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Physico-chemical characteristics of goat and sheep milk☆

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Abstract

Physico-chemical characteristics of milk are related to its composition for a particular animal species. Sheep milk contains higher levels of total solids and major nutrient than goat and cow milk. Lipids in sheep and goat milk have higher physical characteristics than in cow milk, but physico-chemical indices (i.e., saponification, Reichert Meissl and Polenske values) vary between different reports. Micelle structures in goat and sheep milk differ in average diameter, hydration, and mineralization from those of cow milk. Caprine casein micelles contain more calcium and inorganic phosphorus, are less solvated, less heat stable, and lose β-casein more readily than bovine casein micelles. Renneting parameters in cheese making of sheep milk are affected by physico-chemical properties, including pH, larger casein micelle, more calcium per casein weight, and other mineral contents in milk, which cause differences in coagulation time, coagulation rate, curd firmness, and amount of rennet needed. Renneting time for goat milk is shorter than for cow milk, and the weak consistency of the gel is beneficial for human digestion but decreases its cheese yield. Triacylglycerols (TAG) constitute the biggest part of milk lipids (nearly 98%), including a large number of esterified fatty acids. Sheep and goat milk also have simple lipids (diacylglycerols, monoacylglycerols, cholesterol esters), complex lipids (phospholipids), and liposoluble compounds (sterols, cholesterol esters, hydrocarbons). The average fat globule size is smallest (<3.5 μm) in sheep milk followed by goat and cow milk. Five fatty acids (C10:0, C14:0, C16:0, C18:0, and C18:1) account for >75% of total fatty acids in goat and sheep milk. Levels of the metabolically valuable short and medium chain fatty acids, caproic (C6:0) (2.9%, 2.4%, 1.6%), caprylic (C8:0) (2.6%, 2.7%, 1.3%), capric (C10:0) (7.8%, 10.0%, 3.0%), and lauric (C12:0) (4.4%, 5.0%, 3.1%) are significantly higher in sheep and goat than in cow milk, respectively. Principal caseins (CN) in goat, sheep and cow milk are α_{s1}-CN, α_{s2}-CN, β-CN and κ-CN. The main forms of caprine and ovine caseino-macropeptides (CMP), which are the soluble C-terminal derivatives from the action of chymosin on κ-casein during the milk clotting process of cheesemaking, have been identified and are a good source of antithrombotic peptides. Sheep and goat milk proteins are also important sources of bioactive angiotensin converting enzyme (ACE) inhibitory peptides and antihypertensive peptides. They can provide a non-immune disease defence and control of microbial infections. Important minor milk proteins include immunoglobulins, lactoferrin, transferrin, ferritin, proteose peptone, calmodulin (calcium binding protein), prolactin, and folate-binding protein. Non-protein nitrogen (NPN) contents of goat and human milks are higher than in cow milk. Taurine in goat and sheep milk derived from sulphur-containing amino acids has important metabolic functions as does carnitine, which is a valuable nutrient for the human neonate. Mineral and vitamin contents of goat and sheep milk are mostly higher than in cow milk.

Keywords: Goat milk; Sheep milk; Physico-chemical characteristics; Lipids; Proteins; Bioactive peptides; Minerals, Vitamins

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1. Introduction

Dairy goat and dairy sheep farming are a vital part of the national economy in many countries, especially in the Mediterranean and Middle East region (FAO, 2003), and are particularly well organized in France, Italy, Spain, and Greece (Park and Haenlein, 2006). However, large-scale industrialization of the dairy goat and dairy sheep sectors in many countries is limited by low volume and seasonal cyclicity of individual milk production, around 50 kg annually (Juàrez and Ramos, 1986; FAO, 1997).

Information on composition and physico-chemical characteristics of goat and sheep milk is essential for successful development of dairy goat and sheep industries as well as for the marketing the products. There are distinct differences in physico-chemical characteristics between goat, sheep and cow milks. The composition of market cow milk is expected to have minimal changes throughout the year, because the milk entering bulk tank from the cow herds would vary little by seasons because of year-round breeding. On the other hand, this is quite different from sheep and goat milk, which is predominantly produced by seasonal breeding of ewes and does (Haenlein and Wendorff, 2006). Therefore, changes in goat and sheep milk compositions occur by seasons, because towards the end of the lactation, the fat, protein, solids and mineral contents increase, while the lactose content decreases (Brozos et al., 1998; Haenlein, 2001, 2004).

Goat milk differs from cow or human milk in having better digestibility, alkalinity, buffering capacity, and certain therapeutic values in medicine and human nutrition (Haenlein and Caccese, 1984; Park and Chukwu, 1989; Park, 1994). Sheep milk has higher specific gravity, viscosity, refractive index, titratable acidity, and lower freezing point than average cow milk (Haenlein and Wendorff, 2006). Lipids in sheep and goat milk have higher physical characteristics than in cow milk, but there are variations between different reports (Anifantakis, 1986; Park, 2006a).

The purpose of this paper is to review the specific characteristics of physico-chemical properties of goat and sheep milks in comparison with those of cow milk, with emphasis on lipid and protein fractions including bioactive peptides.

2. Basic composition of goat and sheep milk

Compositions of goat, sheep, cow and human milks are different (Table 1), but vary with diet, breed, individuals, parity, season, feeding, management, environmental conditions, locality, stage of lactation, and health status of the udder (Parkash and Jenness, 1968; Schmidt, 1971; Linzell and Peaker, 1971; Larson and Smith, 1974; Posati and Orr, 1976; Underwood, 1977; Jenness, 1980; Haenlein and Caccese, 1984; Juàrez and Ramos, 1986; Park, 1991, 2006a).

Table 1
Average composition of basic nutrients in goat, sheep, cow and human milk

Composition	Goat	Sheep[a]	Cow	Human
Fat (%)	3.8	7.9	3.6	4.0
Solids-not-fat (%)	8.9	12.0	9.0	8.9
Lactose (%)	4.1	4.9	4.7	6.9
Protein (%)	3.4	6.2	3.2	1.2
Casein (%)	2.4	4.2	2.6	0.4
Albumin, globulin (%)	0.6	1.0	0.6	0.7
Non-protein N (%)	0.4	0.8	0.2	0.5
Ash (%)	0.8	0.9	0.7	0.3
Calories/100 ml	70	105	69	68

Data from Posati and Orr (1976), Jenness (1980), Larson and Smith (1974) and Haenlein and Caccese (1984).
[a] Anifantakis et al. (1980).

Sheep milk contains higher total solids and major nutrient contents than goat and cow milk (Table 1). Sheep colostrum in the early post-partum period is also higher in basic nutrients than cow colostrum: fat 13.0% and 5.1%, protein 11.8% and 7.1%, lactose 3.3% and 3.6%, minerals 0.9% and 0.9%, total solids 28.9% and 15.6%, respectively (Anifantakis, 1986).

3. Physico-chemical characteristics

3.1. Comparison of goat, sheep and cow milk

The differences are shown in Tables 1–3. Density of goat milk is comparable to that of cow milk, but is lower than in sheep milk, while both have higher specific gravity, viscosity, titratable acidity, but lower refractive index and freezing point than cow milk (Parkash and Jenness, 1968; Haenlein and Wendorff, 2006). Surface tension of goat milk is within the range of cow milk (Juàrez and Ramos, 1986), but viscosity of goat milk is slightly higher, while that of sheep milk is much higher than in cow milk (Table 2).

Lipids in sheep and goat milk have generally higher physical characteristics than in cow milk (Table 3; Anifantakis, 1986; Park, 2006a). Flavor constituents in sheep milk are similar between the three species, but differ quantitatively over cow milk (Moio et al., 1993).

The unsaponifiable matter of milk fat and acid values are not different between goat and cow milk (Table 3),

Table 2
Some physical properties of goat, sheep and cow milk

Properties	Goat milk[a]	Sheep milk[b]	Cow milk[c]
Specific gravity (density)	1.029–1.039	1.0347–1.0384	1.0231–1.0398
Viscosity, C_p	2.12	2.86–3.93	2.0
Surface tension (Dynes/cm)	52.0	44.94–48.70	42.3–52.1
Conductivity (Ω^{-1} cm^{-1})	0.0043–0.0139	0.0038	0.0040–0.0055
Refractive index	1.450 ± 0.39	1.3492–1.3497	1.451 ± 0.35
Freezing point (−°C)	0.540–0.573	0.570	0.530–0.570
Acidity (lactic acid %)	0.14–0.23	0.22–0.25	0.15–0.18
pH	6.50–6.80	6.51–6.85	6.65–6.71

[a] Juàrez and Ramos (1986).
[b] Kurkdjian and Gabrielian (1962) and Haenlein and Wendorff (2006).
[c] Jenness et al. (1974).

but goat milk has lower iodine values, which reflects its greater amount on lower and unsaturated fatty (Park, 2006a). Cow milk has a higher saponification value and slightly greater refractive index than goat milk, which relates to the longer carbon chains and saturation of the fatty acids (Park, 2006a). The positional distribution of fatty acids in goat milk triglycerides has most of the short chain acids (C4–C8) esterified at position *sn*-3 of the glycerol moiety, while the longer chains (>C10) are at position *sn*-2, and triglycerides are synthesized from a pool of long-chain 1,2-diglycerides (Tziboula-Clarke, 2003).

Goat milk may have lower Reichert Meissl and higher Polenske values than cow milk, suggesting that goat milk fat contains less soluble and more insoluble volatile FA than cow milk fat (Table 3; Park, 2006a), although there are different values in the literature for all three species (Anjaneyulu et al., 1985; Juàrez and Ramos, 1986), and those for sheep milk are sparse (Table 3).

Remeuf and Lenoir (1986) reported that the relative proportions of the major casein components of goat milk are quite different from those in cow milk. Goat milk contains less α_s-casein, and often has more α_{s2} than α_{s1}-casein. The latter is present in highly variable amounts depending on individual goats (Mora-Gutierrez et al., 1991). Proportions of κ-casein and especially β-casein are higher in goat than in cow milk.

Casein contents in goat milk range from 16 to 26 g/L, the proportions of NPN of the total nitrogen content are between 3% and 13%, the ionized calcium levels between 0.07 and 0.19 g/L, the total inorganic phosphorus between 0.45 and 1.0 g/L (Remeuf and Lenoir, 1986),

Table 3
Comparison of physico-chemical characteristics of lipids and micelle structures between goat, sheep and cow milk

Characteristics	Goat milk[a]	Sheep milk[b]	Cow milk[a]
Physico-chemical values[c]			
Unsaponifiable matter of milk fat (%)	0.41 ± 0.02	n.a.	0.41 ± 0.02
Acid value	0.47 ± 0.02	0.22–0.25	0.48 ± 0.05
Iodine value	19–20	20–35	27.09 ± 1.26
Saponification value	228.6 ± 5.24	230–245	232.3 ± 7.61
Reichert Meissl value	19–20	25–31	25–33
Polenske value	1.80 ± 0.35	1.6–1.5	1.4–1.3
Fat globule diameter (μm)	3.49	3.30	4.55
Micelle structure[d]			
Non-centrifugal casein (% of total casein)	8.7	n.a.	5.7
Average diameter (nm)	260	193	180
Hydration of micelle (g/g MS)	1.77	n.a.	1.9
Mineralization of micelle (g/ca/100 casein)	3.6	3.7	2.9

n.a. = not available.
[a] Park (2006a).
[b] Anifantakis (1986).
[c] Anjaneyulu et al. (1985).
[d] Remeuf and Lenoir (1986).

depending on individuals, lactation period, and sample differences (Parkash and Jenness, 1968).

