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Goat's milk-derived bioactive components - a review

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Abstract

A well balanced diet of modern population includes an increased consumption of products from goat's milk, which has composition different from the commonly used cow milk. Goat's milk is characterized by better digestibility, higher buffer capacity than cow's milk and a lower content of αs_1-casein which is responsible for causing allergic reactions. Goat's milk also contains more free amino acids than cow's milk. The advantage of goat's milk is its approximately 30 % higher magnesium content, high selenium content and glutathione peroxidase enzyme, which means that goat's milk has greater antioxidant properties than cow's milk.

Key words: **goat's milk, bioactive components, increasing the content of bioactive ingredients**

Introduction

Goat's milk production accounts for 2 % of world milk production. It should be kept in mind, however, that these are official statistics which do not reflect the individual production and consumption of goat's milk by the people of developing countries s not taken into account (Park and Guo, 2006; Riberio and Riberio, 2010). The largest producers of goat's milk are India (21.6 % of world production) and the Mediterranean countries (18.4 %) (Silanikove et al., 2010). Among the European countries, the largest producers of this milk are Greece (4.5 %), Spain (4.2 %), France (4.1 %) and Italy (4 %). European countries produce 26 % of world goat's milk (Danków and Pikul, 2011; Lasik and Pikul, 2012).

General goat's milk characteristic

Goat's milk is becoming more and more popular due to its better digestabilty, high protein, phosphorus and calcium levels, as well as the fact that more people are experiencing intestinal milk intolerance. The chemical composition of goat's milk is similar to that of cow's milk. The proportion of individual nutrients in goat's and sheep's milk is shown in Table 1.

The physical properties of goat's milk do not differ significantly from cow's milk (Table 2). Goat's milk is characterized by a higher iodine value compared to cow's milk, which indicates a higher content of unsaturated fatty acids than in cow's milk (Wang et al., 2016). The saponification is lower and refractometric index is higher than for cow's milk (Jandal, 1996; Haenlein and Wendorf, 2006; Park et al., 2007; Rayal-Ljutovac et al., 2007).

TABLE 1. Chemical composition of particular types of milk (%) (Pandya and Ghodke, 2007; Raynal-Ljutovac et al., 2007)

Milk	Protein	Fat	Lactose	Mineral components	Dry matter
Goat	3.52	4.25	4.27	0.86	13.00
Sheep	5.81	7.98	4.81	0.90	20.29
Cow	3.50	3.70	4.90	0.70	12.80

TABLE 2. Physical properties of goat's-, sheep's- and cow's milk (Park, 1994; Jandal, 1996; Haenlein and Wendorff, 2006; Park et al., 2007; Raynal-Ljutovac et al., 2007; Wang et al., 2016)

Descriptors	Goat	Sheep	Cow
Active acidity (pH)	6.08-7.06	6.6-6.8	6.5-6.7
Titration acidity (ºSH)	4.4-9.2	6.0-7.5	6.0-8.0
Number of saponification (mgKOH/1g)	228	240	232
Iodine number (gI/100g)	30.44	30.52	27.09
Refractometric index (nD^{20})	1.450	1.349	1.334
Conductivity (Ω/cm)	0.0067	0.0038	0.0040
Freezing point (°C)	-0.556	-0.570	-0.530-0.570
Size of casein micelles (nm)	260	193	175

TABLE 3. Participation of individual protein fractions in goat's-, sheep's- and cow's milk (Tamime et al., 2011)

Protein fractions	Goat	Sheep	Cow
α-s-1 casein (% of casein)	5	16	38
β-s-2 casein (% of casein)	25	15	10
β-casein (% of casein)	50-64	39-47	33-39
κ-casein (% of casein)	10-20	7-10	11-13
α-lactalbumin (% of whey proteins)	40	25	25
β -lactoglobulin (% of whey proteins)	40	51	50
immunoglobulins (% of whey proteins)	18	15	12
IgA (μg/cm^3)	30-80	70-100	140
Ig M (μg/cm^3)	10-40	10-40	50
IgG (μg/cm^3)	100-400	100-500	590
lactoferrin (μg/cm^3)	20-200	20-200	20-200

Protein fraction characteristic

Goat milk contains approximately 3.5 % protein. Goat's milk has seven main groups of proteins: β-casein, α-s-1 casein, α-s-2-casein, κ-casein, α-lactalbumin, β-lactoglobulin, immunoglobulin. The main casein fraction in goat's milk is β -casein (Table 3) (Mohantyet al., 2016).

Casein proteins constitute 80 % of all milk proteins (Jaworski, 1997; Mohanty et al., 2016). Casein micelles are produced in milk cells from polypeptide chains. Calcium ions, which form bonds with the phosphate residues of polypeptide chains, play an important role in their formation. A colloidal solution with casein micelles is stable due to the presence of negative electrical charges in the protein chains. This creates a hydration layer around the micelles (Jaworski, 1997). The nutritional value of casein proteins is similar to meat protein, but it is deficient in methionine and cysteine. Besides carbon, hydrogen, oxygen and nitrogen, it contains sulphur and phosphorus bound organically and comprehensively.

There are some differences between the casein in goat's and cow's milk proteins. They concern not only the absolute content of this fraction, but also the composition and properties.

The important differences in protein polymorphisms have not been discussed nor its significance in human health such as allergies.

