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ORIGINAL PAPER

CONCENTRATIONS OF SELECTED BIOACTIVE COMPONENTS IN TRADITIONAL CHEESES MADE FROM GOAT'S, COW'S AND SHEEP'S MILK*

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Abstract

The aim of the study was to determine the chemical composition of cheeses made with traditional methods in terms of the concentrations of bioactive components. Three types of rennet cheeses featuring on the list of traditional products: sheep's milk cheese – Oscypek, cow's milk cheese – Gołka, and goat's milk cheese – Ser Podkarpacki, were included in the study. The cheeses were obtained in September, from the regions of their production. The study demonstrated that traditional cheeses made from sheep's, cow's or goat's milk have different basic chemical composition, as well as varied concentrations of minerals, vitamins and fatty acids. Sheep cheese had the highest content of dry matter, fat, raw ash, and calcium. Goat cheese contained over twice as much potassium as Oscypek and Gołka. The vitamin E content was similar in all the three products. Sheep's and cow's milk cheeses had higher UFAs concentrations than goat's milk cheese, including MUFAs. However, the highest concentration of polyunsaturated fatty acids (PUFAs), including *n*-3 PUFAs, was noted in sheep cheese. A significantly higher concentration of short- and medium-length fatty acids was found in goat cheese. Both the differences in the initial composition of the material used for its production, that is the milk of three distinct species, as well as the differences in the production technology may be responsible for the diversity of bioactive components in the products studied. Characterized by varied health benefits, the products should be included in every balanced diet.

Keywords: bioactive components, traditional cheeses, goat, cow, sheep, milk.

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INTRODUCTION

Traditional and regional foods are becoming increasingly popular with consumers. Products made according to traditional, home recipes are thought to be delicious, original and, above all, healthy (Knysz et al. 2018). The List of Traditional Products (LTP), managed by the Polish Ministry of Agriculture and Rural Development (www.gov.pl/web/rolnictwo/lista-produktow--tradycyjnych), currently comprises 1892 items, of which 119 are dairy products, mostly cheeses. Among the cheeses, products made from goat's milk are most numerous, and the second largest group are traditional products from mountain sheep farms. An ovine cheese called Oscypek is the most distinctive regional cheese for the Polish consumer. For centuries, it has been made in the same way from raw milk of mountain sheep in the Polish Carpathians region. Like some other cheeses present on the List of Traditional Products, namely Bryndza Podhalańska and Redykołka (both produced in the Podhale region), Oscypek has the status of a food product guaranteed European protection under the Protected Designation of Origin (PDO) scheme. Including the use of traditional tools, nomenclature and practices, the traditional method of making Oscypek is passed from generation to generation. In compliance with the traditional recipe approved by the European Union, the milk for Oscypek must come exclusively from the Polish mountain sheep breed, with an acceptable addition (40% at the maximum) of milk from the Polish Red Cow. Due to the limited availability of sheep's milk, the cheese is made only from May to September. Oscypek has the shape of a double-sided cone, a spindle, with hard, elastic flesh of light creamy colour and a darker rind. Smoked for a few days, Oscypek acquires its unique flavour, and a shiny colour from yellow to light brown.

In the same region where Oscypek is made, Ser Gazdowski is produced from cow's milk (obtained from the Polish landrace called the Polish Red Cow); the cheese is characterized by its delicate flavour. Its name is derived from the word gazda, meaning a farmer, and in the colloquial language it is often referred to as gołka or pucok. Gołka is a cheese in the shape of a cylinder, slightly yellowish after cutting it in half, darker by the rind; the flesh is elastic, soft, with a distinctive smoky smell and a slightly salty taste. Both Oscypek and Gołka are on the List of Traditional Products under the category of dairy products in the Malopolska and Silesia Provinces (southern provinces of the country).

Goat cheeses are most numerous on the LTP. Subcarpathia (the area in southeastern Poland) is particularly rich in this respect. In this region, Bryndza, Wołoski Goat Cheese, Bundz, as well as white and smoked goat matured cheeses from the Bieszczady and Subcarpathia regions are produced from goat's milk. The latter are more and more often made from milk obtained from the native Carpathian breed of goats. Ser Podkarpacki (Subcarpathian cheese) is flattened cylindrical or cuboid in shape, from white to

light cream in colour, whose rind, after being smoked, becomes from light-beige to brown in colour. Its flavour is salty, characteristic of dairy products made from goat's milk, and it may be modified with herbs. Smoked cheese has a distinct smell and smoky flavour.