3.2. Casein micelle characteristics of goat and sheep milk

Micelle structures of goat and sheep milk differ from cow milk in average diameter, hydration and mineralization (Table 3). Caprine casein micelles contain more calcium, inorganic phosphorus, and non-centrifugal casein, are less solvated, less heat stable, and lose β-casein more readily than bovine casein micelles (Jenness, 1980; Remeuf and Lenoir, 1986). Sheep milk is similar to goat milk in micelle characteristics. Average mineralization levels of micelles in goat and sheep milk are higher than in cow milk (Table 3). There is an inverse relationship between the mineralization of the micelle and its hydration, which also means that goat milk is less hydrated than cow milk (Table 3; Soods et al., 1979; Remeuf and Lenoir, 1986).

Juàrez and Ramos (1986) reported soluble casein contents in goat and cow milk are 10% and 1% at 20 °C and 25% and 10% at 5 °C, respectively. O'Connor and Fox (1973) noted that low storage temperatures had a marked influence on the micellar system of milk. Cooling led to a partial solubilization of colloidal calcium phosphate and β-casein. These changes are responsible for different cheesemaking properties of milk, especially a decrease in cheese yield. The β-casein in caprine milk is more soluble on cooling than the homolog in bovine milk (O'Connor and Fox, 1973).

High ionic calcium content and low micellar solvation in caprine milk may contribute to heat instability (Remeuf, 1992), which is considerably less than for bovine milk. Raynal and Remeuf (1998) showed, that if the interactions of casein with whey proteins are excluded, heat treatment up to 90 °C for 10 min has little effect on bovine casein micelles. However, the size of caprine casein micelles begins to increase at 85 °C and after 10 min reaches a value of about 1.25 times of normal and attains it also at 90 °C after only 1 min (Raynal and Remeuf, 1998; Trujillo, 2005). Low casein content and other characteristics such as α_s-casein proportions and micellular size are believed to be responsible for the weak texture of caprine milk yogurt. Horne (1998) proposed a model of casein micelle, which is dependent on a balance between electrostatic repulsion and hydrophobic interaction, where colloidal calcium phosphate crosslinks the caseins and neutralizes negatively charged phosphoserine groups, allowing the formation of hydrophobic interaction between caseins.

3.3. Relationship between physico-chemical properties and rennetability

Cheese making, i.e. renneting properties, of sheep milk are affected by its physico-chemical properties, including pH, larger casein micelle, more calcium per casein weight, and other mineral concentrations in milk, which cause differences in coagulation time, coagulation rate, curd firmness, and amount of rennet needed (Ramos and Juarez, 2003).

Renneting time for goat milk is shorter than for cow milk, and the weak consistency of the gel explains mediocre cheese suitability of goat milk (Parkash and Jenness, 1968; Remeuf and Lenoir, 1986). Renneting time and maximum firmness of the gel are expressed on a scale from 1 to 4, setting speed on a scale from 1 to 9 (Remeuf and Lenoir, 1986). The weight of serum retained in the centrifuged curd is subject to smaller variations between 1 and 2 score. Storry et al. (1983) found, that the maximum firmness of the gel of goat milk is usually much less, and even a gel from goat milk with an equal casein content is not as firm as from cow milk. The casein content of milk has a significant influence on rheological properties of the rennet gel, its setting speed and its maximum firmness. Remeuf and Lenoir (1986) observed significant correlations between casein content and the proportion of α_{s1}-casein, between the casein content and levels of colloidal Ca and inorganic phosphorus, between levels of colloidal Ca and inorganic phosphorus and the firmness of the gel or its setting speed, and between the degree of hydration of the micelles and their mineralization. This confirms similar reverse correlations reported by Storry et al. (1983) for casein content with the quantity of serum retained in the centrifuged curd from goat, cow and sheep milk. Also renneting time was mainly influenced by the pH value of the milk.

Van Hooydonk et al. (1987) reported, that heat and pressure-induced increase of rennet clotting time could be explained by whey protein denaturation and binding with κ-casein, which delays the action of rennet enzymes via repulsion or steric hindrance slowing the enzymatic phase of coagulation. Heating (65–85 °C for 5–35 min) had less pronounced effects on rennet clotting time and rate of curd firming in goat and ewe milk than in cow milk (Raynal and Remeuf, 1998; Montilla et al., 1995), suggesting that heated goat milk has the same crosslinking capacity as unheated milk (Trujillo, 2005).

4. Carbohydrates in goat and sheep milk

Milk sugar, lactose, is the major carbohydrate in goat, sheep and cow milk. It is synthesized from glucose in the

mammary gland with the required active participation of the milk protein α-lactalbumin (Larson and Smith, 1974). Lactose is a valuable nutrient, because it favors intestinal absorption of calcium, magnesium and phosphorus, and the utilization of Vitamin D (Campbell and Marshall, 1975). Lactose is a disaccharide made up of a glucose and a galactose molecule, which may also be present in small free amounts (Park, 2006a). Lactose is of major importance for maintaining osmotic equilibrium between the blood stream and the alveolar cells of the mammary gland during milk synthesis, and secretion into the alveolar lumen and the duct system of the udder (Larson and Smith, 1974). Lactose is found in varying concentrations in the milk of all mammals except for seals.

Lactose content of goat milk is about 0.2–0.5% less than that of cow milk (Posati and Orr, 1976; Haenlein and Caccese, 1984; Chandan et al., 1992). Lactose in sheep milk as in other ruminants is lower at the beginning of lactation in colostrum and towards the end of lactation, contrary to the behavior of fat and protein contents in milk (Pulina and Bencini, 2004; Haenlein and Wendorff, 2006). Compared to cow milk, lactose contents in sheep milk are at about the same level, while fat and protein levels are much higher (Table 1). This makes sheep milk lactose actually less in proportion to their total solids compared to cow milk total solids (22–27% versus 33–40%, respectively) (Ramos and Juarez, 2003).

Milk of most wild or less domesticated mammals usually has more fat and lower contents of lactose than goat milk (Park, 2006b). Cow milk contains minor levels of monosaccharides and oligosaccharides (Chandan et al., 1992). Carbohydrates other than lactose found in sheep and goat milk are oligosaccharides, glycopeptides, glycoproteins, and nucleotide sugars in small amounts (Larson and Smith, 1974), but their functions in sheep and goat milk have been studied little. Milk oligosaccharides have considerable antigenic properties and are valuable in growth promotion of the intestinal flora of the newborn.

Nucleotide sugars in milk are of particular interest, since they are the glycosyl donors for glycosyltransferase in milk and mammary gland, and are the precursors of glycoproteins, glycolipids, and oligosaccharides in the biosynthesis of milk. According to Johke (1974), goats have a remarkably high nucleotide content of about 154 μmol/100 ml in normal milk, followed by sheep (93 μmol/100 ml), and cow milk (68 μmol/100 ml). Colostrum, however had 271 μmol/100 ml for goats, 499 μmol/100 ml for sheep, and 58 μmol/100 ml for cows, respectively, while human milk contained low levels at 5 μmol/100 ml in normal milk and 6 μmol/100 ml in colostrum.

5. Lipids in sheep and goat milk

5.1. General aspects of milk fat

Lipids are the most important components of milk in terms of cost, nutrition, and physical and sensory characteristics that they impart to dairy products. Triacylglycerols (TAG) constitute the biggest group (nearly 98%), including a large number of esterified fatty acids. Consequently, TAG composition is very complex. Along with TAG, the lipid composition of ewe and goat milk presents other simple lipids (diacylglycerols, monoacylglycerols, cholesterol esters), complex lipids (phospholipids) and liposoluble compounds (sterols, cholesterol esters, hydrocarbons) (Park, 2006a; Haenlein and Wendorff, 2006).

Lipids are present in the form of globules, which in ewe and goat milk are characteristically abundant in sizes less than 3.5 μm (Table 3). Some studies found that the average fat globule size is smallest in sheep milk followed by goat milk (65% of globules less than 3 μm) (Mens, 1985) (Table 3). This is advantageous for digestibility and a more efficient lipid metabolism compared with cow milk fat (Park, 1994). Mehaia (1995) reported average fat globule sizes in this decreasing order: cow > ewe > goat, which is not quite consistent with some other research (Anifantakis, 1986; Juàrez and Ramos, 1986). Additionally, bovine milk creams up more rapidly than caprine milk because of agglutination, which causes clustering of the fat globules, but agglutinin is absent in goat milk (Jenness and Parkash, 1971). No appreciable differences have been found in the mechanism of milk fat globule secretion in sheep and goats versus cows. Structure and composition of the membrane is similar in the three species and represents approximately 1% of total milk fat volume (Scolozzi et al., 2003). The phospholipid profile is similar to that of the plasma membrane, which may confirm a common origin. This fraction accounts for roughly 0.8% of total lipids.

5.2. Fatty acids (FA)

Most FA, from acetic (C2:0) to arachidic acid (C20:0), contain an even number of carbon atoms. Five fatty acids (C10:0, C14:0, C16:0, C18:0, and C18:1) account for >75% of total FA in goat and sheep milk (Table 4). Levels of the metabolically valuable short and medium chain FA, caproic (C6:0) (2.9%, 2.4%, 1.6%), caprylic (C8:0)

Table 4
Mean values and minimum and maximum contents of main fatty acids (% in total fatty acid methyl esters) in sheep and goat milk fat

Fatty acid	Sheep milk fat[a]		Goat milk fat[b]	
	Mean	Mininum/maximum	Mean	Minimum/maximum
C4:0	3.51	3.07–3.93	2.18	1.97–2.44
C6:0	2.90	2.68–3.44	2.39	2.03–2.70
C8:0	2.64	2.10–3.27	2.73	2.28–3.04
C10:0	7.82	5.54–9.73	9.97	8.85–11.0
C10:1	0.26	0.23–0.31	0.24	0.19–0.38
C12:0	4.38	3.48–4.92	4.99	3.87–6.18
C12:1	0.04	0.03–0.05	0.19	0.10–0.40
C13:0	0.17	0.13–0.22	0.15	0.06–0.28
C14:0	10.4	9.85–10.7	9.81	7.71–11.2
iso-C15:0	0.34	0.26–0.43	0.13	0.12–0.15
anteiso-C15:0	0.47	0.33–0.60	0.21	0.17–0.24
C14:1	0.28	0.19–0.50	0.18	0.17–0.20
C15:0	0.99	0.89–1.11	0.71	0.46–0.85
iso-C16:0	0.21	0.17–0.26	0.24	0.17–0.40
C16:0	25.9	22.5–28.2	28.2	23.2–34.8
iso-C17:0	0.53	0.44–0.59	0.35	0.24–0.52
anteiso-C17:0	0.30	0.26–0.36	0.42	0.30–0.50
C16:1	1.03	0.74–1.27	1.59	1.00–2.70
C17:0	0.63	0.58–0.70	0.72	0.52–0.90
C17:1	0.20	0.17–0.22	0.39	0.24–0.48
C18:0	9.57	8.51–11.0	8.88	5.77–13.2
C18:1 total	21.1	17.8–23.0	19.3	15.4–27.7
C18:2 total	3.21	2.89–3.57	3.19	2.49–4.34
C20:0	0.45	0.36–0.52	0.15	0.08–0.35
C18:3	0.80	0.52–1.04	0.42	0.19–0.87
C18:2 conjugate total	0.74	0.56–0.97	0.70	0.32–1.17

[a] Goudjil et al. (2004).
[b] Alonso et al. (1999).

(2.6%, 2.7%, 1.3%), capric (C10:0) (7.8%, 10.0%, 3.0%), and lauric (C12:0) (4.4%, 5.0%, 3.1%) are significantly higher in sheep and goat than in cow milk, respectively (Alonso et al., 1999; Goudjil et al., 2004). These FA are associated with the characteristic flavours of cheeses and can also be used to detect admixtures of milk from different species.

