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Characterization and biochemical changes during the ripening of a Spanish hard goat cheese

J. Carballo, J. M. Fresno, J. R. Tuero, J. G. Prieto, A. Bernardo & R. Martín-Sarmiento

Laboratory of Food Technology, Department of Food Hygiene and Food Technology, University of León, 24071 León, Spain

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This paper studies the basic composition and principal physicochemical properties of Valdeteja goat cheese, a hard variety made by artisanal procedures in the north-west of Spain. Biochemical changes during the ripening process have also been investigated.

This cheese shows a high content of total solids (72·53 ± 7·46%) and in fat (59·50 ± 2·08%), and a low pH value (4·50 ± 0·20). Changes throughout ripening are mainly due to transformation reactions of carbohydrates. Almost 65% of lactose was hydrolysed in the curd, around 80% after ten days and 100% on day 17. The D + L lactate content increased quickly in the first five days. Lipids and nitrogen compounds are not degraded much.

INTRODUCTION

Goats' milk could play an important role in the economy of Mediterranean countries if it were transformed into good-quality cheeses. It has been used in cheese making in this region since ancient times. A large variety of home-made goats' cheese is produced there, though only a few types are made on an industrial scale. This is mainly due to a lack of data on production methods and biochemical and microbiological characteristics, which precludes manufacture under controlled conditions.

Like various other countries of the region, Spain produces a large quantity of goats' milk (some 400 million litres per year), which could easily be multiplied by four to five times. However, only a small part of this goes towards the manufacture of goats' cheeses. Although 28 varieties of goats' cheeses (Anon., 1990) are listed in Spain its share of the market is very low, and only one such cheese (Majorero) is produced on an industrial scale. The information available on most of them is scarce and of little value for practical purposes. Only Majorero cheese and a few others (Marcos *et al.*, 1984*a,b*; Martín Hernández *et al.*, 1984; Fontecha *et al.*, 1990) have been studied reasonably extensively.

Data in the literature about Valdeteja cheese refer only to its over-all composition (Martín Hernández *et al.*, 1984; Anon., 1990) and to the changes in the main microbial groups during ripening (Gutiérrez *et al.*, 1988). It is a round, hard-pressed cheese with a mass of 0·8–1·2 kg, which is made in the north-west of Spain from goats' milk by enzymic coagulation. Its prospects of industrialization are very interesting because of its short ripening period (from three to four weeks), easy conservation, and good acceptance by consumers.

The aim of this study is to obtain data on the composition and physicochemical characteristics of Valdeteja cheese and on the changes it undergoes during ripening, in order to establish the basis that would allow its manufacture on a large scale.

MATERIALS AND METHODS

Samples

The cheeses were manufactured by four different artisanal cheesemakers in the following way: whole goats' milk was heated to 35°C, commercial calf rennet was added (20–25 ml per 100 litre of milk), and it was left to coagulate for 105–120 min. The curd was cut into small cubes (1 cm). It was then drained and placed in moulds 14 cm in diameter and 11 cm high and pressed at 1·5 kg per kg of cheese during a period of 12 hours. The salting was carried out with dry salt (30 g per kg). The ripening was carried out by following the artisanal method in an uncontrolled atmosphere at a temperature between 10 and 15°C with a relative humidity of between 70 and 80% (average 13·5°C and 73%) for 27 days.

Sampling was carried out by following the standard FIL-IDF 50:1969.

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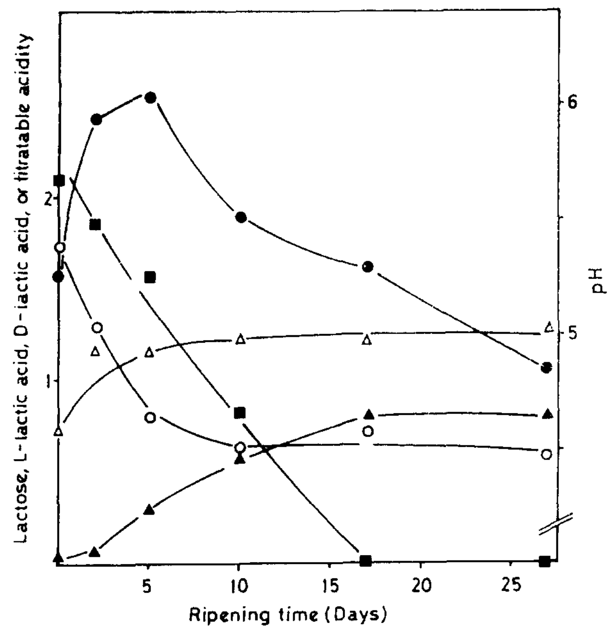

Fig. 1. Evolution of pH (○), titratable acidity (Δ, g of lactic acid/100 g of TS), and lactose (■, % of TS), L-lactate (●, % of TS) and D-lactate (▲, % of TS) contents during the ripening of Valdeteja cheese: average values of the analysis carried out on four batches of cheese.

