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# Characterizing volatile compounds and proteolysis in Gokceada artisanal goat cheese☆

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ABSTRACT

The objective of the study was to determine the gross composition, proteolysis and volatile compounds in Gokceada goat cheese and to provide initial information on its manufacturing and ripening processes. Gokceada goat cheese is traditionally manufactured from raw goat milk in Gokceada (Imbros) island, Canakkale, Turkey. In the present study, 23 commercial samples were characterized. Urea-polyacrylamide gel electrophoresis of the water-insoluble fractions showed that both $\alpha_s$- and β-caseins were extensively decomposed, but β-casein was less degraded compared to $\alpha_s$-casein. RP-HPLC of peptide profiles in the water-soluble fractions demonstrated qualitative and quantitative differences among the samples. Sixty volatile compounds were identified by SPME/GC–MS technique with alcohols and esters as the principal class of volatile components in the cheeses. In general, relatively large variability in gross composition and concentration of volatile aroma was found, which probably reflects lack of standardization in the production of the cheese.



## 1. Introduction

Goat production in Mediterranean countries is particularly important under extensive conditions (Morand-Fehr et al., 1983; Silanikove et al., 2010). The importance of dairy goat farming has been increased in recent years because of increased consumer demand and is supported by central policies (Hayaloglu and Karagul-Yuceer, 2011).

Farmers in Gokceada (island near Dardanelles, Turkey) has traditionally use dairy goat farming as important part of the island economy and goats constituent 30% of total livestock raised in the island (Aktürk et al., 2005). The local goat breed in the island is Gokceada goat, which has high milk yields (Tolu, 2009). The milk is traditionally used to make cheese in small family dairy plants, commonly known as "mandira" in Turkish Gokceada goat cheese is manufactured only for 5–6 months (from April to August) from raw milk which is consumed after about 2 months of ripening. In the past, an home-made kid rennet was used for coagulation; however, presently commercial calf rennet is used. Therefore, lipolysis is not as intensely expressed due to the absence of lipases from the coagulant as in some Italian-type cheeses which are produced by rennet paste. After coagulation of milk, curds are drained with a cotton cloth and pressed for about 6 h; after that it gained an oval shape. Then, the curd is divided into four equal blocks of about 300–500 g each that has one rounded corner. The cheese has acidic and salty taste due to dry-salting (about 2–3 days) and brine-ripening at high concentration of salt at (4–8 °C) for about 2 months or more.

The objective of the study was to obtain first information on the cheese composition at the end of traditional ripening processes in terms of gross composition, proteolysis levels and volatile compounds.

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## 2. Materials and methods

### 2.1. Chemical analysis of cheese samples

Twenty-three samples of Gokceada goat cheese were collected from different retails in Gokceada island, Canakkale, Turkey. The samples were sealed under vacuum and transported to the laboratory at Food Engineering Department, Inonu University, Turkey. The samples were stored at 4 °C until analysis and all analyses were performed within two weeks. Cheese samples were analyzed in duplicates: moisture was analyzed by the oven drying method at 102 °C (IDF, 1982), fat by the Van Gulik method (Ardo and Polychroniadou, 1999) and total nitrogen by the micro-Kjeldahl method (IDF, 1993). For pH measurement, 10 g of sample was macerated in 10 mL of distilled water and the pH of the resultant slurry was measured using a digital pH meter (pH 211, Microprocessor pH Meter, Hanna Instruments, Italy). Titratable acidity (as % of lactic acid) was measured according to AOAC (1995).

### 2.2. Proteolysis

The water-soluble nitrogen (WSN) and 12% trichloroacetic acid-soluble nitrogen (TCA-SN) fractions as % of total nitrogen of the cheese were determined by the methods described by Kuchroo and Fox (1982) and Polychroniadou et al. (1999), respectively. The water-insoluble fractions of the cheeses were freeze-dried and then analyzed by urea-polyacrylamide gel electrophoresis (urea-PAGE) using Protean II XI vertical slab gel unit (Bio-Rad Laboratories Ltd., Watford, UK) according to the method of Andrews (1983) and the gels were stained directly by the method of Blakesley and Boezi (1977) with Coomassie Brilliant Blue G-250. The WSN fractions of the cheeses were freeze-dried and analyzed by reverse-phase high performance liquid chromatography (RP-HPLC) as described by Hayaloglu et al. (2011).