The most important factor between the intrinsic and extrinsic variables to modulate milk FA composition is the feed, in particular adding lipid supplement to the diet as recently reviewed for cows (Jensen, 2002), goats (Chilliard et al., 2003), and sheep (Bocquier and Caja, 2001). Changes in FA profile of ovine and caprine milk fat may not differ substantially from the pattern described for cow milk. If there are differences between ruminants, then goats appear to be the exception rather than ewes or cows (Chilliard and Ferlay, 2004). To increase levels of polyunsaturated fatty acids (PUFA) in milk, dietary PUFA oil intake and factors which decrease their hydrogenation in the rumen have been successful for goat milk, such as trapping of FA in vegetable cells, high forage/concentrate ratios, and PUFA rich protected fat (Chilliard and Ferlay, 2004; Sanz Sampelayo et al., 2004). Chiofalo et al. (2004) found increases of monounsaturated fatty acids (MUFA) in milk after the administration of olive cake to ewe feed.

5.2.1. *Odd-number and branch-chain saturated fatty acids*

The main point of quantifying other minor milk lipid components, branch-chain (BCFA) and odd-number chain saturated fatty acids is, that volatile BCFA lend characteristic flavours to many dairy foods. Their amounts in cheese are dependent on the composition of the milk fat substrate. BCFA concentration in sheep milk fat (2.0% of total FA; Goudjil et al., 2004) was made up of six different acids: *iso*-C14, *iso*- and *anteiso*-C15, *iso*- and *anteiso*-C17, and *iso*-C16, which are also predominant in bovine milk (Jensen, 2002). Thirty-six BCFA (mostly monomethylates) were quantified in goat milk (Alonso et al., 1999). Of these, the most important quantitatively (>0.1%) were the same as in sheep milk (Table 4). Different authors (Massart-Leen et al., 1981; Wolf, 1995) have emphasised the wide

range of monomethyl-branched components, other than *iso*- and *anteiso*-FA, mainly with methyl substitution of C4 and C6, which are present in caprine milk fat but are absent in bovine milk. Alonso et al. (1999) identified and quantified 30 minor BCFA (ranging from 0.004 to 0.765 mg/g of total FA) by gas chromatography/mass spectrometry (GC/MS). Of these BCFA, 25 were identified as monomethyl BCFA, two were dimethyl BCFA, and four were ethyl BCFA. Noteworthy in ethyl BCFA was the presence of 4-ethyloctanoate. This acid and 4-methyloctanoate lend characteristic (goaty and muttony) flavours to dairy products, but other BCFA such as 3-methylbutanoate, 4-methylpentanoate, and 8-methylnonanoate, also identified in bovine milk, determine the characteristic flavour of dairy foods (Ha and Lindsay, 1991; Park, 2001; Whetstine and Drake, 2006).

5.2.2. Mono-unsaturated trans fatty acids (MUTFA, TFA)

TFA content in milk fat ranges from 2.5% to 5% of total FA, depending on the species and the season. In general, sheep milk presented the highest quantities, after cow and finally goat milk fat. In recent years, TFA intake has been associated with the risk of coronary heart disease. The main daily source of TFA consumed by humans is partially hydrogenated vegetable fats and oils, although these compounds also occur naturally in caprine, ovine and bovine milk. Monoene TFA are the majority in all species. However, the isomer profile of hydrogenated vegetable fats is very different.

During hydrogenation of vegetable fats a range of *trans* mono-unsaturated FA are principally formed (e.g. *trans*-9C18:1, elaidic acid), while the main TFA in milk fat is *trans*-11C18:1, vaccenic acid (TVA) (IDF, 2005). The importance of TVA lies in its role as a precursor in the synthesis of the main isomer of the nutritionally valuable conjugated linoleic acid (CLA), rumenic acid (RA) (*cis*-9 *trans*-11C18:2), which occurs in the mammary gland (Griinari and Bauman, 1999) and also in some human tissues (Turpeinen et al., 2002).

The proportion of vaccenic acid in milk fat total TFA is similar in the three species (around 45–60%; Wolf, 1995; Alonso et al., 1999; Precht et al., 2001; Jensen, 2002; Goudjil et al., 2004). Elaidic acid is only present in considerably smaller amounts (average 4.3%, 4.7%, 6.1%) of total TFA in cow, sheep and goat milk fat, respectively (Precht et al., 2001). In contrast to the majority of hydrogenated vegetable oils, which are rich in *trans*-9 and *trans*-10C18:1 FA, the consumption of dairy products provides very little intake of these components.

5.2.3. Octadecadienoic isomers

Mean linoleic acid content (*cis*-9 *cis*-12C18:2) accounts for 70–75% of total C18:2, excluding CLA, in goat, sheep and cow milk (Jensen, 2002; Chilliard and Ferlay, 2004; Goudjil et al., 2004), whereas the rest of the *trans* C18:2 isomer group represents slightly more than a quarter of this fraction in sheep milk fat and 0.5–0.9% of the total FA (Goudjil et al., 2004; Luna et al., 2005a). The data reported for cow milk for the *trans* C18:2 isomer group are similar or slightly higher, although the range of variation is large (0.6–1.1), because these isomers vary with diet (Precht and Molkentin, 2000). In goat milk the available data on *trans* C18:2 isomer content are lower than in ewe milk fat: 0.2–0.5% of the total FA (Chilliard et al., 2003; Chilliard and Ferlay, 2004).

5.2.4. Conjugated linoleic acid (CLA)

The generic name CLA is a collective term embracing all positional and geometric isomers of linoleic acid, which contain a conjugated double bond system. Data from animal models have been used to suggest that the RA isomer is responsible for CLA anticarcinogenic properties, as well as antiatherogenic effects (Khanal, 2004; Parodi, 2004; Lee et al., 2005b), whereas the *trans-10 cis-12* CLA isomer has lean body mass-enhancing properties (Belury, 2002; Pariza, 2004). Total CLA mean content seems to decrease in the following order: ewe > cow > goat milk fat, 1.08%; 1.01% and 0.65%, respectively (Jahreis et al., 1999), but information about small ruminants is too scant to offer a full picture.

Milk CLA concentration in different ruminant species varied with the season mainly due to variations in feeding factors (Chilliard and Ferlay, 2004). The greatest seasonal differences were measured in sheep milk, 1.28% in summer and 0.54% at the end of the winter period (Jahreis et al., 1999). Milk fat has been reported to contain not only the highest level of the beneficial CLA, but also the highest content of TVA (physiological precursor of CLA) (Jahreis et al., 1999).

RA in cow milk represents approximately 80% of total CLA. The remaining 20% consist of several minor isomers of which *trans-7 cis-9* and *trans-11 cis-13*C18:2 are the most prominent (Parodi, 2003; Khanal, 2004). Most studies on ewe milk fat (Prandini et al., 2001; Barbosa et al., 2003) have quantified them by GC and shown that the GC peak can include more than one component and minor CLA isomers masked by the RA peak (Luna et al., 2005a). The combination of GC/MS of fatty acid methyl esters (FAME) and 4,4-dimethyloxazoline derivatives (DMOX) with silver-ion high performance liquid chromatography (Ag^+-HPLC) of FAME have

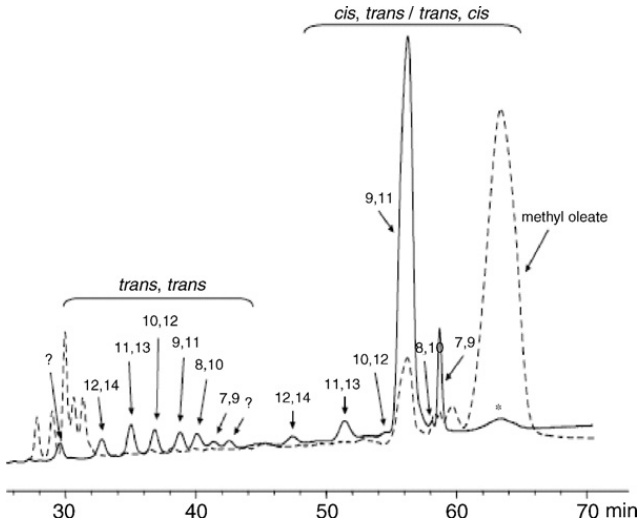

Fig. 1. Ag^+-HPLC profile of sheep milk fat fatty acid methyl esters using UV detector at 234 nm (solid line) and 205 nm (broken line) and three columns in series. Asterisk represents methyl oleate (Luna et al. (2005a) with permission of Cambridge Univ. Press).

reported CLA isomer profiles in five different herds of ewes (Luna et al., 2005a). RA represented more than 75% of total CLA; *trans*-11 *trans*-13, *cis*/*trans* plus *trans*/*cis* 11–13, and *cis*/*trans* plus *trans*/*cis* 7–9 were the main isomers after RA. Minor amounts of 8–10 and 10–12C18:2 isomers were also found (Fig. 1).

Table 5 shows the range of the relative composition of CLA isomers in ewe milk fat by Ag^+-HPLC (Luna et al., 2005a) similar to that reported in cow milk (Parodi, 2003; Khanal, 2004). In goat milk fat, although there are several papers reporting data on total CLA (Mir et al., 1999; Jahreis et al., 1999; Chilliard et al., 2002; Chilliard and Ferlay, 2004), there is no information about minor isomers.

Table 5
Relative composition (% of total conjugated linoleic acid) determined by silver-ion high performance liquid chromatography of conjugated linoleic acid (CLA) isomers in sheep and cow milk fat

CLA isomers	Sheep milk fat[a]	Cow milk fat[b]
12-*Trans*, 14-*trans*	1.31–3.47	0.9–2.8
11-*Trans*, 13-*trans*	1.21–5.08	2.3–4.2
10-*Trans*, 12-*trans*	1.17–1.77	0.5–0.6
9-*Trans*, 11-*trans*	1.13–1.99	1.5–2.0
8-*Trans*, 10-*trans*	1.05–1.37	0.3–0.4
7-*Trans*, 9-*trans*	0.48–0.61	0.6–2.4
12–14 (*c*, *t*/*t*, *c*)	0.52–1.83	0.4–0.8
11–13 (*c*, *t*/*t*, *c*)	0.76–4.23	–
10–12 (*c*, *t*/*t*, *c*)	0.28–0.41	0.4–1.1
9–11 (*c*, *t*/*t*, *c*)	76.5–82.4	76.5–83.5
8-10 (*c*, *t*/*t*, *c*)	0.11–0.71	0.3–1.0
7-9 (*c*, *t*/*t*, *c*)	3.31–9.69	3.6–6.7

c, *t*/*t*, *c* corresponds to the sum of *cis*–*trans* plus *trans*–*cis* C18:2 isomers.
[a] Luna et al. (2005a).
[b] Parodi (2003) and Khanal (2004).

The interest in increasing CLA content and changing the fatty acid profile in milk by dietary manipulation may provide a value-added human food. Although the CLA content in dairy products is affected by many factors, animal feeding strategies and specifically diets with oil seed or oil supplements rich in PUFA have been effective in enriching milk of the three dairy species (Stanton et al., 2003; Khanal and Olson, 2004; Chilliard and Ferlay, 2004), especially of dairy goats (Chilliard et al., 2005) and dairy ewes (Luna et al., 2005b). Effects of feeding fresh forages and the seasonal changes of Mediterranean natural pastures on FA, especially on CLA composition and its precursors in sheep milk have been reported (Addis et al., 2005; Cabiddu et al., 2005; Nudda et al., 2005). Enhancing CLA contents by dietary changes results also in lower proportions of saturated FA and greater amounts of mono-unsaturated FA (including TVA) and PUFA. Generally, free oils are more effective than whole or treated oilseeds (Chilliard et al., 2002).

Milk yield and fat and protein content responses to lipid supplements are, however different between the three dairy species. Milk fat content increased in general without a change in milk yield in dairy goats, whereas the response in cows was an increase in milk yield and either an increase or a decrease in milk fat content (Chilliard et al., 2002). In ewes fed a linseed supplement no changes were observed in milk yield and protein content, but the fat content decreased slightly throughout lactation (Luna et al., 2005b). In ewes fed olive cake, a positive effect on milk yield and no changes in milk composition were reported (Chiofalo et al., 2004).