Casein micelles contain 94 % protein, and the remaining 6 % consists of calcium, phosphorus, magnesium and citrate, depending on the animal species. The casein micelles found in goat's milk are characterized by a higher calcium and phosphorous content and greater diameter than cow's milk micelles. They also have greater susceptibility to solvation and less thermal stability, which makes clotting difficult (Park et al., 2007). In cow's milk, αs1-casein constitutes the largest ratio in casein proteins (Table 3), and is responsible for triggering allergic reactions (Litwińczuk, 2004; Nongonierma and FitzGerald, 2015). Its share in the total nitrogen of goat's milk is 25 %, in cow's milk it is 38 % (Tziboula-Clarke, 2003; Mituniewicz-Małek et al., 2011). In goat's milk the level of this protein fraction is often much lower, and for some breeds it is completely absent. This makes goat's milk a good substitute for cow's milk in some allergies or intolerances. Goat's milk is dominated by the β-casein fraction. Its level in goat's milk is 50-64 % relative to total casein protein, compared to cow's milk, which accounts for 33-39 % (Tziboula-Clarke, 2003; Mituniewicz-Małek et al., 2011). The content of α-s-2 casein in goat's milk varies between 10-30 % of total casein, while casein-κ 10-20 %. For comparison, the level of these fractions in cow's milk is 10 % and 11-13 %, respectively (Wszołek, 2006). The whey proteins in goat's milk include: β-lactoglobulin, α-lactalbumin, immunoglobulins IgG, Ig, IgM, serum albumin, lactoferrin and lysozyme. β-lactoglobulin is composed of 162 amino acids and is structurally distinctly different from animal species. The level of β-lactoglobulin in goat's milk is lower than in sheep's and cow's milk. On the other hand, α-lactalbumin content is higher in goat's milk compared to sheep's and cow's milk (Morgan et al., 2001; Park, 2006; Herrero and Requena, 2006). β-lactoglobulin has anti-carcinogenic properties. It is responsible for the binding of many chemicals, vitamin A, mercuric chloride, long-chain fatty acids and supports the activity of lipolytic enzymes. It does not dissolve in water, and reduces the oxidation of fats in dairy products. α-lactalbumin is a carrier of calcium and other elements, binds zinc, cobalt and magnesium ions. It also has antitumor and antimicrobial properties, improves mood, helps to overcome stress, helps to fall asleep, and has a protective effect against gastric ulcers (Milewski and Kędzior, 2010). Accompanied by apoptosis, it acts as an anti-tumor and immunological agent. It is involved in the synthesis of lactose. Whey proteins contain significant amounts of exogenous lysine and sulfuric amino acids, i.e. cystine and cysteine (Molina et al., 2003; Cabiddu et al., 2005; Haenlein and Wendorff, 2006).

Peptides formed during digestion in the digestive tract have beneficial effects for human health and prevent many diseases (Kuczyńska et al., 2009). The amount of non-proteinaceous nitrogen compounds, i.e. urea, uric acid, free amino acids, creatine and creatinine in goat's milk is on average 8.7 %, in sheep's milk 13 %, and cow's milk 5.2 % (Rashida et al., 2004; Mituniewicz-Małek et al., 2011). The high content of easily digestible non-protein nitrogen in goat's milk results in faster growth of lactic bacteria and a faster rate of acidification. Goat's milk also contains more free amino acids than cow's milk. The free amino acid content in goat's milk varies from 16.02 to 20.7 mg/100 g of amino acids. The percentage of free amino acids in the total amount of non-proteinaceous nitrogen compounds is about 17 %. The proportion of individual free amino acids in goat's milk is varied and comprises threonine (5.1-16.1 %), glutamic acid (17.1-27.5 %), glycine (9.0-28.5 %) and valine (1.4-25.4 %). There is no cystine in free amino acids and tryptophan is present in very small amounts (Table 4). Another valuable non-protein amino acid, taurine, which is about 20 times higher than in cow's milk, is worth mentioning. Taurine is involved in the stabilization of cell membranes, has antioxidant properties and also stimulates glycolysis and glycogenesis (Redmond et al., 1998; Ahmed et al., 2015). Goat's milk contains an average of 6.62 mg/100 g of taurine as a free amino acid, while in cow's milk it is 0.16-1.00 mg/100 g (Szczepanik and Libudzisz, 2000; Ziarno and Truszkowska, 2005; Silanikove et al., 2010).

TABLE 4. The content of selected amino acids in goat's-, sheep's- and cow's milk in 100 g of milk (Park et al., 2007)

Amino acids (g)	Goat	Sheep	Cow
Isoleucine	0.207	0.338	0.199
Leucine	0.317	0.587	0.220
Lysine	0.290	0.513	0.261
Methionine	0.080	0.155	0.083
Phenylalanine	0.155	0.284	0.159
Threonine	0.163	0.268	0.149
Tryptophan	0.044	0.084	0.046
Valine	0.240	0.448	0.220

Lipid fraction characteristic

Milk fat is synthesized in the mammary gland from blood plasma components: acetate, β-hydroxybutyrate, triacylglycerols and chylomicrons and in smaller amounts from lipoproteins, sterols, phospholipids, free glycerol and free fatty acids (Szulc et al., 2010). In terms of quantity, this is the least stable component of milk. The fat in goat's milk is in the form of an emulsion consisting of fatty balls of a smaller diameter than that of sheep's and cow's milk. It does not contain the enzyme agglutinin, which causes the fat globules to stick together when milk is cooled. In the acylglycerols of goat's milk lipids, the highest proportion of triacylglycerols is 97.8 % (Table 5). Di- and monoacylglycerols are respectively 2.2 % and 0.9 % of goat's milk lipids. In goat's milk lipids, triacylglycerols dominate, with very small amounts of mono-, diacylglycerols, phospholipids and cholesterol. In goat's milk the content of phospholipids is much higher than in sheep's milk (Jandal, 1996; Bonczar and Paciorek, 1999). As with the other ingredients of milk's fat, the content depends on a number of factors (environmental, physiological and genetic).