The aim of the study was to determine and compare the chemical composition of regional rennet cheeses made with traditional methods: sheep cheese – Oscypek, cow's milk cheese – Gołka, and the Subcarpathian goat cheese Ser Podkarpacki, in terms of concentrations of selected bioactive components.

MATERIAL AND METHODS

Three types of rennet cheese found on the List of Traditional Products: Oscypek – sheep cheese, Gołka – cow's milk cheese, and Ser Podkarpacki, goat cheese, were included in the study. The cheeses were produced in September, in the regions of their production: Oscypek and Gołka in the Podhale region, and goat cheese came from a farm in the Subcarpathian region. Analyses of the composition of the cheeses (6 pieces of every type) were performed at the Central Laboratory of the National Research Institute of Animal Production. The cheeses were lyophilized and a pre-drying rate was determined prior to the analyses. The total protein content was determined by the Kjeldahl method, total fat content by the Soxhlet method, water content by the method of drying the sample at 102°C for 4 h, and the total ash content using the method of incineration of a sample at 550°C (AOAC, 2007). The content of vitamins A and E was determined using the reversed-phase HPLC method. The method of flame atomic absorption was adopted to determine the levels of calcium, magnesium and potassium in milk and dairy products (PN-EN ISI 6869:2002). The separation and determination of fatty acids were performed in a VARIAN 3400 gas chromatograph using a Flame Ionization Detector (FID), and an RTX 2330 capillary column (105 m x 0.32 mm x 0.2 μm). The analytical settings were as follows: the column programming temperature within the range of 140-210°C, injector port temperature: 250°C, carrier gas: helium (flow 3 ml min^{-1}), the injection 0.7 mcl. For CLA determination, acids standards of Lardon Fine Chemicals AB were used. Other acids were determined with Sigma-Aldrich standards. The results were statistically analysed using the Statistica package version 10 and a one-way analysis of variance. The tests were performed at $p \leq 0.05$ and $p \leq 0.01$ levels of significance.

RESULTS

The results of the chemical composition analysis of the three types of cheese studied are presented in Table 1. Considerable variability

Table 1

Chemical composition (mean ± standard deviation) of cheeses

Chemical composition	Cow's milk cheese	Goat's milk cheese	Sheep's milk cheese
Dry matter (%)	61.93^{aB} ± 2.23	44.01^{A} ±2.07	65.75^{Aa}±2.67
Ash (%)	4.33^{a} ± 0.45	4.14^{A}±0.64	$5.41A^{aA}$±0.66
Fat (%)	22.92^{a}±6.87	18.68^{A}±2.22	27.85^{aA}±2.57
Protein (%)	31.89^{B}±4.64	17.99^{AB}±1.43	30.87^{A}±2.01
Ca (g kg^{-1})	4.98^{AB}±0.75	6.64^{AB}±0.33	9.40^{A}±1.14
Mg (g kg^{-1})	0.22^{AB}±0.02	0.43^{B}±0.03	0.39^{A}±0.07
K (g kg^{-1})	0.77^{B}±0.18	1.64^{AB}±0.13	0.64^{A}±0.12
Vitamin A (ug g^{-1})	1.71^{a}±0.23	2.45±0.75	2.66^{a}±0.50
Vitamin E (ug g^{-1})	6.66±2.47	6.35±1.68	6.77±1.67

A, *B* – $p \leq 0.01$; *a*, *b* – $p \leq 0.05$ – the mean values designated with the same letters in rows are statistically significantly different

in the content of the majority of components was observed. Oscypek had the highest amounts of dry matter, fat, and raw ash. Oscypek and Gołka contained similar amounts of total protein. Goat cheeses had the lowest concentrations of basic components, but they contained over twice the amount of potassium (1.64 g kg^{-1}) found in Oscypek and Gołka (0.64-0.77g kg^{-1}). Traditional goat cheese contained more calcium. Similarly to vitamin A, the least amount of Mg was found in Gołka. The amount of vitamin E was similar in all the three products (6.35-6.77 μg g^{-1}).