However, the changes in FA composition were similar in the three species. Cows fed fish oil was more effective than plant oils for enhancing milk fat CLA contents (Chouinard et al., 2001). The responses were further increased when fish oil was fed in combination with supplements rich in C18:2n-6 (Abu-Ghazaleh et al., 2003, 2004; Jones et al., 2005). A slight increase in the level of ω-3 FA in goat milk fat occurred when goats were fed fish oil (Kitessa et al., 2001), but the levels of these supplements in the diet should be low and protected against ruminal biohydrogenation in order to avoid a decrease in milk yield and fat and protein contents. To date, data on CLA enhancement in ewes or goats by adding fish oil supplements are, however, limited (Mozzon et al., 2002).

5.3. Triacylglycerols

The TAG structure of milk is responsible for the rheological properties of milk fat and its behaviour during

Table 6
Triacylglycerol composition of sheep, goat and cow milk fat (wt%)

Triacylglycerol	Cow[a]	Sheep[b]	Goat[c]
C_{26}	0.22	0.72[d]	0.49
C_{28}	0.57	1.6	1.23
C_{30}	1.13	2.52	2.47
C_{32}	2.56	3.63	4.06
C_{34}	5.95	6.03	6.20
C_{36}	10.8	9.64	9.40
C_{38}	12.5	12.8	12.1
C_{40}	9.87	12.0	12.6
C_{42}	6.87	9.02	12.5
C_{44}	6.47	8.08	11.6
C_{46}	7.32	6.77	8.1
C_{48}	9.12	6.67	5.84
C_{50}	11.3	7.63	5.85
C_{52}	10.0	8.43	4.92
C_{54}	4.99	4.48	2.01

[a] Precht (1992).
[b] Goudjil et al. (2003a).
[c] Fontecha et al. (1998).
[d] Cholesterol included.

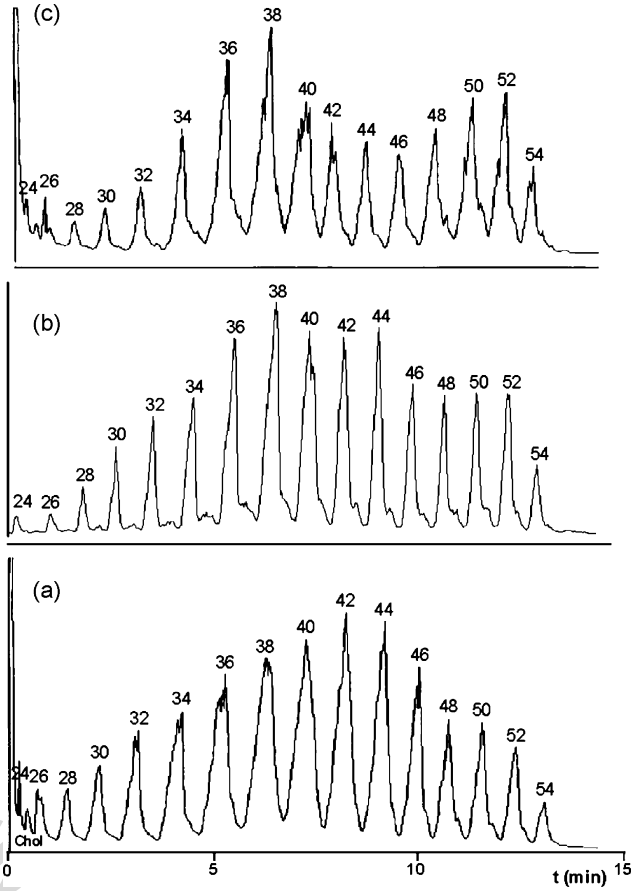

Fig. 2. Chromatographic profiles of goat (a), sheep (b) and cow (c) milk fat triacylglycerols (TAG). Cholesterol included in C24 or near C26 TAG.

melting and crystallization. Their composition is of interest, because it can be used to verify the origin of milk fat. TAG are almost invariably accompanied by small amounts of di- and mono-glycerides, mainly at position 1 and 2 molecules, probably being intermediates in the biosynthesis of TAG.

Table 6 shows the average TAG composition of sheep and goat milk fat compared with cow milk fat. The TAG of the three species present a wide range of molecular weights and chain lengths with carbon atom numbers beyond C26–C54. The TAG content in sheep milk has a bimodal distribution with a maximum at C36–C38 and C50–C52, and a minimum at C44–C46 (Partidario et al., 1998; Goudjil et al., 2003a). The chromatographic TAG profile of sheep milk (Fig. 2) shows similarities to that reported for cow milk (Precht, 1992). In goat milk the TAG content increased with the number of carbon atoms, reaching maximum (about 13% of total TAG) at C40–C42. Beyond this point, the TAG of goat milk decreased, but not uniformly, given that the values for C48 and C50 were similar (Fig. 2) (Fontecha et al., 1998).

Ewes and goats had a higher percentage of C26–C36 TAG than cow milk (24% versus 21%) (Fig. 2). Percentages of C38–C44 TAG also were higher in goat than in sheep and cow milk (49% versus 42% and 36%, respectively), however, percentages of C46–C54 TAG were lower in goat and sheep than in cow milk (27% and 34% versus 43%). These differences are related to the need for a TAG composition with appropriate melting points for fat secretion.

Multiple regression equations based on TAG contents of milk samples have been proposed to detect foreign fats in sheep and goat milk fat and in cheeses (Fontecha et al., 1998; Goudjil et al., 2003a). Their study is interesting, because TAG composition can change during cheese ripening, if there is selective lipolysis. In sheep cheeses with low lipolysis levels, the proposed equations were suitable for testing the genuineness of the fat (Fontecha et al., 2006).

Regarding the molecular species of TAG in goat and sheep milk using more than one chromatographic technique and MS (Ruiz-Sala et al., 1996; Fontecha et al., 2000, 2005), it has been established, that in goat milk fat the most important TAG in quantitative terms are medium-chain FA (C8, C10, C12) and C18:1 as unsaturated FA (Fontecha et al., 2000). In sheep milk fat the primary TAG are composed of three fatty acids, C4, C16 and C18:1 (Najera et al., 1999; Fontecha et al., 2005), the same as in cow milk (Spanos et al., 1995; Fraga et al., 1998). Concentrations of TAG in which the FA C8, C10 or C12 were esterified was highest in goat > sheep > cow milk fat.

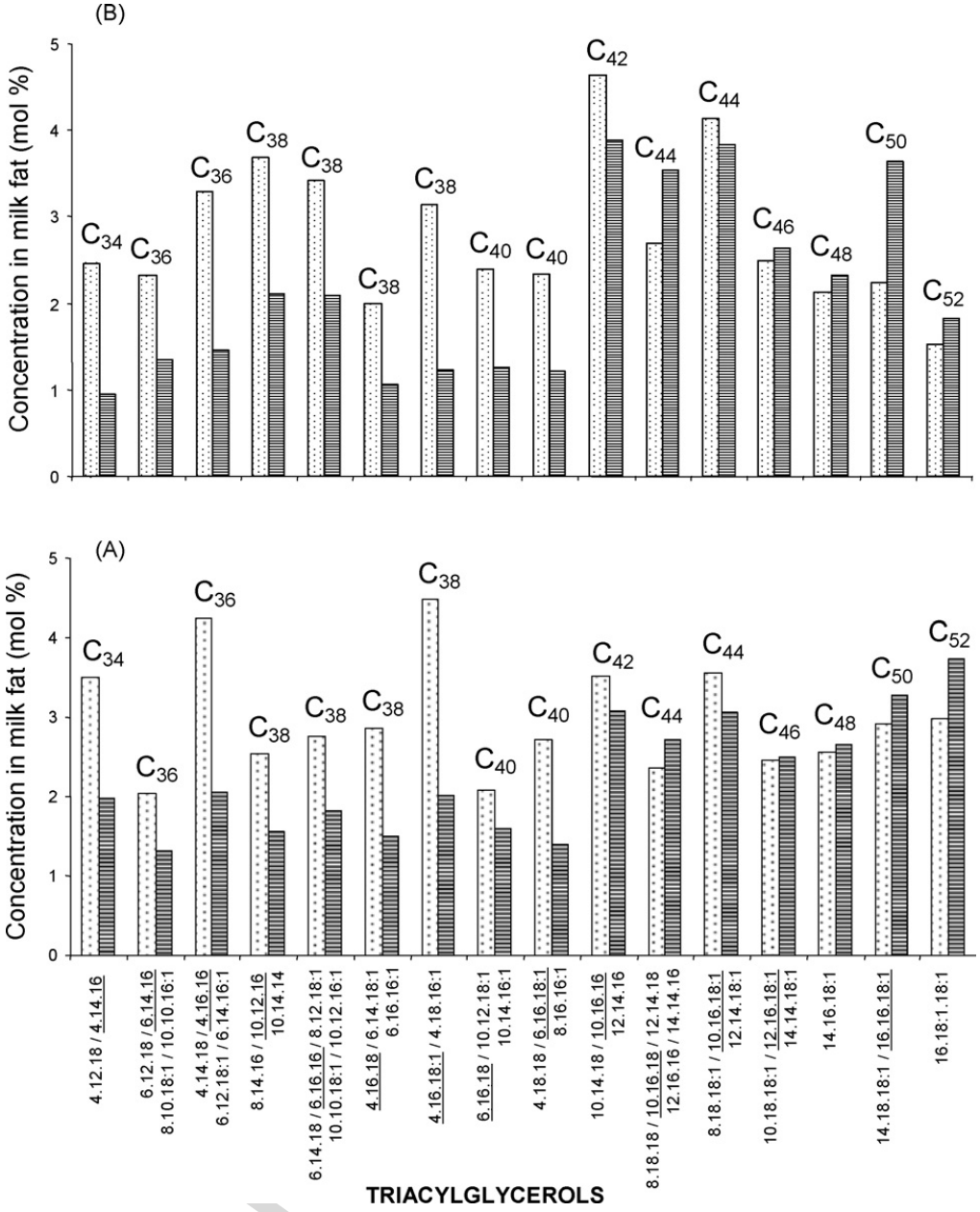

Fig. 3. Experimental (pointed bars) and random (dark bars) distribution of the main triacylglycerols in caprine (A) and ovine (B) milk fats. (From Fontecha et al., 2005; with permission of Elsevier Publ.).

5.3.1. Fatty acid distribution in TAG in ovine and caprine milk

The FA distribution in TAG in bovine milk is non-random (Christie, 1995), but there is no corresponding evidence for the distribution of FA in TAG in ovine or caprine milk. In order to compare the experimental and theoretical distributions of FA in TAG for ovine and caprine milk fat, the TAG content (Fontecha et al., 2000, 2005) was compared with the theoretical (random) distribution of the TAG calculated from experimental molar percentages of FA in total milk fat following the procedure of Gresti et al. (1993).

Fig. 3 shows the experimental and random theoretical values of the most abundant TAG (molar content >1.5%) (Fontecha et al., 2005). The comparison of theoretical and experimental values reveals a non-random distribution of the FA in the TAG of sheep and goat milk fat. TAG containing a short-chain FA, e.g., C4 or C6 (CG peaks C34–C40) are synthesized preferentially to TAG containing three medium- or three long-chain FA. This relates to the fact, that only one short-chain acid (C4 or C6) occurs per TAG molecule and stereospecific studies have shown, that short-chain FA in ruminant mammary glands are esterified only in position

Table 7
Concentrations of different sterols found in goat and sheep milk fat (mg/100 g fat)

Relative retention time	Identification	Mean ± S.D.	
		Goat milk fat[a]	Sheep milk fat[b]
1.00	Cholesterol	341.8 ± 15.6	288.4 ± 42.2
1.11	Lathosterol	1.47 ± 0.35	1.81 ± 0.82
1.15	Desmosterol	1.39 ± 0.49	0.41 ± 0.30
1.32	Dihydrolanosterol	2.25 ± 0.38	4.15 ± 2.40
1.44	Lanosterol	9.75 ± 1.64	6.86 ± 1.88

[a] Fraga et al. (2000).
[b] Goudjil et al. (2003b).

sn-3, whereas medium- and long-chain FA are esterified in all three glycerol positions. The differences between experimental and theoretical values in C42–C46 TAG, which include most C10 and C12 acids, are close to unity (Fig. 3). This result is probable, because in cow milk medium-chain FA can be esterified in all three positions of the TAG molecule (preferentially sn-1 or sn-2), since they are occurring in relatively small amounts, and which is reflected in the higher milk fat melting point.