### 2.3. Volatile composition by solid-phase microextraction (SPME)

Frozen cheese samples were sliced into small granules and placed immediately in glass bottles in a freezer at −20 °C. A duplicate 3.0 g portion of the sample was then placed in a 15 mL vial, followed by 10 μL of internal standard containing 81 ppm of 2-methyl-3-heptanone in methanol (Sigma–Aldrich Co., USA) and allowed to equilibrate at 40 °C for 30 min. Extraction of volatiles was carried out using a solventless extraction technique (Pawliszyn, 1997). The method is suitable for the isolation of volatiles from the sample matrix and has been used in various configurations for characterization of the samples. Essentially, extraction is achieved by inserting a 75 μm carboxen-polydimethylsiloxane (CAR/PDMS) fiber (Supelco, Bellefonte, PA, USA) into the vial and exposing it to the headspace for 30 min at 40 °C. The fiber was positioned at 3.0 scale units in each run. Desorption of the extracted volatiles was carried out on a Shimadzu GC-2010 gas chromatography–QP-2010 mass spectrometry system (Shimadzu Corporation, Kyoto, Japan) and run in split (ratio was 1:20) mode. During desorption, the fiber remained in the injector for 2 min at a temperature of 250 °C, with helium as the carrier gas at a flow rate of 1.0 mL/min. The volatile compounds were separated on a DB-Wax column (60 m × 0.25 mm × 0.25 μm; J&W Scientific, Folsom, CA, USA). The oven was held at 40 °C for 2 min, then increased for 5 °C per min to 240 °C and held for 6 min at 240 °C, to give a run time of 48 min. The mass spectrometer was set to record at 33–450 amu (threshold 1000) at a sampling rate of 1.11 scans/s. The volatile compounds were identified by calculation of the retention index (RI) of each compound, using an *n*-alkane series ($C_{10}$–$C_{26}$) under the same conditions (Kovats, 1958; Arn and Acree, 1998). The peak identifications were based on comparison of the mass spectra of unknown compounds with those in Wiley 7 (7th edition) and NIST/EPA/NIH 02 mass spectral library. Identifications were also confirmed by comparing retention times with reference standards when available. Thirty-five authentic standard compounds (Sigma Chemical Co., St. Louis, MO) were used to confirm volatiles in cheese samples. The RI values were also compared with those described in the literature determined under the same conditions for matching the compounds. The amount was calculated by the comparison of the peak area of the internal standard and the unknown compounds. Each compound was expressed as μg/100 g of cheese.

### 2.4. Statistical analysis

Data from volatile components were analyzed using multivariate statistical techniques to simplify interpretation of the data from GC–MS. Principal component analysis (PCA) was performed using a covariance matrix and varimax rotation between the cheeses. The concentrations of volatile components (GC–MS) were used as variables. PCA was carried out using SPSS package program version 9.0 for Windows (SPSS Inc., Chicago, IL).

## 3. Results and discussion

### 3.1. Chemical composition and pH

A large variability in all chemical parameters was found, which was most likely related to lack of standardization in the manufacture process of the cheese (Table 1). The pH values that ranged from 3.75 to 6.26 with mean value of 4.71 ± 0.66 (Table 1) are consistent with typical pH found in other goat's milk cheeses (Tzanetakis et al., 1995; Franco et al., 2003; Asteri et al., 2010). Though, in some cases much lower (4.3) and higher (5.2) pH values were reported by Bontinis et al. (2008) and Fresno and Alvarez (2012) for Greek raw milk (Xinotyri) and Spanish raw milk (Majorero) cheeses, respectively. The mean values of the cheese samples for titratable acidity, moisture, salt, salt-in-dry matter, fat-in-dry matter and total protein contents were 1.34 ± 0.57% (as lactic acid), 50.27 ± 5.37%, 5.42 ± 2.84%, 11.17 ± 5.98%, 47.30 ± 7.08% and 18.97 ± 3.56%, respectively. These values are consistent with brined-type of cheese. Moisture, salt-in-dry matter and fat-in-dry matter contents were found to be in accordance with the values reported by Atasoy and Turkoglu (2009) for Urfa cheese made by using raw goat milk at 90 d of ripening. Protein content was about 38% (on a dry matter basis) and similar protein content were found by Saldo et al. (2002) for a Spanish caprine milk cheese.

### 3.2. Proteolysis

The WSN fraction of the cheese includes non-casein proteins, casein-derived peptides, amino acids, amines, or ammonia whereas the TCA-SN fraction contains medium- or small-sized casein-derived peptides and amino acids (Fox et al., 1993; Hayaloglu et al., 2011). These two fractions increase during the ripening of cheese due to enzymatic (Hayaloglu et al., 2011). In the present study, these variables varied over a wide range: WSN (3.48–16.56%) and TCA-SN fractions (2.49–13.80%). The averaged values for WSN and TCA-SN were 9.26 ± 4.06% and 5.50 ± 2.57%, respectively (Table 1). However, these values are consistent with previous reports reporting: Fresno et al. (1997) for a Spanish artisanal goat cheese, Faccia et al. (2012) for Cacioricotta goat milk cheese using calf rennet and by Mallatou et al. (2004) for Teleme cheese made using goat's milk but lower than the WSN levels reported by Tzanetakis et al. (1995) and Delgado et al. (2011a). Similarly, to variation in WSN, the TCA-SN values varied over a wide range among the samples, likely due to the lack of standardization in ripening process. Similar values for the TCA-SN were reported by Fresno et al. (1997) for a Spanish craft goat cheese, Olarte et al. (2000) for Cameros goat's milk cheese,