More unsaturated than saturated acids were found in the fat of the cheeses studied: in Oscypek and Gołka these acids amounted to more than 66-68%, whereas in the fat of ser podkarpacki, to more than 78% (Table 2). The sheep and cow cheeses contained more UFA, including more MUFA, than the goat cheese. Oscypek, on the other hand, had the highest amount of PUFA, including the *n*-3 PUFA fraction. A significantly higher concentration of short- and medium-length saturated fatty acids (SCSFA): $C_{8:0}$, $C_{10:0,}$ and C_{12} was found in the goat cheese. Gołka contained more C_{14} and C_{16} acids, while unsaturated $C_{16\text{-}1}$, $C_{18\text{-}1}$, $C_{18\text{-}2}$ acids were predominant in Gołka and Oscypek. The percentage of specific CLA isomers was different depending on a cheese type. The concentration of the c9-t11-CLA isomer was

Table 2

Fatty acid profile (mean±standard deviation) of cheeses (%)

Fatty acids	Cow's milk cheese	Goat's milk cheese	Sheep's milk cheese
C_{8}	3.523^{aB} ± 0.110	9.928^{AB}±1.632	6.472^{Aa}±0.273
C_{10}	3.166^{aB} ± 0.005	16.765^{AB}±2.033	6.518^{aA}±0.008
C_{12}	4.646^{AB} ± 0.001	5.612^{B}±0.456	4.378^{A}±0.035
C_{14}	13.766^{AB}±0.256	11.243^{B}±1.031	11.848^{A}±0.427
C_{16}	29.180^{A}±a0.195	26.463^{a}±2.150	24.653^{A}±0.176
$C_{16\text{-}1}$	1.303^{B}±0.265	0.628^{AB}±0.238	1.105^{A}±0.008
C_{18}	13.820^{B}±0.010	8.542^{AB}±1.762	12.596^{A}±0.023
$C_{18\text{-}1}$	26.920^{B}±0.001	17.968^{AB}±2.082	27.216^{A}±0.015
$C_{18\text{-}2}$	1.246^{a}±0.028	1.551^{a}±0.165	1.485±0.023
$gama_{18\text{-}3}$	0.026±0.010	0.022±0.004	0.026±0.018
C_{20}	-	0.002^{A}±0.004	0.090^{A}±0.004
$C_{18\text{-}3}$	1.473^{a}±0.030	0.826^{Aa}±0.342	1.761^{A}±0.012
CLA c9-t11	0.366^{Aa}±0.001	0.136^{Ba}±0.068	1.185^{AB}±0.099
CLA t10-c12	0.306^{AB}±1.470	0.002^{B}±0.004	0.006^{A}±2.271
CLA c9-c11	0.010^{AB}±1.470	0.005^{B}±0.005	0.062^{AB}±2.271
CLA t9-t11	-	0.015^{A}±0.005	0.053^{A}±2.026
C_{22}	0.063^{A}±0.225	0.082^{B}±0.022	0.148^{AB}±0.540
$C_{20\text{-}4}$	0.080^{a}±0.107	0.123^{a}±0.026	0.105±0.299
$C_{22\text{-}1}$	0.013±0.287	0.007±0.004	0.008±0.366
EPA	0.093^{a}±0.291	0.048^{A}±0.008	0.116^{aA}±2.969
DHA	-	0.025±0.007	0.163±0.050
SFA	68.166^{B}±0.030	78.642^{AB}±2.847	66.705^{A}±0.043
UFA	31.833^{B}±0.005	21.357^{AB}±2.847	33.295^{A}±0.010
MUFA	28.243^{B}±0.197	18.607^{AB}±2.266	28.328^{A}±0.081
PUFA	3.596^{A}±0.110	2.752^{A}±0.619	4.966^{A}±0.273
PUFA-6	1.343^{a}±0.005	1.698^{a}±0.198	1.612±0.008
PUFA-3	1.566^{a}±0.001	0.896^{Aa}±0.355	2.041^{A}±0.035
DFA	45.653^{B}±0.256	29.897^{AB}±2.476	45.891^{A}±0.427
UFA/SFA	0.466^{B}±0.195	0.272^{AB}±0.049	0.501^{A}±0.176
MUFA/SFA	0.416^{B}±0.265	0.238^{AB}±0.036	0.423^{A}±0.008
PUFA/SFA	0.053^{A}±0.010	0.035^{A}±0.009	0.075^{A}±0.023
PUFA 6/3	0.883^{B}±0.001	2.036^{AB}±0.429	0.796^{A}±0.015