5.4. Sterol fraction

Sterols are a minor fraction of total lipids in milk, the main sterol being cholesterol (300 mg/100 g fat, equivalent to 10 mg/100 ml cow milk). Small quantities of other sterols have been reported in cow milk (Jensen, 2002) including vegetable sterols (IDF, 1992). The sterol fraction of milk is of nutritional interest because high levels of cholesterol in plasma are associated with an increasing risk of cardiovascular disease. Through analyses of the sterol fractions adulterant vegetable fats can be detected in milk and dairy products.

Values reported for the cholesterol content of sheep and goat milk vary considerably due to different breeds and the use of different analytical techniques. Concentrations of sterols in goat and sheep milk fat from different herds are shown in Table 7, determined by GC using MS for identification of minor compounds (Fraga et al., 2000; Goudjil et al., 2003b). Variation is considerable but comparable to that found in cow milk fat. Minor sterols represent 3–5% of the total sterol fraction. Some small GC peaks in the chromatograms had a relative retention time similar to campesterol and β-sitosterol, but mass spectra could not be assigned to these sterols, and they could not be identified either.

6. Proteins in goat and sheep milk

6.1. General characteristics of milk proteins

The average protein content in sheep milk (5.8%, w/w) is higher than in goat (4.6%, w/w) or cow milk (3.3%, w/w). Protein contents vary widely within species, and are influenced by breed, stage of lactation, feeding, climate, parity, season, and udder health status. Goat and sheep milk contains about 0.7–1.0% and 0.4–0.8% N, respectively, which is distributed in fractions, whose importance varies in terms of dairy technology and human nutrition. Proteins in sheep milk account for approximately 95% of total N and 5% is non-protein N. Goat milk has a higher level of non-protein N and less casein-N than sheep and cow milk. This is responsible for low cheese yield and weak yogurt structure and texture (Guo, 2003), while sheep milk has a very good clotting ability.

The principal proteins in sheep and goat milk are about the same as in cow milk. Milk proteins occur in two distinct phases. One is an unstable micellar phase composed of caseins, as suspended micelles, averaging about 190 nm in diameter. They are interlinked by calcium phosphate and small amounts of magnesium, sodium, potassium and citrate, which diffuse light and lend the milk its opaque white appearance. The other is a soluble phase composed of whey proteins. The caseins precipitate at pH 4.6 at room temperature, whereas under the same conditions the whey proteins (β-lactoglobulin, α-lactalbumin and serumalbumin) remain soluble. Summaries of the characteristics of sheep and goats milk have been published (Anifantakis, 1986; Juàrez and Ramos, 1986; Alichanidis and Polychroniadou, 1996; Guo, 2003; Ramos and Juarez, 2003; Tziboula-Clarke, 2003; Haenlein, 2004; Park, 2006a).

Table 8
Comparison of structural features of the four caseins in bovine, ovine and caprine milk (Martin et al., 2003)

Caseins	Bovine			Ovine			Caprine		
	Amino acids[a]	Amino acids[b]	P sites[c]	Amino acids[a]	Amino acids[b]	P sites[c]	Amino acids[a]	Amino acids[b]	P sites[c]
α_{s1}-Casein	199	15	9/9	199	15	10/10	199	15	11/11
α_{s2}-Casein	207	15	17/?	208	15	17/13	208	15	16/?
β-Casein	209	15	6/5	207	15	6/6	207	15	6/6
κ-Casein	169	21	5/3	171	21	5/3	171	21	6/3

[a] Number of amino acid residues of the mature chain of the protein.
[b] Number of amino acid residues of the signal peptide.
[c] Number of phosphorylation sites (putative/actual).

6.2. Caseins

6.2.1. Caseins in goat milk

The principal caseins in goat milk are about the same as in the milk of sheep or cows, α_{s1}-CN, α_{s2}-CN, β-CN and κ-caseins. The amino acid composition and their sequence has been determined by cDNA analysis. Table 8 shows the comparison of structural features of four caseins from cow, sheep and goat milk (Martin et al., 2003).

Casein composition in goat, sheep and cow milk is influenced by genetic polymorphisms on the α_{s1}-, α_{s2}-, β-, and κ-casein loci. Polymorphism of α_{s1}-CN is one of the most interesting and extensively studied in goat and cow milk (Grosclaude et al., 1987). The types of pertinent mutations are single nucleotide substitutions, deletions, or large insertions. Eight of the currently identified alleles in goat milk (A, B_1, B_2, B_3, B_4, C, H and L) are associated with a high level of α_{s1}-CN (3.5 g/l milk), two (E and I) with medium levels (1.1–1.7 g/l), and two (F and G) with low levels (0.45 g/l). The O_1 and O_2 are "null" alleles and produce no α_{s1}-CN in goat milk (Chianese et al., 1997; Grosclaude and Martín, 1997). Instead, goat milk may have α_{s2}-CN, for which seven alleles have been identified, and which also are associated with three different casein synthesis levels. A, B, C, E and F alleles produce "normal" α_{s2}-CN contents (2.5 g/l), the D allele causes reduced α_{s2}-CN contents, and the O allele has no detectable amounts of this casein in goat milk.

Recently, Gomez-Ruiz et al. (2004) used a capillary electrophoresis method (CE) for the quantitative determination of α_{s1} and α_{s2}-casein in goat milk with different genotypes. A good correlation was found between quantities of α_{s1}-Cn described for each genotype in the literature and the quantities calculated with the CE method. Moatsou et al. (2004) studied the characteristics of the casein fractions of two Greek indigenous goat breeds and two highly selected Alpine and Saanen breeds. The two indigenous breeds had an α_{s1}-CN relative percentage content at the level reported for caprine milks with high alleles (20.7% and 25.6%), but β-casein was the main casein fraction (<50%).

Polymorphisms of β-casein have also been studied by Chianese et al. (1993b), and several alleles expressing different levels have been found. The origin of this heterogeneity depends on multiple phosphorylation of the peptide chain giving 4P, 5P and 6P forms, but some goat milk may be totally devoid of this protein. Studies about the aptitude for coagulation of individual milks with "null" β-casein showed, that longer rennet coagulation times were needed than for normal milk and weaker curd firmness occurred. A review about the heterogeneity of sheep and goat milk proteins and their relation to characteristics of the micelle and their influence on cheese making has been published by Piredda and Pirisi (2005).

Polymorphisms of caprine κ-casein have been studied by Yahyaoui et al. (2003). They characterized and genotyped four variants in different Spanish, French and Italian goat breeds. Alleles A and B are the most frequent variants with highest prevalence of the B variant, except for the Canaria breed, where the A allele is more frequent. Also, two new variants F and G have been identified in some Italian breeds.

6.2.2. Caseins in sheep milk

Caseins (α_{s1}-CN, α_{s2}-CN, β-CN and κ-CN) are the major proteins in sheep milk (76–83% of total proteins). The heterogeneity of caseins is determined either by the presence of genetic variants or by other factors such as a discrete phosphorylation level, variation in the extent of glycosylation of the κ-CN fraction, and the coexistence of proteins with different chain lengths.

A review of the genetic polymorphisms of sheep milk proteins and their influence on technological properties of the milk has been published by Chianese (1997) and Amigo et al. (2000). There are five polymorphic variants

of α_{s1}-CN, designated A–E in line with the nomenclature used for cow or goat milk caseins (Chianese et al., 1996). The α_{s1}-CN D had previously been described as the Welsh variant because of its discovery in the Welsh mountains by King (1966). This is the least phosphorylated genetic variant. The less numbers of phosphate groups explains its longer migration time on capillary electrophoresis at acid pH and slow migration on alkaline polyacrylamide gel (Recio et al., 1997a, b, c). Variant α_{s1}-CN C differs from variant α_{s1}-CN A in the amino acid substitution of Ser for Pro at position 13, which determines the loss of the phosphate group on site 12 of the protein chain. Two variants of α_{s2}-CN, A and B, have also been described, differing in replacement of amino acids Asn_{49} and Lys_{200} by Asp_{49} and Asn_{200}. In addition, a variant with high electrophoretic mobility and low molecular weight has been found in the Manchega sheep breed (Chianese et al., 1993a).

Ovine β-CN is formed by 209 amino acids and a non-genetic polymorphism occurs due to varying degrees of phosphorylation, with six and five phosphate groups for β1 and β2, respectively. Three genetic variants, A–C, were described by Chianese et al. (1996). The only sequence difference found between A and C was a substitution of the amino acid Glu at position 2 in variant A for Gln in variant C, but no sequence data for the B variant are yet available. Stability of the micelle and the availability and distribution of Ca are affected by the extent of phosphorylation of the caseins.

Sequencing of ovine κ-casein has shown that 171 amino acid residues form it. No genetic variants have been found in κ-casein, but non-genetic polymorphisms occur due to varying degrees of glycosylation at three different Thr residue sites (positions 135, 137 and 138) and two phosphorylation sites (Ser P^{151} and Ser P^{168}). This casein fraction also contains γ-caseins, the product of breakdown of β-caseins by plasmin (Chianese, 1997).

6.3. Whey proteins

Sheep milk whey proteins account for 17–22% of total proteins. The major whey proteins are β-lactoglobulin (β-Lg) and α-lactalbumin (α-La). Immunoglobulins, serum albumin and proteose–peptones are present in smaller concentrations. The latter are products of the breakdown of β-casein by plasmin. Another soluble protein found in small amounts and presenting antibacterial properties is lactoferrin. Serum albumin and immunoglobulins are not specific to milk and are considered to be the same as those found in blood. In the case of rennet whey, caseino-macropeptides are also present, produced by the chymosin action on link 105–106 of κ-casein.

The major whey protein, β-lactoglobulin, in sheep milk consists of a polypeptide chain of 162 amino acids. Three genetic variants, β-Lg A–C have been described. Ovine β-Lg B and A differ in a single amino acid exchange, His for Tyr at position 20; β-Lg C is a subtype of ovine β-Lg A with a single exchange, Arg for Gln at position 14 (Bell and McKenzie, 1967; Erhardt et al., 1989). The three variants can be separated by isoelectric focusing and by capillary electrophoresis (Recio et al., 1997c). The ovine β-Lg alleles A and B are present in almost all breeds, whereas allele C is rather rare and confined to a few specific breeds (Amigo et al., 2000). The influence of β-Lg polymorphism on the composition and technological behavior of sheep milk has been studied by Recio et al. (1997c).

In goat milk, the nucleotide sequence cDNA and amino acid sequence of β-Lg has been described by Folch et al. (1993). Pena et al. (2000) reported the existence of two genetics variants of β-Lg in Spanish and French Saanen goats. Studying the composition of whey from different indigenous Greek sheep and goat breeds, Moatsou et al. (2005) found that the principal characteristics were low α-La percentages. The β-Lg percentage of goat acid whey was lower than in sheep or cow acid whey. The α-La in sheep and goat milk are closely homologous to cow α-La. It is a metallo-protein containing one atom of Ca per molecule and is physiologically important because of its requirement in lactose synthesis. Two genetic polymorphic variants, α-La A and B, have been described, although the B variant is rare. Cosenza et al. (2003) have detected an additional silent allele at the goat α-La locus.