TABLE 5. The proportion of fat fractions in goat's-, sheep's- and cow's milk (Blasi et al., 2008; Tamime et al., 2011)

Fat fractions	Goat	Sheep	Cow
Triacylglycerols	97-99	96-99	96-99
Diacylglycerols	2.2	0.4-1.4	0.3-1.6
Monoacylglycerols	0.9	0.5	0.002-0.1
Compound lipids	1-3	1-2.1	1-2.3
Phospholipids	0.44	0.043	0.2-1.0
Glycolipids	0.08	-	0.0-0.07
Cholesterol	0.03	0.03	0.02

The cholesterol content in the milk fat of selected mammalian species is presented in Table 5 (Strzałkowska et al., 2012). Cholesterol comprises a small fraction of the total lipid content of goat's milk. It is an indispensable component of the cellular membranes of the myelin sheath of plasma lipoproteins and neural tissue. It also participates in the synthesis of vitamin D and bile acids (Bonczar et al., 2002; Strzałkowska et al., 2009). It has been argued that fat milk clearly affects the risk of cardiovascular disease among humans. Cholesterol levels in raw milk and dairy products depend on a number of factors. The animal's individual characteristics, diet, health and lactation contribute directly to the cholesterol level in milk. In dairy products, this cholesterol content is determined by the technology used (homogenization, heat treatment, storage), starter culture type and initial fat content in the milk (Rao and Reddy, 1984; Bonczar et al., 2011; Atti et al., 2006). The cholesterol level in goat's milk is 10 to 20 mg/100 mL (for comparison, cow's milk contains 10 mg/100 mL) (Park, 2000). Table 6 gives the percentage of the six fractions of phospholipids present in goat's and sheep's milk. Three of them, phosphatidylcholine, phosphatidylethanolamine and sphingomyelin, are present in the highest amounts. Phosphatidylserine, phosphatidylinositol and lysophospholipid constitute a small percentage of milk fat.

TABLE 6. Basic fractions of phospholipids of goat's- and sheep's milk (Jandal, 1996)

fractions of phospholipids (% phospholipids)	Goat	Sheep
Phosphatidylethanolamine	33.20	36.00
Phosphatidylserine	6.70	3.10
Phosphatidylcholine	25.70	29.00
Phosphatidylinositol	5.60	3.10
Lysophospholipid	0.50	-
Sphingomyelin	29.90	28.30

In goat's milk fat, compared to sheep's milk, there are more mono- and polyunsaturated fatty acids (Table 7), which results in the milk having more beneficial nutritional value (Ryniewicz et al., 2000; Pieniak-Lendzion and Niedziółka, 2004). In comparison to sheep milk, goat's milk has higher content of cephalin that was a source of easily absorbable phosphorus (Szczepanik-Wiatr and Libudzisz, 1996).

The content and composition of fatty acids are also largely dependent on the composition of the feed. In milk fat, attention should be paid to the content of conjugated linoleic acid dienes, which have the capacity to inhibit carcinogenesis, as well as counteract atherosclerosis and osteoporosis. Their proportion in goat's milk is 0.84 % and in cow's 0.55 % (Jandal, 1996; Patkowska-Sokoła et al., 2000; Blasi et al., 2008; Tamime et al., 2011; Yao et al., 2016). The term CLA is defined by the positional group of geometric isomers of linoleic - octadiene (C18: 2) with conjugated diene (Tsiplakou et al., 2006). These CLA isomers include cis9, trans11 isomer, and trans10, cis12 C18: 2 (Szumacher-Strabel, 2005; Szumacher-Strabel et al., 2011). The cis9 isomer, trans11 C18: 2 is the major CLA isomer and constitutes in milk 75-90 % of all isomeric forms. The percentage content of the second trans10, cis12 C18: 2 isomer is significantly lower, ranging from 5 to 20 % (Szumacher-Strabel, 2005; Tsiplakou et al., 2006; Renna et al., 2011; Lu et al., 2016).

The richest sources of CLA are animal products, including meat and ruminant milk, whereby it is found in a significantly lower contents in foods of plant origin (Jahreis et al., 1999; Serafeimidou et al., 2012; Albenzio et al., 2016). Dairy products contain approximately 2.9-6.1 mg CLA/g fat, whereas in vegetable oils it ranges from 0.2-0.7 mg/g fat (Prandini et al., 2011). The data in Table 7 show that sheep's milk has a higher CLA content (1.1-3.0) than goat's milk (0.58-1.1) and cow's (0.41-2.5). There is a higher amount of CLA in fermented beverages compared to unfermented milk (Prandini et al., 2007). This is due to the ability of microorganisms used in the fermentation of milk products to produce CLA. Studies on CLA concentrations in fermented dairy products have shown that strains such as *Bifidobacterium, Lactococcus, Lactobacillus, Streptococcus* and *Propionibacterium* have this property (Prandini et al., 2007). In addition to the type of strains used, the number and the parameters of the fermentation process and the type of feed used are also important (Prandini et al., 2007; Szumacher-Strabel et al., 2011; Serafeimidou et al., 2012).