Key: under Table 1

nearly 10 times higher in the sheep cheese than in the goat cheese, whereas t10-c12-CLA was predominant in the cow cheese. The concentration of other isomers (c9-c11-CLA and t9-t11-CLA) was also higher in Oscypek.

DISCUSSION

Cheeses are the most diverse and numerous group of dairy products. They are a rich source of many nutrients, and, primarily, highly valuable protein, easily digestible fat, as well as many minerals, especially calcium and phosphorus (Brodziak et al. 2018). Cheese components have been demonstrated to potentially provide important health benefits. Calcium, present in large amounts in cheeses, has a positive effect on various disorders such as osteoporosis (Heaney 2000), or dental caries (Kato et al. 2002), and it also helps in losing weight (Walther et al. 2008). Some fatty acids such as conjugated linoleic acid (CLA) have demonstrated to display anti-carcinogenic and anti-atherogenic properties (Battacharaya et al. 2006). Bioactive peptides produced during cheese ripening exhibit biological properties including antioxidant, antimicrobial, anti-inflammatory and immunomodulatory activity (López-Expósito et al. 2012). Ripened cheeses are free of lactose and therefore they are suitable for lactose-intolerant people (Walther et al. 2008). Cheeses are considered to be suitable for almost all age groups (Knysz et al., 2018). In Poland, the most popular are rennet cheeses, commonly known as 'yellow cheeses', and curd cheeses (the so-called 'white cheeses'). Polish consumers, however, more and more often buy regional cheeses. These cheeses are often produced directly on farms where traditional methods of animal breeding are used. Studies indicate that the way in which ruminants are fed has a dramatic impact on the quality and chemical composition of milk, as well as its applicability for cheese production. The use of roughage, and green pasture in particular, is of considerable significance in this regard (Martin et al. 2005). The quality of the milk for processing affects the physicochemical and sensory properties of cheese, as well as its productivity (Fekadu et al. 2005). Studies on different kinds of cheese indicate the significant impact of a pasture type on cheese qualities. Active substances present in plants may penetrate into milk and cheese, giving them a characteristic flavour and smell (Carpino et al. 2004). The chemical composition of a cheese and its variability, particularly as regards lipid-soluble components (fatty acids, carotenoids, retinol, α-tocopherol), depends mainly on the conditions under which milk is produced (Lucas et al. 2008) and on the animal species from which milk is obtained (Chilliard, Lamberet 2001, Lucas et al. 2006*a*).

Oscypek is the most recognizable traditional cheese. In compliance with the EU's Council Regulation (2006), the dry matter percentage in Oscypek cannot be lower than 56%. In the present study, the smoked Oscypek contained 65.75% of dry matter. In the study by Kędzierska-Matysek et al.

(2014), Oscypek contained 64.07% of dry matter, 29.09% of protein and 47.22% of fat in dry matter. Drożdż (2001) obtained similar results of chemical composition to the data presented in this study. His study indicated that Oscypek contained 27.30% of water, 29.09% of protein, and 22.54% of fat. The results of the our study concerning dry matter, protein and fat content correspond with the data achieved by Przygoda et al. (2009), who assessed the nutritional value of selected traditional food products, concluding that the Oscypek cheeses made from sheep's milk and in those made from a mixture of sheep's and cow's milk had the mean dry matter content of 66%, protein 29%, fat 27%, and ash 6.6%. Kawęcka and Sosin-Bzducha (2014), on the other hand, indicated that Oscypek cheeses from other mountain breeds – Coloured Mountain Sheep (CMS) and Podhale Zackel (PZ), contained 59.29-60.46% of dry matter, 21.3-27.06% of fat and 25.47-31.85% of protein. The percentage of raw ash in the sheep's cheeses studied amounted to 5.8%.