6.4. Caseino-macropeptides (CMP)

Caseino-macropeptides (CMP) are soluble C-terminal fragments derived from the action of chymosin on κ-casein during the milk clotting process in cheesemaking. As precursors of κ-casein, they are a heterogeneous mixture because of genetic variations and differently glycosylated and phosphorylated forms.

The amino acid sequences of CMP from different species are well established (Jollés et al., 1974; Stewart et al., 1984). They are characterized by the absence of aromatic amino acids (Phe, Trp, and Tyr) and Arg, and by high levels of acidic and hydroxyl amino acids (Mercier et al., 1976). Less is known about post-translational modifications of CMP from sheep and goat milk. An excellent review about the physicochemical, technological, biological and nutritional aspects of κ-casein

macropeptides from sheep and goat milk has been published by Manso and López-Fandiño (2004). Moreno et al. (2000, 2001) characterized ovine and caprine CMP by chromatographic techniques. The most abundant ovine (90%) and caprine CMP components (77%) were the diphosphorylated carbohydrate-free form, followed by monophosphorylated species. In the case of ovine CMP, non-phosphorylated and triphosphorylated forms were also found in small quantities (Moreno et al., 2000). The similarities between the sequences of caprine and ovine CMP would imply, that both species have the same phosphorylation sites, Ser_{151} and Ser_{168} (Mercier et al., 1976; Rasmusen et al., 1997). About 30% of ovine and caprine CMP are glycosylated, compared to 60% of bovine CMP. The lower level of glycosylation of ovine and caprine CMP may support the hypothesis that the attachment of more than one phosphate residue inhibits the glycosylation process. The glycosylated forms of ovine and caprine CMP (Moreno et al., 2000, 2001) are similar to those found in bovine CMP (Saito and Itoh, 1992; Mollé and Leonil, 1995) except for the substitution of *N*-acetyl neuraminic by glycolyl neuraminic. The content of *N*-acetyl neuraminic and glycolyl neuraminic (sialic acid) in CMP is interesting in terms of bioactivity. Large amounts are found in the brain and in the central nervous system in the form of gangliosides and glycoproteins, contributing to the functioning of cell membranes, membrane receptors and to normal brain development.

7. Bioactive peptides derived from goat and sheep milk proteins

7.1. General aspects of bioactive peptides

Enzymatic hydrolysis of milk proteins can release fragments able to exert specific biological activities, such as antihypertensive, antimicrobial, opioid, antioxidant, immunomodulant, or mineral binding. Such protein fragments, known as bioactive peptides, are formed from the precursor inactive protein during gastrointestinal digestion and/or during food processing (Korhonen and Pihlanto-Leppälä, 2003). Due to their physiological and physico-chemical versatility, milk peptides are regarded as highly prominent components for health promoting foods or pharmaceutical applications.

7.2. Angiotensin converting enzyme (ACE) inhibitory peptides

Among the known bioactive peptides, those with angiotensin converting enzyme (ACE) inhibitory properties have received special attention due their potentially beneficial effects in the treatment of hypertension. ACE is a multifunctional enzyme, located in different tissues, and able to regulate several systems that affect blood pressure. It is responsible for generating vasopressor angiotensin II and the inactivation of the vasodepressor bradykinin.

Milk proteins are the main source of ACE inhibitory peptides. Several techniques have been applied for releasing these peptides from milk proteins:

(a) hydrolysis with digestive enzymes of mammalian origin,
(b) hydrolysis with enzymes of microbial and/or plant origin,
(c) fermentation of milk with proteolytic starter cultures,
(d) successive combination of hydrolysis with fermentation,
(e) chemical synthesis based on combinatorial library designs of peptides having similar structures to those known to inhibit ACE.

Most publications on ACE inhibitory and/or antihypertensive peptides have used peptides from cow milk (Korhonen and Pihlanto-Leppälä, 2003; Gobbetti et al., 2004; Silva and Malcata, 2005; Meisel, 2005). However, in recent years, the sheep and goat milk proteins have become an important source of ACE inhibitory peptides (Table 9).

7.3. ACE inhibitory peptides derived from whey proteins

Studies about the ACE inhibitory activity of hydrolysates of β-Lg from sheep and goat milk with enzymes of digestive and microbial origin have been carried out by Hernández-Ledesma et al. (2002). Higher activities were observed for caprine and ovine β-Lg hydrolysates obtained with enzymes of microbial origin than for those prepared with digestive enzymes. Four new caprine β-Lg derived peptides with ACE inhibitory activity were purified and identified from the hydrolysate prepared with termolisin (Table 9). These peptides corresponded to β-Lg fragments *f*(46–53), *f*(58–61), *f*(103–105), and *f*(122–125), and their IC_{50} values (protein concentration needed to inhibit original ACE activity by 50%) ranged from 34.7 to 2470 μM. Of special interest is peptide LLF, included within the sequence of opioid peptide β-lactorphin (YLLF), which is considered a "strategic zone" partially protected from digestive breakdown (Hernández-Ledesma et al., 2002). Recently, Chobert et al. (2005) have investigated the

Table 9
Sequence of bioactive peptides derived from ovine and caprine milk proteins

Peptide fragment	Sequence	Biological activity	Reference
Ovine α_{s1}-CN *f*(86–92)	VPSERYL	ACE-inhibitory	Gómez-Ruiz et al. (2002)
Ovine α_{s1}-CN *f*(102–109)	KKYNVPQL	ACE-inhibitory	Gómez-Ruiz et al. (2002)
Caprineα_{s1}-CN *f*(143–146)	AYFY	ACE-inhibitory	Lee et al. (2005a)
Ovine α_{s2}-CN *f*(165–170)	LKKISQ	Antibacterial	López-Expósito et al. (2006)
Ovine α_{s2}-CN *f*(165–181)	LKKISQYYQKFAWPQYL	Antibacterial	López-Expósito et al. (2006)
Caprine α_{s2}-CN *f*(174–179)	KFAWPQ	ACE-inhibitory	Quirós et al. (2005)
Ovine α_{s2}-CN *f*(184–208)	VDQHQAMKPWTQPKTKAIPYVRYL	Antibacterial	López-Expósito et al. (2006)
Ovine α_{s2}-CN *f*(202–204)	IPY	ACE-inhibitory	Gómez-Ruiz et al. (2002)
Ovine and caprine α_{s2}-CN *f*(203–208)	PYVRYL	Antibacterial	López-Expósito et al. (2006)
		ACE-inhibitory	Quirós et al. (2005)
		Antihypertensive	Recio et al. (2005)
Ovine α_{s2}-CN *f*(205–208)	VRYL	ACE-inhibitory	Gómez-Ruiz et al. (2002)
Ovine and caprine β-CN *f*(47–51)	DKIHP	ACE-inhibitory	Gómez-Ruiz et al. (2005, 2006)
Ovine β-CN *f*(58–68)	LVYPFTGPIPN	ACE-inhibitory	Quirós et al. (2005)
Caprine κ-CN *f*(59–61)	PYY	ACE-inhibitory	Lee et al. (2005a)
Ovine and caprine κ-CN *f*(106–111)	MAIPPK	ACE-inhibitory	Manso and López-Fandiño (2003)
Ovine and caprine κ-CN *f*(106–112)	MAIPPKK	ACE-inhibitory	Manso and López-Fandiño (2003)
Ovine κ-CN *f*(112–116)	KDQDK	Antithrombotic	Qian et al. (1995)
Caprine β-Lg *f*(46–53)	LKPTPEGD	ACE-inhibitory	Hernández-Ledesma et al. (2002)
Caprine β-Lg *f*(58–61)	LQKW	ACE-inhibitory	Hernández-Ledesma et al. (2002)
Caprine β-Lg *f*(103–105)	LLF	ACE-inhibitory	Hernández-Ledesma et al. (2002)
Caprine β-Lg *f*(122–125)	LVRT	ACE-inhibitory	Hernández-Ledesma et al. (2002)
Ovine and caprine LF *f*(17–41)	ATKCFQWQRNMRKVRGPPVSCIKRD	Antibacterial	Vorland et al. (1998)
Ovine and caprine LF *f*(14–42)	QPEATKCFQWQRNMRKVRGPPVSCIKRDS	Antibacterial	Recio and Visser (2000)

ACE inhibitory activity of ovine β-Lg hydrolysates by trypsin.

Manso and López-Fandiño (2003) evaluated the ACE inhibitory activities of bovine, caprine and ovine κ-CMP and their tryptic hydrolysates. The results indicate that these κ-CMP exhibit moderate ACE inhibitory activity, that increased considerably after digestion under simulated gastrointestinal conditions. In addition, active peptides can be produced from CMP via proteolysis with trypsin. Peptides MAIPPK and MAIPPKK, corresponding to κ-CN fragments *f*(106–111) and *f*(106–112), respectively, were identified (Table 9). These peptides showed a moderate activity, but their digestion under simulated gastrointestinal conditions allowed the release of potent ACE inhibitory peptide IPP (IC_{50} value of 5 μM). These findings might help promote κ-CMP as multifunctional active ingredients, broadening the potential uses of rennet whey from various sources.

7.4. ACE inhibitory peptides derived from caseins

Caseins are also an important source of peptides with ACE inhibitory activity after enzymatic hydrolysis and/or milk fermentation. Recently, different proteolytic enzymes were used by Lee et al. (2005a) to hydrolyse goat milk casein. The peptic hydrolysate was found to be the most active and several ACE inhibitory peptides were isolated from it (Table 9). Peptides released from sheep and goat milk by fermentation with different proteolytic starter cultures have been isolated and characterised by different authors.

Proteolytic enzymes of lactic acid bacteria and yeasts involved in milk fermentation during kefir manufacture can be responsible for the release of a number of peptides. Sixteen peptides were identified in a commercial caprine kefir by HPLC coupled to tandem mass spectrometry. Two of these peptides, with sequences PYVRYL [α_{s2}-CN *f*(203–208)] and LVYPFTGPIPN [β-CN *f*(58–68)], showed potent ACE inhibitory activity with IC_{50} values of 2.4 and 27.9 μM, respectively (Table 9). The first of these peptides also had potent antihypertensive activity in spontaneously hypertensive rats (Recio et al., 2005). The results demonstrate the influence of digestion on the formation of new ACE inhibitory peptides (Quirós et al., 2005).

A few papers deal with the ACE inhibitory activity of peptides liberated from casein during cheese ripening. Cheeses are an important source of milk protein derived peptides, because of the diversity of the proteolytic systems in cheese ripening and the intensity of proteolysis during ripening.

An 8-month-old Manchego cheese from ovine milk was analysed by Gómez-Ruiz et al. (2002), and several peptides with ACE inhibitory activity were identified. Studying different Spanish cheeses (Cabrales, Idiazábal, Roncal, Manchego, Mahón from sheep milk, and a goat milk cheese) from diverse technologic processes, their ACE inhibitory activity was essentially concentrated in the 1 kDa permeate. In isolating the major peptides a total of 41 peptides were identified by mass spectrometry, most of them being derived from α_{s1}-casein and β-casein. On the basis of their structure, several of these peptides were selected and chemically synthesized. All showed moderate or low ACE inhibitory activity. Peptide DKIHP, corresponding to β-CN *f*(47–51) was found in all cheeses with the exception of Mahon cheese. This peptide had the highest inhibitory activity, with an IC_{50} value of 113.1 μM (Gómez-Ruiz et al., 2005, 2006).

7.5. Antimicrobial peptides

Bioactive proteins and peptides derived from milk have been reported to provide a non-immune disease defence and control of microbial infections (McCann et al., in press). It is generally accepted, that the total antibacterial effect in milk is greater than the sum of the individual contributions of immunoglobulin and non-immunoglobulin defence proteins such as lactoferrin (LF), lactoperoxidase, lysozyme, and peptides. This may be due to the synergistic activity of naturally occurring proteins and peptides in addition to peptides generated from inactive protein precursors (Gobbetti et al., 2004). It has been proved, that milk proteins can also act as antimicrobial peptide precursors, and in this way might enhance the organism's natural defences against invading pathogens. Consequently food proteins can be considered as components of nutritional immunity (Pellegrini, 2003).