Conjugated linoleic acid and, more important, its isomers, exhibits a number of physiological and biological functions that have a beneficial effect on the human body. The general effect of CLA contributes to reducing the risk of heart disease, atherosclerosis, cancer or obesity. In addition to anti-atherogenic and anticancer activity, CLA has antioxidant activity that is significantly higher than α-tocopherol. It also supports the immune system, contributes to the reduction of body fat or muscle mass, and also demonstrates bacteriostatic properties to *Listeria monocytogenes* (Prandini et al., 2007; Tsiplakou et al., 2006; Szumacher-Strabel et al., 2011). Vaccenoic acid (C18: 1 trans-11) is an oleic acid isomer, the double bond is in the Δ11 position. Regardless of the cis or trans configuration, the source of the isomers of this acid are primarily lipids of meat and ruminant milk (Przybojewska and Rafalski, 2003). It is the second intermediate in the biocohydration process of unsaturated fatty acids into stearic acid, making it a major source of cis9 synthesis, CLA trans11 (Meluchowa et al., 2008; Castro et al., 2009). The biological activity of vaccenium isomers (VA) is associated with its anti-carcinogenic and anti-atherosclerotic properties. Both the cis and trans isomer of vaccenoic acid slow down the progressive growth of tumor cells, but the trans form of this isomer is characterized by greater inhibitory potency, unlike the cis form (Przybojewska and Rafalski, 2003; Ciołkowska et al., 2012).

The average diameter of the goat's milk fat is 2.76 µm (0.73 µm to 8.58 µm) and, in the case of cow's milk fat, there is an average of 3.51 µm (in the range of 0.92 µm to 15.75 µm). Approximately 90 % of goat's milk's fat globules reach a diameter of less than 5.21 µm and 90 % of the fat globule curd has a diameter of less than 6.42 µm. Thanks to this, goat's milk is characterized by high nutritional value and digestibility, which also results from higher levels of goat's milk in short- and medium-chain fatty acids and their better distribution in triacylglycerides (Ziarno and Truszkowska, 2005; Collomb et al., 2006; Gorissen et al., 2012).

TABLE 7. Content of the main fatty acids in goat's-, sheep's- and cow's milk (Jandal, 1996; Collomb et al., 2006; Kuczyńska et al., 2009; Tamime et al., 2011)

Fatty acids (%)	Goat	Sheep	Cow
Saturated fatty acids	75.3	30.6-33.2	62.7-74.8
Monounsaturated fatty acids	20.7	11.8-12.2	20.8-28.0
Polyunsaturated fatty acids	3.4	1.8-3.2	3.8-4.0
CLA	0.84	1.10	0.55

TABLE 8. Fatty acids content (%) in different types of milk (Jandal, 1996; Anti et al., 2006)

Fatty acids	Goat (%)	Sheep (%)	Cow (%)
$C_{4:0}$	3.6	4.0	3.3
$C_{6:0}$	2.9	2.6	1.6
$C_{8:0}$	2.7	2.5	1.3
$C_{10:0}$	8.4	7.5	3.0
$C_{12:0}$	3.3	3.7	3.1
$C_{14:0}$	10.3	11.9	9.5
$C_{16:0}$	24.6	25.2	26.5
$C_{16:1}$	2.2	2.2	2.3
$C_{18:0}$	12.5	12.6	14.6
$C_{18:1}$	28.5	20.0	29.8
$C_{18:2}$	2.2	2.1	2.5

Goat's milk contains more short chain fatty acids than cow's milk. In terms of the general profile, fatty acids such as C4: 0, C6: 0, C8: 0, C10: 0, C12: 0, C14: 0 and C18: 2 are present in greater amounts in goat's milk than in sheep's milk (Table 8). C18: 0 and C18: 1 fatty acids are present in smaller amounts (Ziarno and Truszkowska, 2005). The content of C6: 0, C8: 0 and C10: 0 in goat's milk is about 15 % relative to the total fat content of this milk. For comparison, cow's milk contains about 6 % of the listed fatty acids in relation to the total fat content (Danków and Pikul, 2011). It should be noted that goat's milk has a specific aroma due to the high content of free fatty acids (5.65 mg/dm^3). For the formation, the 'goat aroma' also corresponds to the goat's milk enzyme, i.e. lipoprotein lipase. It is located on the surface of fatty beads (46 %), milk serum (46 %) and on the casein micellar surface (8 %). Hence, goat's milk is more easily liable to lipolysis and is more susceptible to spontaneous lipolysis due to milk cooling.