It was concluded in the study that cow's milk cheese contained less fat and dry matter than Oscypek, but more than the compared goat cheese. In their studies comparing the quality of two cheese types: Oscypek and Ser Gazdowski, Kędzierska-Matysek et al. (2014) demonstrated differences in the dry matter content, which was lower in Gołka than in Oscypek (59.23%), similarly to the content of protein (25.83%). The researchers, however, did not observe any differences in the fat content between the sheep's milk cheese and cow's milk cheese. According to Kudełka (2014), the mean fat content in Gołka, made from cow's milk, was 28.4%. Similar values, i.e. 27.67% of fat, were obtained in a study by Wszołek and Bonczar (2002). The study performed in 2017 by Ochrem et al. indicated that the percentage of protein in traditional cheeses produced in the Podhale region varied, and ranged from 15.72% in fresh cheeses (Bundz type – made from sheep's milk) to as much as 25.35% in smoked Oscypek type cheeses. Not only are cheeses a highly valuable protein source containing almost all exogenous amino acids in quantities covering the needs of an adult, but also, depending on a cheese type, 100 g of this product covers 30-100% of a daily requirement of the organism for calcium. It was concluded in our study that the calcium content in Oscypek was higher than in goat cheese and twice as high as in cow's milk cheese. Comparing the content of micro- and macroelements in Italian and Polish cheeses made from the milk of different animal species (including cow's milk cheeses: Parmigiano-Reggiano, Grana Padano, and Fontina; a buffalo's milk cheese Caciotta Stagionata, and a sheep's milk Pecorino Toscano Stagionato), Kędzierska-Matysek et al. (2018) concluded that in comparison to cheeses made from the milk of other species, Italian cow's milk cheeses had the highest copper levels, whereas sheep's milk cheese had the highest amount of iron. The highest content of magnesium and the lowest content of potassium were observed in buffalo's and sheep's milk cheeses. According to Milewski et al. (2016), sheep and goat cheeses have different chemical composition, nutritional value and sensory character-

istics. Milk and dairy products are an important source of lipid-soluble vitamins, vitamins A and E in particular. Numerous studies prove that milk obtained from ruminants grazing on pasture contains more vitamins than that obtained from animals fed with TMR (Nozière et al. 2006, Radkowska et al. 2018). In comparison with preserved pasture, fresh pasture sward has higher levels of vitamin E and provitamin A (Nozière et al. 2006). Hence, an increase of the content of these vitamins in milk and its products is observed on farms that use grazing during the summer feeding season. The studies conducted by Milewski et al. (2016) indicated that sheep's milk cheese is a rich source of vitamins A and E. In comparison with cow's and goat's milk, due to higher mean fat levels, sheep's milk has a higher percentage of lipophilic vitamins, while goat's milk has the lowest vitamin E concentration (Raynal-Ljutovac et al. 2008). In the present study, the vitamin E content was similar in all the three products. Revilla et al. (2014) analyzed the vitamin A and E content in cheeses produced with the same technology from milk obtained directly from Spanish farms rearing dairy cattle, sheep and goats. The authors found that cheeses made from cow's milk had the highest amount of vitamin A, whereas goat cheeses had the highest content of vitamin E. The curing period affected levels of both vitamins only in the case of cow's milk cheeses. The studies by Lucas et al. (2006*a*,*b*) revealed that the vitamin E content in cow's and goat's milk cheese is not dependent on the technology applied, but rather on the milk's composition, which is influenced by rearing systems, including feeding (hay vs. pasture).

