-10 times higher in O milk than in A milk (*figure 4*).

3.5. Coagulation

The rennet coagulation of milks was studied on individual milks collected during three successive samplings. Coagulation times varied from 8 to 13 min, i.e. by $\sim 30\%$. No relation was found with the A or O milk group nor with the TNM level (not shown). On the contrary, the fir-

Table IV. Relative proportions (percentage of weight) of the different fatty acid classes in the total fatty acids (TFA) and the free fatty acids (FFA) and lipolysis level (FFA/TFA %) in A and O milks (mixed milks of each type, $n = 3$).

Tableau IV. Proportions relatives (% en poids) des différentes classes d'acides gras dans les acides gras totaux (TFA) et les acides gras libres (FFA). Taux de lipolyse (FFA/TFA %) dans les laits A et O (mélange des trois laits de chaque type).

		A milk	O milk
TFA % (w)	Normal saturated	75.9	74.9
	Branched saturated	2.0	1.9
	Mono-unsaturated	19.8	20.7
	Poly-unsaturated	2.2	2.4
FFA % (w)	Normal saturated	79.9	74.2
	Branched saturated	1.7	1.4
	Mono-unsaturated	16.6	21.4
	Poly-unsaturated	1.8	3.0
FFA / TFA %		0.4	1.9

Figure 3. Composition of total fatty acid and free fatty acid fractions (percentage weight) in A and O milks ($n = 3$).

Figure 3. Composition des fractions d'acides gras totaux et acides gras libres (% poids) dans les laits A et O ($n = 3$).

Figure 4. Molar concentration of free fatty acids in A and O milks ($\mu\text{mol kg}^{-1}$ milk).

Figure 4. Concentration molaire des acides gras libres dans les laits A et O ($\mu\text{mol kg}^{-1}$).

ming time of the curd (*figure 5a*) and its maximum firmness (*figure 5b*) were related to TNM.

Therefore A milks with their higher overall TNM had shorter times of firming and higher firmness. Nevertheless, the comparison on *figure 5* of A and O milks having the same TNM level ($27\text{--}28 \text{ g kg}^{-1}$), shows that O milks had lower perfor-

mances. This means that the specific composition of the A milk casein, containing α_{s1} CN and structured in micelles of a smaller size, favoured the aggregation of curd and enhanced its firmness. When TNM in milks was lower than $\sim 25 \text{ g kg}^{-1}$, the firming times are long, meaning a poor ability to aggregate, and experimental values were dispersed, meaning that curd

Figure 5. Rennet coagulation of A (■) and O (□) individual milks. **a.** Firming time (K 20, min). **b.** Curd firmness (aR, cm). 30 °C. Chymosin added 50 µg mL⁻¹ milk.

Figure 5. Coagulation présure des laits A (■) et O (□). Laits individuels. **a.** Temps de raffermissement (K 20, min). **b.** Fermeté du caillé (aR, cm). 30 °C. Chymosine 50 µg mL⁻¹.

formation did not proceed well. The casein concentration seemed to be the limiting factor for rennet coagulation in these milks. The aggregation of micelles could not proceed correctly. It has been likewise demonstrated that an ultrafiltration of milk, even to a low concentration factor, could improve the coagulation parameters of low TNM goat milks [18].

3.6. Volatile fraction

Twelve compounds were separated in the acidic volatile fraction and identified as free fatty acids from C4 to C12. The amounts extracted in the volatile fraction roughly corresponded to 2–5% of the total free fatty acid in milks (figures 4, 6). The level of each compound was by 2–6 times higher in O milk than in A milk. Standard deviations were low, highlighting the difference between the two milks. Levels were higher than the specific organoleptic threshold of the compounds, so that the results confirmed the differences in flavour previously observed, comparing A and O milks through organoleptic tests

(results not shown). Branched chain fatty acids, as 4 methyl C8 and 4 ethyl C8, reported as having a high specific goat flavour [2] were not detected (sensitivity threshold of the analysis: ~ 10 µg kg⁻¹ milk). As a matter of fact, it has been previously observed by the authors that these compounds are not present as free fatty acids in fresh drawn milk and that they can only be detected after a 24 h incubation time of the milks (results not published).

In the neutral fraction were characterized 32 compounds, including eight aldehydes, seven alcohols, three cetones and dimethylsulfide. Some of them were at higher levels in O milks, however a notable difference was obtained only for nonanal and 2-undecenal. All compounds in the neutral fraction were at levels lower than their organoleptic threshold.

4. CONCLUSION

The comparison of milks having a high level of α_{s1} CN (A milk) with milks totally deprived of α_{s1} CN (O milks) although carried on with a small number of goats, allo-

Figure 6. Molar concentration of aroma compounds extracted in the acidic volatile fraction of A milk (■) and O milk (□). $\mu\text{mol kg}^{-1}$ milk. Bars: standard deviations.