Carbohydrates fraction characteristic

80 % of lactose is produced from glucose in the Golgi apparatus and 20 % from acetate. This disaccharide supports the absorption of calcium in the lower sections of the small intestine, facilitates the conversion of calcium ions to erythrocytes and improves the absorption of magnesium, phosphorus and other elements. In addition, it has a positive effect on the body's utilization of vitamin D and is a natural source of glucose, which is involved in the synthesis of important structural relationships of the nervous system. Many people suffer from lactose intolerance. This condition is due to a decrease in the activity or the absence of β-galactosidase enzyme. Some symptoms of lactose intolerance are bloating, abdominal pain, diarrhoea, nausea and vomiting (Ziarno and Truszkowska, 2005). Lactose intolerance usually occurs after ingestion of 7-15 g. Intolerant people are advised to consume milk in the form of fermented beverages containing hydrolysed lactose (up to 50 % of its original content) and active β-galactosidase produced by lactic acid bacteria (Ziarno, 2006). The proportion of lactose in goat's milk is 0.2-0.5 % smaller than in cow's milk (Pandya and Ghodke, 2007). Goat's milk contains between 250 and 300 mg/L of oligosaccharide, four or five times more than cow's milk, but much less than breast milk (5-8 g/L). The oligosaccharides present in goat's milk have a complex structure, whose profile is similar to that of human milk oligosaccharides. For this reason, they can be used successfully to produce infant milk for newborns (Martinem-Ferez et al., 2005; Silanikove et al., 2010).

TABLE 9. Average content of minerals (mg/100 g) of goat's-, sheep's- and cow's milk (Park, 2007)

Minerals (mg/100 g)	Goat	Sheep	Cow
Calcium	134	193	122
Phosphorus	121	158	119
Magnesium	16	18	12
Potassium	181	136	152
Sodium	41	44	58
Chlorine	150	160	100
Sulfur	28	29	32
Iron	0.07	0.08	0.08
Copper	0.05	0.04	0.06
Manganese	0.032	0.007	0.02
Zinc	0.56	0.57	0.53
Iodine	0.022	0.02	0.021
Selenium (μg)	1.33	1.0	0.96

Minerals and vitamins

Mineral components include mineral salts as well as salts of organic acids. They affect the physical properties of milk, mainly non-protein stability. The main mineral components found in goat's milk are calcium, phosphorus, potassium and chlorine (Table 9).

Goat's milk is characterized by iron and copper deficiency. This can lead to anemia in children, who are given only one of these types of milk (Pełczyńska, 1995; Szczepaniak and Libudzisz, 2000). The levels of potassium and chlorine in goat's milk, which are high in relation to cow's milk, can contribute to the excess of these elements in the diet and the potential for intestinal disturbances. Hence, for infant feeding goat's milk should be diluted 2:1 (Danków and Pikul, 2011). The advantage of goat's milk is about 30 % higher magnesium content (15-18 mg/100 g) which is responsible for many enzymatic reactions in living organisms. In addition, it reduces tension in the nervous system, protects against lead accumulation and improves the body's resistance to the influence of biometeorological factors (Borek-Wojciechowska, 1994). The high selenium (0.013 mg/kg) and glutathione peroxidase enzyme (57.3 mU/mL) content give goat's milk strong antioxidant properties (Haenlein and Wendorf, 2006; Park et al., 2007). Goat's milk is considered a good source of retinol, B vitamins, especially B1, B2, vitamin C and niacin (Table 10).

TABLE 10. Average content of vitamins in 100g of goat's-, sheep's- and cow's milk (Park, 2006; Raynal-Ljutovac et al., 2008)

Vitamins	Goat	Sheep	Cow
Retinol (A) (mg)	0.04	0.08	0.04
Vitamine D (μg)	0.06	0.18	0.08
Tocopherol (E) (mg)	0.04	0.11	0.11
Thiamine (B_1) (mg)	0.05	0.08	0.04
Riboflavin (B_2) (mg)	0.14	0.35	0.17
Niacin (B_3) (mg)	0.20	0.42	0.09
Pantothenic acid (B_5) (mg)	0.31	0.41	0.34
Pyridoxine (B_6) (mg)	0.05	0.08	0.04
Biotin (B_8) (μg)	2.0	No data	2.0
Folic acid (μg)	1.0	5.0	5.3
Cobalamin (B_{12}) (μg)	0.06	0.71	0.35
Ascorbic acid (C) (mg)	1.3	5.0	1.0

The ability to increase the content of bioactive ingredients in processed milk

The nutritional value of goat's milk is high. It is used as an alternative to cow's milk in the diet of children and adults. As a result of the species specificity, goat's milk lipids are characterized by a higher content of short- and medium-chain fatty acids, which are faster to digest (Blasi et al., 2008). Goat's fatty acids profile is specific due to a unique cholesterol metabolism, which facilitates the dissolution of cholesterol in bile acids. Goat's milk is used in the diet of people suffering from cardiovascular disease and epilepsy, and in premature babies (Park, 1994; Jandal, 1996; Park, 2006). Allergy to goat's milk is about 72-73 % lower than to cow's milk with respect to α-lactalbumin and about 96 % with respect to β-lactoglobulin (Mituniewicz-Małek et al., 2011). It has been shown that in children aged 6-13 years who received approximately 1 L of raw goat's milk every day for 5 months, mineralization and bone density improved and vitamin A content in serum plasma and blood plasma increased. In addition, studies in Western countries show that goat's milk provides relief for rheumatism (Piendziak-Lendzion and Niedziółka, 2004). Thanks to its nutritional and dietary value, goat's milk is especially recommended for population suffering from allergies, convalescents and children. Under natural conditions, goats eat nearly 450 plant species, many of which contain medicinal substances and important micronutrients (Milewski and Kędzior, 2010). The nutritional value of milk is closely related to its composition. It is believed that differences in the basic composition of milk are related to different needs of the individual species of young mammals. Therefore, the level of the most important components of milk fluctuates and is linked to genetic and non-genetic factors, i.e. environmental and nutritional factors (Pijanowski, 1980; Litivczuk, 2004; Danków and Pikul, 2011).