The research by Milewski et al. mentioned above (2016) indicated that sheep cheese is a rich source of PUFAs, while goat cheese has a lower content of SFAs and OFAs, more beneficial UFA/SFA and DFA/OFA ratios, as well as a lower atherogenic index (AI). The presence of short- and medium-length saturated fatty acids (SCSFA) is a unique characteristic of dairy fat. Butyric $C_{4:0}$, caproic $C_{6:0}$, caprylic $C_{8:0}$, capric $C_{10:0}$, and lauric $C_{12:0}$ acid belong to the most important SCSFAs of dairy fat. Sheep and goat cheeses have higher concentrations of these acids than cow's milk cheeses, according to Park et al. (2007). Examining the authenticity of traditional sheep's milk cheeses on the basis of selected physicochemical parameters, Kudełka (2014) observed differences in profiles of fatty acids between specific types of cheeses. The researcher noted a higher content of short-chain fatty acids $C_{4:0}$-$C_{10:0}$ (especially capric acid) in sheep cheeses, and the lowest concentrations of EFAs ($C_{18:2}$ and $C_{18:3}$) in the cheese made from cow's milk. As in the present study, Kudełka (2014) noted that $C_{14:0}$, $C_{16:0}$ acids were predominant in Gołka. The fat in traditional Portuguese sheep cheeses had high concentrations of medium chain fatty acids, with 6-10 carbon atoms (Partidário et al. 2008). Conjugated linoleic acid (CLA) is a polyunsaturated fatty acid with valuable health properties. As regards people's health, among other characteristics, CLA prevents obesity and sclerosis, has anticancer properties, and stimulates the immune system. Primarily, it has been found in the muscle tissue and in the milk of ruminants, with the highest amounts of it noted in sheep's

milk (Shingfield et al. 2010, Kawęcka, Krupiński 2014). The study conducted by Aguilar et al. (2014) comparing fatty acids profiles in cheeses made from sheep's, cow's, and goat's milk indicated that compared with cow's and goat's milk cheeses, sheep's milk cheese had a higher content of $C_{18:1}$ trans isomers. The $C_{18:1}$ trans isomer content in sheep cheese is similar to that reported in Italian (Nudda et al. 2005) and Spanish (Luna et al. 2005) cheeses. This may be due to feeding practices. It is possible that those cheeses came from farms where the sheep were fed with fresh pasture plants or supplemented with oilseeds. When pasture inclusion increases in the total diet, linear increases in $C_{18:3n3}$, $C_{18:1\ t11}$ and $C_{18:2\ c9t11}$, and decreases in $C_{10:0}$-$C_{16:0}$ are observed (Chilliard et al. 2007). The differences in the FA profile between cow's milk cheeses and goat's milk cheeses can be partly explained by differences in the regulation of mammary cells between caprine and bovine species, particularly in the elongation process of FA, which are synthesized *de novo* by the 'fatty acid synthase' complex (Chilliard et al. 2003).

As far as nutrition is concerned, appropriate ratios and proportions of specific groups of acids in products are of special importance. The *n-6:n-3* PUFA ratio is especially important for people's health, and it should be within the range 1 to 4, according to Bergamo et al. (2003). In the research conducted, the *n*-6:*n*-3 PUFA ratio in sheep cheeses was within the range of the recommended feeding standards. Likewise, the study by Aguilar et al. (2014), comparing FA profiles in cheeses made from sheep's, cow's, and goat's milk, demonstrated that the *n*-6:*n*-3 ratio was higher in goat cheese than in sheep and cow's milk cheese. The PUFA:SFA ratio in the samples of cheeses studied by these authors was similar for all species, but lower than recommended by the World Health Organisation (WHO), according to which its value should be over 0.45. In our study, the lowest PUFA:SFA ratio was recorded in goat cheese.

CONCLUSIONS

1. The study indicated that traditional rennet cheeses made from sheep's, cow's and goat's milk have different basic chemical composition as well as varied concentrations of minerals, vitamins and fatty acids.

2. Sheep cheese had the highest content of dry matter, fat, raw ash, calcium and polyunsaturated fatty acids (PUFA), including *n*-3 PUFA.

3. Goat cheeses had over twice as much potassium as Oscypek and Gołka and a significantly higher concentration of short- and medium-length fatty acids was found in these products.

4. The variability may be due to both the differences in the initial chemical composition of the material used for production, i.e. the milk of the three species, and differences in the basic cheese production technology.

5. Characterized by various health benefits, products made from milk obtained from sheep, goats and cows should be included in every balanced diet.

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