7.6. Antimicrobial peptides derived from whey proteins

Peptides derived from lactoferrin (LF) are antibacterial peptides from milk proteins that have attracted more attention during the last decade. The first report that demonstrated the enzymatic release of antibacterial peptides with more potent activity than the precursor LF dates from Tomita et al. (1991). Shortly afterwards, the antibacterial domains of bovine LF *f*(17–41) and human LF *f*(1–47), called, respectively, bovine and human lactoferricin (LFcin), were purified and identified (Bellamy et al., 1992). These peptides showed a potent antimicrobial activity against a wide range of Gram-positive and Gram-negative bacteria (Wakabayashi et al., 2003).

In the case of caprine and ovine species, first approaches consisted in the chemical synthesis of fragment *f*(17–41) of caprine LF, which displayed antibacterial activity, although to a lesser extent than the bovine counterpart (Vorland et al., 1998). Hydrolysis of caprine and ovine LF by pepsin resulted in antibacterial hydrolysates, and a homologous peptide to LFcin, corresponding to fragment *f*(14–42), was identified in the caprine LF hydrolysate. Caprine LFcin showed lower antibacterial activity than bovine LFcin against *Escherichia coli* but comparable activity against *Micrococcus flavus* (Table 9). The region corresponding to the LFcin within the sequence of ovine LF was hydrolysed by the action of pepsin, and hence, the activity observed in the ovine LF hydrolysate could be caused by other LF fragments (Recio and Visser, 2000). In addition to these studies, El-Zahar et al. (2004), obtained a peptic hydrolysate of ovine α-La and β-Lg, that inhibited the growth of *Escherichia coli* HB101, *Bacillus subtilis* Cip5262 and *Staphylococcus aureus* 9973 in a dose-dependent manner, but responsible peptides were not identified.

7.7. Antimicrobial peptides derived from caseins

In the same way as whey proteins, caseins are also a source of antimicrobial peptides (López-Expósito and Recio, 2006). In a preliminary study, an ovine β-casein hydrolysate with pepsin, trypsin and chymotrypsin showed inhibition of bioluminescent production by *Escherichia coli* JM103, but the peptides responsible for this activity have not been identified (Gómez-Ruiz et al., 2005, 2006).

Recently, four antibacterial peptides were identified from a pepsin hydrolysate of ovine α_{s2}-casein (López-Expósito et al., 2006). The peptides corresponded to α_{s2}-casein fragments *f*(165–170), *f*(165–181), *f*(184–208) and *f*(203–208), being the fragments *f*(165–181) and *f*(184–208) homologous to those previously identified in the bovine protein (Recio and Visser, 1999) (Table 9). These peptides showed a strong activity against Gram-negative bacteria. Of them, the fragment *f*(165–181) was the most active against all bacteria tested. The peptide corresponding to ovine α_{s2}-casein *f*(203–208) is a good example of multifunctional peptides, because it exhibited not only antimicrobial activity, but also potent antihypertensive and antioxidant activity (Recio et al., 2005). These results can be extended to caprine proteins, because the amino-acid sequence of these peptides is the same.

7.8. Antithrombotic peptides

Cardiovascular diseases, including thrombosis, are among the most important causes of mortality of adults in industrialized countries. Fibrinogen plays an important role in coagulation of blood, particularly because it binds to specific glycoprotein receptors located on the surface of the platelets, which allows them to clump. Some structural similarities have been found between the sequence of fibrinogen and the sequence of the undecapeptide *f*(106–116) derived from bovine κ-casein. These analogies seem to be important for the inhibitory effect of the aggregation of ADP-activated platelets, as well as of the binding of human fibrinogen γ-chain to a specific receptor site on the platelet surface, shown by the κ-casein fragment called casoplatelin (Jollès et al., 1986). Two smaller fragments from casoplatelin were identified in tryptic hydrolysates of κ-casein. One of them, named casopiastrin and corresponding to fragments *f*(106–110), inhibited fibrinogen binding (Mazoyer et al., 1992). However, the fragment *f*(106–111) can prevent blood clotting through inhibition of platelet aggregation, and is not able to affect fibrinogen binding to the platelet receptor (Fiat et al., 1993).

The κ-caseino-macropeptide is one of the main components of whey and it is obtained as a by-product in cheesemaking. The κ-CMP from several animal species have been reported as a good source of antithrombotic peptides. Qian et al. (1995) found two very active sequences with inhibitory activity of human platelet aggregation induced by thrombin and collagen after hydrolysing ovine κ-CMP with trypsin (Table 9). Furthermore, bovine, ovine and caprine κ-CMP and their hydrolysates with trypsin were found to be inhibitors of human platelet aggregation (Manso et al., 2002). In this work, the hydrolysate obtained from ovine κ-CMP showed the strongest effect, but the peptides responsible of this activity were not identified.

7.9. Other biological activities of peptides from goat and sheep milk proteins

A number of peptides with opioid activity have been isolated and identified from hydrolysates of bovine casein and/or whey proteins with different enzymes. These peptides can modulate social behaviour, increase analgesic behaviour, prolong gastrointestinal transient time by inhibiting intestinal peristalsis and motility, exert antisecretory action, modulate amino acid transport, and stimulate endocrine responses such as the secretion of insulin and somatostatin (Clare and Swaisgood, 2000). Several of these peptides have also revealed inhibitory effects of proliferation and/or inductor effects of apoptosis in different carcinoma cell lines (Kampa et al., 1997; Mader et al., 2005).

It has been claimed that casein phosphopeptides (CPP) can form soluble organophosphate salts and may function as carriers for different minerals, especially calcium in the intestine (Sato et al., 1986). Furthermore, it has been shown that calcium binding CPP can have anticariogenic effects by inhibiting caries lesions through recalcification of the dental enamel, along with competition of dental plaque forming bacteria for calcium (Reynolds, 1987).

Recently, studies have centred their interest in the identification of peptides derived from caseins and whey proteins with potent antioxidant activity acting by different mechanisms. These peptides are released by enzymatic hydrolysis (Suetsuna et al., 2000; Rival et al., 2001a,b; Hernández-Ledesma et al., 2005) and milk fermentation (Kudoh et al., 2001).

Due to the great homology among the sequences of bovine, ovine, and caprine milk proteins, it would be predictable that the peptides reported as bioactive agents and released from bovine proteins are also within sheep and goat proteins. More studies would be very interesting to isolate these peptides even more and demonstrate their great potential activities as opioid, mineral binding, antioxidant and anticarcinogenic compounds for use as functional foods in human nutrition.

8. Minor proteins and NPN compounds

8.1. Minor proteins

Important minor proteins include immunoglobulins, lactoferrin, transferrin, ferritin, proteose peptone, calmodulin (calcium binding protein), prolactin and folate-binding protein, etc. Lactoferrins constitute a family of homologous glycoproteins present in milk of all vertebrate species. Lactoferrin is the major iron binding protein in human and mare milk, whereas transferrin is predominant in milk from rats and rabbits (Renner et al., 1989). Guinea pig, mouse, cow, goat, and sow milks contain nearly the same amount of lactoferrin and transferrin (Fransson et al., 1983) and prolactin (Table 10). Human milk contains more than 2 mg lactoferrin/ml, which amounts to 10–100 fold more than in goat milk (Park, 2006a,b). Transferrin contents of goat and cow milks are 20–200 μg/ml, while human milk contains less than 50 μg/ml (Table 10). Assaying by radioimmunoassay, Malven (1977) reported that mean prolactin contents (μg/ml) of goat and cow milk were 44 ± 5 (S.E.) and 50 ± 1, respectively.

Table 10
Some minor protein contents in goat, cow and human milk

Proteins	Goat	Cow	Human
Lactoferrin (μg/ml)	20–200	20–200	<2000
Transferrin (μg/ml)	20–200	20–200	<50
Prolactin (μg/ml)	44	50	40–160
Folate-binding protein (μg/ml)	12	8	–
Immunoglobulin			
IgA (milk: μg/ml)	30–80	140	1000
IgA (colostrum: mg/ml)	0.9–2.4	3.9	17.35
IgM (milk: μg/ml)	10–40	50	100
IgM (colostrum: mg/ml)	1.6–5.2	4.2	1.59
IgG (milk: μg/ml)	100–400	590	40
IgG (colostrum: mg/ml)	50–60	47.6	0.43
Non-protein N (%)	0.4	0.2	0.5

Adapted from Remeuf and Lenoir (1986), Renner et al. (1989) and Park (2006a,b).

Folate-binding protein concentrations of goat milk are higher than those of cow milk, causing actual folate content to be lower in the former than in the latter (Table 10; Ford et al., 1972; Renner et al., 1989). Goat milk contains about 12 μg/ml of folate-binding protein, which is a glycoprotein with about 22% carbohydrates (Ford et al., 1972; Rubinoff et al., 1977), and binds 9.2 μg folic acid/mg of protein (Jenness, 1980).

Immunoglobulins IgGs, IgA and IgM are also present in goat milk. Goat milk has similar ranges of immunoglobulins to those of cow and sheep milk and colostrums (Table 10). In the colostrum of cow milk, IgG predominates forming about 80–90% of total immunoglobulins, while the proportion of IgM is about 7% and IgA 5%. IgG_1 accounts for 80–90% of IgG, IgG_2 for 10–20% (Renner et al., 1989). The level of all isotypes diminishes rapidly postpartum, whereas IgG predominates also in mature milk as shown in Fig. 4.

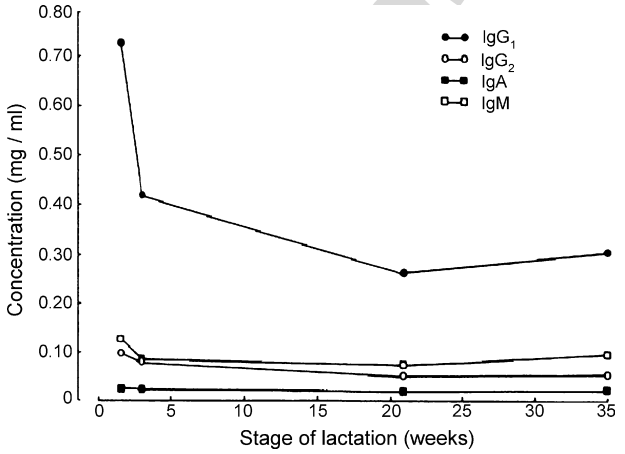

Fig. 4. Immunoglobulin isotype concentrations in milk during lactation (Guidry and Miller, 1986).

Among minor whey proteins, caprine milk also has proteose–peptones like bovine and other species milks. The proteose–peptone fraction has been characterized as a mixture of heat-stable acid-soluble (at pH 4.6) phosphoglycoproteins insoluble in 12% trichloroacetic acid (Rowland, 1937).

8.2. NPN compounds

Non-protein nitrogen (NPN) contents of goat and human milks are higher than in cow milk (Table 10). NPN is composed of several nitrogenous compounds, and its components (mg N/100 ml) in cow milk include: 0.17 ammonia N, 6.54 urea N, 0.19 creatinine, 3.55 creatin, 1.55 uric acid, 2.20 α-amino N, and 5.63 unaccountable N, respectively (Rowland, 1937; Jenness and Patton, 1976; Park, 2006a,b). Goat and sheep milk vary somewhat in the contents of these NPN components compared to cow milk, partially due to factors in their diet such as protein and NPN levels.