The most important genetic factor is race, which is the main cause of changes in the content of individual components of milk, but also determines the amount of raw material. The milk composition can be modified by crossbreeding or by breeding selection (Krzyżewska, 2011). Genetic factors directly affect physiological factors. Among the physiological factors determining the chemical composition of milk is the lactation phase. The most important differences are observed during the initial lactation period, when the glands secrete colostrum. Its composition almost completely deviates from the milk secreted in later periods. Moreover, the age of animals and the time between the feeding of the offspring and the milk, as well as the state of health of the female, are also important. The most important environmental factors include the climatic conditions, the way of feeding and the season. The greatest variations are in the content and composition of milk fat (Litivczuk, 2004; Danków and Pikul, 2011). Recently, there has been a growing interest in research aimed at increasing the bioactive ingredients in milk and dairy products, not only from cow's milk. One of the ways this can be achieved is by supplementing ruminant diets under controlled conditions to alter the fatty acid composition and by using membrane processes to alter the composition of milk proteins.

Controlled animal nutrition

The way of feeding animals has a significant influence on the formation of biologically active ingredients in milk. There are three ways of feeding animals: pasture, ecological and barn. Increasing the proportion of fodder feed in animal feed reduces the milk fat content while increasing the protein level. A common method for increasing the amount of unsaturated fatty acids in milk is the addition of oilseeds, sea algae or fish oil to the feed (Krzyżewska, 2011). Due to the over-reaction of bio-hydrogenation of fatty acids to the feed, fats are added in the form of calcium salts of fatty acids. There are different nutritional strategies affecting the quantitative and qualitative composition of lipids in ruminant milk. One of them is the intensification of processes occurring naturally in the animal's body, i.e. the creation of optimal conditions for the development of microflora in the rumen (Szumacher-Strabel, 2010). The ruminal lipolysis process depends on the presence of *Butyrivibrio sp.* bacteria. Ruminal protozoa, mainly *Epidinium spp.*, also play an important role. They constitute approximately 30 % of the yield. The source of biologically active compounds in ruminant milk are mainly unsaturated fatty acids, which are the substrate for the biohydrogenation and *de novo* synthesis of fatty acids in the mammary gland. Fats that increase the pool of unsaturated fats include fresh green fodder. Using flax seed, rape and soy in the animal feed and reducing the content of lauric and myristic acids as well as palmitic acid and rapeseed or flax seed oil can also facilitate the biophyhydrogen process (Cieślak et al., 2009; Cais-Sokolinska et al., 2011). The reduction of polyunsaturated n-6 acid to n-3 acids in milk can be achieved by the presence in the feed of saturated short-chain fatty acids, as they inhibit the conversion of n-6 acids, thus affecting the ratio of n-3 to n-6 favourably.

Traditional summer grazing on pastures or fortification of fodder with sunflower, flaxseed or corn oil contributes to an increase in CLA in milk (Kuczyńska and Puppel, 2009). The main pathway for CLA formation is the biohydrogenation of unsaturated (linoleic, linolenic, oleic) acids in the rumen and the endogenous synthesis of vaccenic acid in the mammary gland (Castro et al., 2009; Szumacher-Strabel et al., 2011). The bio-hydrating process occurs in the rumen of ruminants in the presence of bacteria of the genus *Butyrivibrio fibrisolvens* or *Megasphaera elsdenii*. Mono- and polyunsaturated fatty acids are isomerized by bacterial enzymes. The first stage of the biohydrogenation process ends with the formation of vaccenoic acid, which is the second intermediate. The resulting vaccenic acid is hydrogenated under the influence of microorganisms into stearic acid (Szumacher-Strabel, 2005; Ciołkowska et al., 2006). The second way to produce significant amounts of CLA, as much as 65 % of the cis9 isomer, trans11 C18: 2, is through endogenous synthesis in the milk gland. This process occurs with the participation of Δ9-desaturase (Meluchova et al., 2008; Castro et al., 2009).

Membrane separation as a method to change a composition of processed milk

One technique of standardizing milk which has been greatly appreciated in recent years is membrane separation. It is known that the composition of milk fluctuates depending on the season, lactation period, race and other factors, and membrane techniques enable effective normalization of milk components without the need for additives. The most commonly used membrane filtration methods in the dairy industry include microfiltration, ultrafiltration, nanofiltration and reverse osmosis (Kurkowska, 2001).

In the diaphragm separation processes, mainly liquids containing many components with different dispersion levels in solution are used, therefore these methods are widely used in dairy technology. As a result of the flow of raw material through the membrane unit, two streams are formed: a permeate consisting of water and substances permeating through the membrane and retentate, or a stream containing the same components that form the retentate enriched with the components retained on the membrane. The concentration of the dry substance in the permeate is always lower than in the feed stream and the concentration of the retentate components is always greater than in the feed. The retentate is often called the concentrate (Saboya and Maubois, 2000).

Transport through the membrane is achieved by using the right driving force. The propulsion of mass transport through the membrane is the difference in chemical potential on both sides of the membrane. This difference can be caused by differences in pressures, concentrations, temperatures or electrical potential. In membrane techniques, the transport of molecules is caused by a difference of potential on both sides of the membrane, and the separation is due to the difference in the transport rate of the solution's components (Saboya and Maubois, 2000; Coutinho et al., 2009).