Figure 6. Concentration molaire des composés d'arôme extraits dans la fraction volatile acide des laits A (■) et O (□) ($\mu\text{mol kg}^{-1}$ lait). Barres : écarts types.

wed to demonstrate which milk characteristics were related to α_{s1} CN. These results confirm those already obtained comparing the A variant with low producing variants, such as E and F [4, 12, 20]. Amongst the differences observed between the milks, some can be explained by the presence of the α_{s1} CN itself in the milk, as the rennet coagulation characteristics (particularly firmness and time of firming), as they highly depend on TNM level and on the total casein content.

Some other differences noticed between A and O milks remained unexplained. Thus, A milk is different not only from O milk, but also from E and F milks, regarding to fatty acid composition, lipase activity and/or specificity and plasmin-like activity. This means that differences in the physiological activity of the mammary gland take place associated with the A variant, the nature of which is not presently known.

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REFERENCES

- [1] Boulanger A., Etude biochimique et génétique des protéines du lait de chèvre, Thèse de Dr 3^e cycle, Univ. Paris VIII, 1976.
- [2] Brennan C.P., Ha J.K., Lindsay R.C., Aroma properties and thresholds of some branched-chain and other minor volatile fatty acids occurring in milk fat and meat lipids, *J. Sens. Stud.* 4 (1989) 105–120.
- [3] Brown J.R., Law A.J.R., Knight C.H., Changes in casein composition of goat's milk during the course of lactation: physiological interferences and technological implications, *J. Dairy Res.* 62 (1995) 431–439.
- [4] Delacroix-Buchet A., Degas C., Lamberet G., Vassal L., Influence des variants AA et FF de la caséine α_{s1} caprine sur le rendement fromager et les caractéristiques sensorielles des fromages, *Lait* 76 (1996) 217–241.
- [5] Dumont J.P., Adda J., Isolement des constituants de l'arôme des fromages: comparaison des méthodes, *Lait* 52 (1972) 311–323.
- [6] Etievant P., Bayonove C., Aroma compounds of pomaces and wines from the variety Muscat de Frontignan, *J. Sci. Food Agric.* 34 (1983) 393–403.

- [7] FIL-IDF, Determination of total phosphorus content in cheese, Standard no. 33 B, (1982)
- [8] Folch J., Less M., Sloane Stanley G.H., A simple method for the isolation and purification of total lipids from animal tissues, *J. Biol. Chem.* 226 (1957) 497-509.
- [9] Forss D.A., Jacobsen V.M., Ramshaw E.H., Concentration of volatile compounds from dilute aqueous solutions, *J. Agric. Food Chem.* 15 (1967) 1104-1107.
- [10] Gandemer G., Morvan-Mahi B., Meynier A., Lepercq M., Quantitative and qualitative analysis of free fatty acids in meat and meat products using ion exchange resin, in : 37th Int. Congr. Meat Sci. Technol. Kulmbach, Germany, 3, 1991, pp. 1139-1142, .
- [11] Grosclaude F., Mahé M.F., Brignon G., Di Stasio L., Jeunet R., A mendelian polymorphism underlying quantitative variations in goat α_{s1} casein, *Genet. Sel. Evol.* 19 (1987) 399-411.
- [12] Lamberet G., Degas C., Delacroix-Buchet A., Vassal L., Influence de caractères liés aux allèles A et F de la caséine α_{s1} caprine sur la flaveur chèvre: fabrications fromagères avec échange de protéines et de matières grasses, *Lait* 76 (1996) 349-361.
- [13] Mahé M.F., Grosclaude F., α_{s1} CN D, another allele associated with a decreased synthesis rate at the caprine α_{s1} casein locus, *Genet. Sel. Evol.* 21 (1989) 127-129.
- [14] Needs E.C., Ford G.D., Owen A.J., Tuckley B., Anderson M., A method for the quantitative determination of individual free fatty acids in milk by ion exchange resin adsorption and gas liquid chromatography, *J. Dairy Res.* 50 (1983) 321-329.
- [15] Pierre A., Michel F., Le Graet Y., Variation in size of goat milk casein micelles related to casein genotype, *Lait* 75 (1995) 489-502.
- [16] Remeuf F., Contribution à l'étude des aptitudes fromagères du lait de chèvre, Thèse de Dr Ingénieur, INA Paris-Grignon, 1988.
- [17] Remeuf F., Influence du polymorphisme génétique de la caséine α_{s1} caprine sur les caractéristiques physico-chimiques et technologiques du lait, *Lait* 73 (1993) 549-557.
- [18] Remeuf F., Verdalet-Guzman I., Lenoir J., Technological adjustment of goat milk containing low synthesis-rate α_{s1} -casein variants, *Int. Dairy J.* 5 (1995) 381-392.
- [19] Rowland S.J., The determination of the nitrogen distribution in milk, *J. Dairy Res.* 9 (1938) 42-46.
- [20] Vassal L., Delacroix-Buchet A., Bouillon J., Influence des variants AA, EE et FF de la caséine α_{s1} caprine sur le rendement fromager et les caractéristiques sensorielles de fromages traditionnels: premières observations, *Lait* 74 (1994) 89-103.
- [21] Wolff R.L., Fabien R.J., Utilisation de l'isopropanol pour l'extraction de la matière grasse de produits laitiers et pour l'estérification subséquente des acides gras, *Lait* 69 (1989) 33-46.