Free amino acids (FAA) represent 10–20% of the NPN in milk, and their concentration is 5–8 mg/100 ml (Renner et al., 1989). FAA mainly consist of the non-essential amino acids glutamic acid, glycine, aspartic acid and alanine, while the other amino acids are present as FAA only in very low concentrations (Renner et al., 1989). Among the FAA, taurine and carnitine, which do not occur as protein-bound amino acids, are important because of their essential physiological functions in the newborn.

Taurine is one of the final metabolic products of sulphur-containing amino acids, which occurs as free amino acid in various mammalian tissues. Normal cow milk contains 0.6 mg/100 ml (1 μmol/100 ml), and cow colostrum has 8 mg/100 ml (Erbersdobler et al., 1983).

Human mature milk contains significantly more taurine (30 μmol/100 ml) than cow milk or the milk of other species, sheep 14, horse 3, rabbit 14, guinea pig 17, but less than the milk of cat 287, dog 181, and mouse 75 μmol/100 ml, respectively (Gaull, 1982). Taurine may act as a membrane stabiliser and growth modulator in recognition of the high concentrations found in fetal tissues (Naismith et al., 1986). An established function of taurine is the formation of bile salts, which facilitate the digestion and absorption of lipids (Renner et al., 1989).

Carnitine is a critically important nutrient for the human neonate, since the endogenous synthesis from lysine appears to be lower than in adults (Renner et al., 1989). Baltzell et al. (1987) reported that carnitine plays an important role in facilitating the transport of fatty acids into mitochondrial matrix for oxidation, in the initiation of ketogenesis, and in the maintenance of thermogenesis. Carnitine is synthesized in human liver and kidney from lysine and methionine (Borum, 1985). Reports on carnitine contents of goat and sheep milk are scarce. Cow milk has higher carnitine than human milk, which is 160–270 versus 30–80 nmol/ml, respectively. Cow milk based baby food formulae contain 60–250 nmol/ml (Renner et al., 1989).

9. Minerals

Mineral contents of goat and sheep milk are much higher than those of human milk. Goat milk contains about 134 mg Ca and 121 mg P/100 g (Table 11), while human milk has only one-fourth to one-sixth of these two major minerals. The concentrations of macro-minerals may not fluctuate much, but they vary depending on the breed, diet, individual animal, stage of lactation, and status of udder health (Park and Chukwu, 1988). Substantial changes in contents of the major minerals in goat milk were found during the first 7 weeks of lactation by Maraval and Vignon (1982). Overall, goat milk has more Ca, P, K, Mg and Cl, and less Na and S contents than cow milk (Table 11; Haenlein and Caccese, 1984; Park and Chukwu, 1988; Chandan et al., 1992).

Mineral concentrations are very different between milk and blood. K, Ca, and P in milk are higher, but Na and Cl are lower than in blood because of active pumping mechanisms. The Na–K pump regulates K osmolarity between blood cytoplasm and milk. The Ca pump transports Ca from the basal membrane into the cytosol and furtheron into the Golgi apparatus of the mammary alveolar cells to build casein micelles (Pulina and Bencini, 2004). These movements of ions, lactose and water between blood, intracellular alveolar fluids and milk are very important for the normal osmotic balance of a healthy udder and they are correlated to the amounts of milk yield (Pulina and Bencini, 2004).

A high inverse relationship exists between lactose content and the molar sum of Na and K contents of goat or other species milks (Konar et al., 1971; Park and Chukwu, 1988). Chloride has been shown to be positively correlated with K and negatively with lactose. Potassium content of goat milk was 1.50–1.80 g/l in studies by Konar et al. (1971) and not affected by stage of lactation, while citrate concentration decreased during lactation. No major minerals of goat milk were affected by parity except for Na level, which was 15–20% lower than in the first lactation (Maraval and Vignon, 1982). Citrate is a kind of harbinger of lactogenesis in goats (Peaker and Linzell, 1975), where its level in mammary secretion increases sharply from virtually nil to normal 150–200 mg/100 ml on the day of parturition (Peaker and Linzell, 1975). Total carbon dioxide and carbonate in freshly drawn goat milk was 3.4 mM, of this CO_2,

Table 11
Mineral and vitamin contents (amount in 100 g) of goat, sheep and cow milk as compared with human milk

Constituents	Goat	Sheep	Cow	Human
Mineral				
Ca (mg)	134	193	122	33
P (mg)	121	158	119	43
Mg (mg)	16	18	12	4
K (mg)	181	136	152	55
Na (mg)	41	44	58	15
Cl (mg)	150	160	100	60
S (mg)	28	29	32	14
Fe (mg)	0.07	0.08	0.08	0.20
Cu (mg)	0.05	0.04	0.06	0.06
Mn (mg)	0.032	0.007	0.02	0.07
Zn (mg)	0.56	0.57	0.53	0.38
I (mg)	0.022	0.020	0.021	0.007
Se (μg)	1.33	1.00	0.96	1.52
Al (mg)	n.a.	0.05–0.18	n.a.	0.06
Vitamin				
Vitamin A (IU)	185	146	126	190
Vitamin D (IU)	2.3	0.18 μg	2.0	1.4
Thiamine (mg)	0.068	0.08	0.045	0.017
Riboflavin (mg)	0.21	0.376	0.16	0.02
Niacin (mg)	0.27	0.416	0.08	0.17
Pantothenic acid (mg)	0.31	0.408	0.32	0.20
Vitamin B_6 (mg)	0.046	0.08	0.042	0.011
Folic acid (μg)	1.0	5.0	5.0	5.5
Biotin (μg)	1.5	0.93	2.0	0.4
Vitamin B_{12} (μg)	0.065	0.712	0.357	0.03
Vitamin C (mg)	1.29	4.16	0.94	5.00

Data from Posati and Orr (1976), Park and Chukwu (1988,1989), Jenness (1980), Haenlein and Caccese (1984), Debski et al. (1987), Coni et al. (1999), Gebhardt and Matthews (1991) and Park (2006a).

1.9 mmol/l was in the form of bicarbonate ion (Linzell and Peaker, 1971).

Trace mineral contents of goat milk are also affected by diet, breed, individual animal, and stages of lactation (Park and Chukwu, 1989). Mean levels of Mn, Cu, Fe, and Zn in goat milk were 0.032, 0.05, 0.07, 0.56 mg/100 g (Table 11), while Anglo-Nubian goat milk contained significantly higher levels of Cu and Zn than French-Alpine goat milk (Park and Chukwu, 1989). Among trace minerals, Zn was in greater amounts, but goat and cow milk had more Zn than human milk (Park and Chukwu, 1989). Levels of Fe in goat and cow milk are significantly lower than in human milk (Table 11), whereas goat and cow milk contain significantly greater iodine contents than human milk, which would be important for human nutrition, since iodine and thyroid hormones are involved in the metabolic rate of physiological body functions (Underwood, 1977).

Positive correlations were determined between levels of Co and P, K, Na, Ca, Al and Mg in Norwegian bulk goat milk (Brendehaug and Abrahamsen, 1987). Goat and human milk contain higher levels of Se than cow milk (Table 11). Small amounts of Se (<3%) are associated with the lipid fraction of milk. Glutathione peroxidase is higher in goat than in human and cow milk. Total peroxidase activity (associated with glutathione peroxidase) was 65% in goat milk as opposed to 29% for human and 27% for cow milk (Debski et al., 1987).

Sheep milk has around 0.9% total minerals or ash compared to 0.7% in cow milk (Table 1). The levels of Ca, P, Mg, Zn, Fe, and Cu are higher in sheep than in cow milk, while the opposite appears to be the case for K, Na, and Mn (Table 11). In general, mineral contents of sheep milk seem to vary much more than those of cow milk (Rincon et al., 1994) due to feeding differences and months of the year. The trace minerals in sheep milk have not been extensively studied even though they may be of considerable nutritional and possibly human health interests.

In a discriminant analysis of mineral compositions of 360 raw milk samples, distinct and highly significant differences were found for 120 cow milk samples compared to 120 sheep milk samples, while there was some 10% overlap between sheep and goat milk samples (Jay, 2000). Two discriminant functions with eight quantitative mineral variables were used to plot the milk analyses on a graph, which showed clear separation by species for identifying the origin of milk or milk mixtures in the market place (Jay, 2000; Haenlein and Wendorff, 2006).

Heavy metals in sheep milk have been studied. Total dietary intake of Pb was 15% of permissible limits in Italy, and from sheep cheese, like Pecorino, <0.05% of total intake (Coni et al., 1999). Lead is a contaminant from automobile exhausts on pastures along highways that sheep may be grazing. However, Cd in sheep milk was significantly higher than in cow milk, possibly due to feed sources or different metabolism between the two species. Platinum contents in sheep milk were considered high (Table 11) and possibly due to the grazing along highways, but the effects of platinum in human nutrition have not been studied (Coni et al., 1999; Haenlein and Wendorff, 2006).

9.1. Distribution of minerals between the soluble and colloidal phases

The salt balance in sheep and goat milk is interesting as a contribution to the knowledge of nutritional characteristics of these types of milk, and to the retention of these elements in the curd during cheesemaking. In samples from different herds in mid- lactation from farms in the Madrid region, the percentages of Ca, Mg and P in the soluble phase of goat milk were 33%, 66% and 39%, respectively (Fuente et al., 1997). In European breeds, soluble Ca ranged from 30% to 38% (O'Connor and Fox, 1977; Remeuf, 1993). The levels of Mg and P were 66% and 39%, respectively, close to that found in previous studies. Percentages of Ca, Mg and P in the soluble phase of sheep milk were: 21%, 56%, 35%, respectively, within the variation reported in the literature (Pellegrini et al., 1994). In both species, most of the Zn (92% in sheep and 88% in goats) and Mn (93% in sheep and 89% in goats) were found in the micellar fraction (Fuente et al., 1997). The distribution of Fe and Cu differed more. The soluble phase of sheep milk contained 29% Fe and 44% in goat milk. Sheep milk contained more soluble Cu (33%) than did goat milk (18%) (Fuente et al., 1997).

10. Vitamins

Goat and sheep milk have higher amounts of Vitamin A than cow milk (Table 11). Because goats convert all β-carotene into Vitamin A in the milk, caprine milk is whiter than bovine milk. Goat milk supplies adequate amounts of Vitamin A and niacin, and excesses of thiamin, riboflavin and pantothenate for a human infant (Table 11; Ford et al., 1972; Parkash and Jenness, 1968). If a human infant fed solely on goat milk, the infant is oversupplied with protein, Ca, P, Vitamin A, thiamin, riboflavin, niacin and pantothenate in relation to the FAO-WHO requirements (Jenness, 1980). Vitamin B levels in goat and cow milk are a result of rumen synthesis, and are somewhat independent of diet (Haenlein and Caccese, 1984; Mann, 1988).

Compared to cow milk, goat milk has significant deficiencies in folic acid and Vitamin B_{12}, which cause "goat milk anemia" (Collins, 1962; Davidson and Townley, 1977; Jenness, 1980; Park et al., 1986). Levels of folate and Vitamin B_{12} in cow milk are five times higher than those of goat milk, and folate is necessary for the synthesis of hemoglobin (Collins, 1962; Davidson and Townley, 1977). Vitamin B_{12} deficiency can cause a megaloblastic anemia in infants (Parkash and Jenness, 1968), but the anemia has been attributed mainly to folate deficiency in goat milk. Goat and cow milk are both deficient in pyridoxine (B_6), Vitamins C and D, and all these deficient vitamins must be supplemented to baby nutrition from other sources (McClenathan and Walker, 1982).

In heat treatment of goat milk, Lavigne et al. (1989) reported that high temperature short time pasteurization (HTST) of goat milk was the best processing method to preserve vitamins as well as to extend shelf-life of the milk, although some losses of thiamine, riboflavin and Vitamin C occurred.

Vitamin contents in sheep milk are mostly higher than in cow and goat milk, except for carotene (Table 11), however, research data on vitamins in sheep milk are sparse.

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