Industrial production of fermented milk drinks requires a specific dry matter content in the processed milk. It is recommended that its content in milk for yoghurt production is 14-18 %. The chemical composition of the milk purchased for processing is not constant and is subject to seasonal variations. It is therefore necessary to standardize the dry matter content of milk. The most commonly used method for increasing it is the addition of skimmed milk powder. Other means of normalizing the processed milk include evaporation of milk, added milk or added milk proteins. Alternative methods for increasing dry matter content in milk are membrane techniques. Currently, the most commonly used for standardizing milk is ultrafiltration (Kowalska et al., 2000; Domagała and Wszołek, 2008). This allows for a high concentration of milk components, standardizing their contents and changing their proportions.

Another membrane technique commonly used in the dairy industry is microfiltration. The wide range of microfiltration membrane pores (0.1-10 μm) allows the separation and fractionation of milk components to be used. At present, microfiltration is used to remove microorganisms from the milk, allowing it to produce pure microbiological milk. This process removes 99.91 % of the total bacteria from the milk, completely eliminating sulphite-reducing spores and dead cells and other microbial contaminants. It leaves the more drastic heat treatment and thus allows valuable nutrients to be retained in the milk. Milk produced on the basis of a microfiltration technique that has an extended shelf life is called Extender Shelf Life (Śmietana et al., 2004). In addition, microfiltration can be used to separate casein micelles from whey proteins using a suitably selected membrane (pore size 0.1-0.2 μm). This creates the opportunity to separate or thicken casein proteins for cheese production and to modify the proportion of whey protein in the casein of processed milk. Membranes used in microfiltration can be prepared from inorganic materials, i.e. ceramics, metals, glass and organic polymers. Because of the material that made up the membrane, the following can be used (Żulewska, 2010):

/ cellulose acetate with hydrophilic properties, so that they are characterized by low susceptibility to formation of sediment on the membrane,
/ polysulphones with high thermal resistance,
/ polyamides with greater tolerance to the pH of the microfiltered material
/ ceramics with high chemical and thermal stability (up to 130 °C).

The greatest benefit of using membrane techniques for the standardization and removal of micro-organisms from milk is the absence of high temperatures and chemical or biological agents that can contribute to the degradation of valuable components. The use of membrane processes in dairying reduces production costs through lower energy and raw materials consumption. Modules for the process are not expensive, but easy to use and guarantee high performance. It is possible to use this kind of filtration for every production scale due to the modular construction of the process. The use of techniques using membrane separation methods provides the production of new products with increased bioactive ingredients, beneficial functional, sensory and nutritional properties, as well as the management of by-products (Tziboula et al., 1998; Kurkowska, 2001; Debon et al., 2010).

Design of fermented dairy beverages with increased participation of bioactive ingredients

In recent years the food market has been under increased pressure to expand its range of functional and convenient food. Increasing public awareness of healthy diets generates changes in dietary habits, in turn leading to changes in the production of all foods. This also applies to milk processing companies, who seek to increase the range of fermented milk drinks. Products come not only from cow's milk, but also from small-ruminant milk. These drinks contain a properly selected microflora, both technologically and nutritionally (Minervini et al., 2009).

The content of biologically active ingredients in a dairy product is the result of several factors. Feeding animals plays a very important role in this case. Modification of feed composition directly influences the chemical composition of milk. The aspect most susceptible to change is milk fat. Biologically active compounds present in milk fat are produced by bioreacting unsaturated fatty acids in the rumen. In the case of ruminants, using a suitably composed feed, we determine the composition of the ruminal microflora, which in turn determines the direction of fermentation and the composition of the milk. By utilizing milk-rich bioactive ingredients in processing, we can design a product with a higher nutritional value (Cieślak et al., 2009; Szumacher-Strabel, 2010). Nutritional methods for changing milk constituents can also be applied to the regulation of protein content. They involve the modification of animal feeds in such a way that the amino acid composition of the milk produced corresponds to the body's needs for all essential amino acids. Cais-Sokolińska et al., (2011) in their study of the effect of oilcake on goat's milk, found that this supplement reduced cholesterol content. Significant differences were observed in the composition of sheep's and goat's milk obtained under winter and summer (pasture) feeding conditions. Szumacher-Strabel et al., (2011) found that ruminant milk was characterized by higher C18: 0 and C18: 1 acids during summer and lower C4: 0 to C16: 0 content. Moreover, Jahreis et al., (1999) showed that goat's and sheep's milk in spring and summer exhibited a significantly higher content of conjugated linoleic acid dienes compared to autumn and winter months.

Over the past 20 years a number of new whey protein products have been researched. These proteins have a high biological value, higher than soy proteins, eggs or milk casein (Smithers, 2008; Bhat and Bhat, 2011). Their properties and biological value are mainly related to the high content of branched exogenous amino acids such as isoleucine, leucine and valine, which stimulate the synthesis of muscle proteins. Whey proteins have many healthy properties. However, they contain β-lactoglobulin, which is a milk allergen. Inoculation of milk with lactic acid bacteria leads to protein hydrolysis. Some strains also exhibit the properties of β-lactoglobulin decomposition in milk. It has also been found that some probiotic strains are capable of increasing tolerance to this allergen and affecting the distribution of proteins in the intestinal mucosa (Pescuma et al., 2010). Kirjavainen et al., (2003) have shown that supplementation of food for children with *Lactobacillus GG* causes a significant reduction or even elimination of milk allergy. Fermented milk is a metabolically active product and exhibits changes in storage (acidification, loss of viability of starter cultures). Increased whey protein content improves the viability of starter cultures, which is important in the design of functional foods with a high nutritional value (Smithers, 2008). Larger whey protein buffer capacity is likely to protect against secondary acidification of products during refrigerated storage. Research by Pescuma et al., (2010) in the field of whey protein-fortified milk drinks indicates that an increase in whey protein content improved the growth and proteolytic activity of *Lactobacillus delbrueckii* subsp. *bulgaricus*. As a result of protein fermentation, essential amino acids such as leucine, valine, isoleucine, lysine and threonine were released. Leucine, isoleucine and valine provide energy to the muscles and accelerate the synthesis of alanine and glutamic acid during stress caused by trauma, infection or intense exercise. Leucine, lysine, tryptophan, isoleucine and threonine also act as metabolic glucose regulators and affect protein metabolism, which increases their weight control (Pescuma et al., 2010).

Whey proteins are widely used in the production of dietary foods, especially high protein supplements for children, athletes and convalescents. They are also used for the production of thin edible coatings suitable for storing fruits and vegetables. Functional properties of whey proteins include water retention capacity, foaming ability, emulsifying properties and gel formation, as well as viscosity improvement. These proteins are used in the production of yoghurts, cheeses, creams, sausages and bakery products (Glinowski, 2004; Livney, 2010). In yogurt production they improve yogurt flavor, texture, nutritional value, syneresis reduction, prolongs life, extend probiotic viability, reduce costs and reduce the addition of non-dairy ingredients such as starch, gelatine and pectin (Glibowski, 2004; Onwulata and Tomasula, 2006). Fortification of yoghurts with whey proteins increases the water-binding capacity. The higher content of this fraction of milk proteins results in a more homogeneous microstructure. The smaller pore diameter makes it difficult to migrate the solution from the depth of yogurt to the surface.

Whey proteins are often defined as ideal proteins from the nutritional point of view, because they contain essential amino acids for the proper functioning of the human body and bioactive peptides. The amino acid composition of whey protein is almost identical to the essential amino acids in the correct diet, so their participation in the design of new dairy products has increased (Gad and Sayed, 2009; Fluegel et al., 2010).

Increasing the functional properties of fermented milk drinks can also be achieved by using probiotic bacteria for their production. To manufacture a product with the desired organoleptic qualities and to preserve the pro-health properties of probiotic cultures, they must be carefully selected. The characteristics that they should have are: moderate acidogenic activity, milk growth ability, antagonism to food spoilage bacteria, and good survival during refrigerated storage. Fermented milk beverages made with probiotic microflora are a functional food due to their documented properties, ie. lactose intolerance, inhibition of pathogenic bacteria development, hypocholesterolemia, normalization of intestinal motility disorders and inhibition of bacterial nitroreductase which catalyses nitrosamines synthesis (Lacroix and Yildirim, 2007; Reid, 2008; Thirabunyanon et al., 2009; Aureli et al., 2011).

Conclusion

Global production of goat's milk stands at about 16 million tons per year. Outside the cheese industry goat's milk is used more often for the production of fermented milk drinks. These drinks are currently the fastest growing branch of the dairy industry. This is due to the growing consumption of such products, estimated at an increase of about 0.7 % per year on a global scale.

Conscious and rational diets among modern population has resulted in an increased interest in products made from goat's milk, which has a composition different to the commonly used cow's milk. Goat's milk is characterized by easier digestibility and a higher buffer capacity than cow's milk. In the latter, the largest part of the casein is casein-αs_1, which is responsible for causing allergic reactions. Its contribution to the total nitrogen in goat's milk casein is 25 %, while in cow's milk it is 38 %. The casein-αs_1 content in goat's milk protein fraction is much smaller in the case of certain breeds or even absent. The result is that the goat's milk can be a good alternative for cow's milk allergy in some cases. Moreover, goat's milk fat is present in the form of an emulsion consisting of fat globules of a smaller diameter than is the case in cow's milk. It does not contain an enzyme agglutinin, which causes clumping of the fat globules when the milk is cooled. Compared to cow's milk, goat's milk fat contains more mono- and polyunsaturated fatty acids, which results in this milk having beneficial nutritional characteristics. Goat's milk also contains more short-chain fatty acids than cow's milk. In conclusion, because of its characteristic and functional properties, goat's milk products should be a significant part of a healthy and balanced daily diet.

Bioaktivni sastojci kozjeg mlijeka

Sažetak

Uravnotežena prehrana suvremenih potrošača sve češće podrazumijeva i povećanu konzumaciju proizvoda od kozjeg mlijeka koje se svojim sastavom znatno razlikuje od kravljeg. Kozje mlijeko karakteriziraju bolja probavljivost, veći puferski kapacitet u odnosu na kravlje mlijeko te niži udjel αs_1-kazeina kojeg se smatra odgovornim za brojne alergijske reakcije. Osim toga, kozje mlijeko u usporedbi s kravljim sadrži i znatno veće količine slobodnih aminokiselina. Neke od ostalih prednosti kozjeg mlijeka nad kravljim su oko 30 % više magnezija, visoke koncentracije selena i enzima glutation-peroksidaze koji pridonose većem antioksidacijskom kapacitetu.

Ključne riječi: **kozje mlijeko, bioaktivni sastojci, bioactive components, povećanje sadržaja bioaktivnih sastojaka**

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