Analytical methods

The following methods for the determination of the basic composition of the milk were used: total solids, FIL-IDF 21B:1987; protein, FIL-IDF 20A:1986; fat, FIL-IDF 105:1981; lactose, FIL-IDF 28A:1974; NaCl, FIL-IDF 12A:1969; ash, by incineration at 535 ± 15°C. The titratable acidity was measured using a phenolphthalein solution at 1% (0·5 ml per 10 ml of milk) as indicator.

The analysis of the cheese samples was done by the following procedures: total solids, FIL-IDF 4A:1982; protein, FIL-IDF 25:1964; fat, FIL-IDF 5B:1986; lactose, FIL-IDF 43:1967; ash, FIL-IDF 27:1964; NaCl, FIL-IDF 17A:1972; acidity index of the fat, FIL-IDF 6A:1969. The AOAC 14022:1975 method was followed for pH determinations and the AOAC 16228:1975 method for the titratable-acidity determinations. The D and L lactic acids were analysed by the enzymatic method by using the Boehringer kit (Boehringer Mannheim GmbH, Mannheim, Germany). The Aw value was calculated from the chemical-composition data by using the Rodríguez Tuero *et al.* (1989) equation. The T.B.A. number was determined as described by Tarladgis *et al.* (1960). The Dulley and Grieve (1974) method was used in order to analyse the short-chain free-fatty-acid content. The casein breakdown was studied by using the Andrews electrophoretical procedure (1983), and the technique of El-Shibiny and Abd El-Salam (1976) was followed in the quantitation of caseins and their degradation products. Total nitrogen (TN) was determined by the Kjeldahl method in a Tecator 1007 + 1002 apparatus. The Vakaleris and Price procedure (1959) was followed for the extraction of soluble nitrogen (SN) and the Johnson method (Lichstein & Oginsky, 1965) for its determination. This

Table 1. Composition of Valdeteja cheese and of the milk used in its manufacture*

Component	Milk (% w/w)	Cheese (g/100 g TS)
Total solids (TS)	13·66 (± 0·57)	72·53 (± 7·46)†
Protein	3·61 (± 0·70)	35·56 (± 2·06)
Fat	4·67 (± 0·70)	59·50 (± 2·08)
Lactose	4·73 (± 0·73)	0·00
Ash	0·76 (± 0·03)	6·15 (± 0·94)
NaCl	0·24 (± 0·01)	2·89 (± 0·67)

* The data are average values obtained in the analysis of 30 batches. The figures in brackets are standard deviations.
† Expressed as g/100 g of cheese.

Table 2. Changes in Aw and in total solids, ash, and NaCl contents of Valdeteja cheese during ripening†

	Ripening time (days)					
	0	2	5	10	17	27
Total solids (TS, %)**	45·2 ± 1·4	48·2 ± 1·5 ($p < 0·05$)	56·5 ± 1·9 ($p < 0·001$)	57·8 ± 0·7 ($p < 0·001$)	66·3 ± 1·5 ($p < 0·001$)	72·4 ± 3·2 ($p < 0·001$)
Ash (% of TS)**	3·41 ± 0·44	5·94 ± 0·76 ($p < 0·01$)	5·16 ± 0·57 ($p < 0·01$)	5·18 ± 0·35 ($p < 0·01$)	5·00 ± 0·88 ($p < 0·05$)	5·39 ± 1·09 ($p < 0·05$)
NaCl (% of TS) Surface*	1·83 ± 0·38	3·62 ± 0·82 ($p < 0·05$)	2·54 ± 0·35 (n.s.)	2·95 ± 0·23 ($p < 0·01$)	2·77 ± 0·57 (n.s.)	3·09 ± 0·66 ($p < 0·05$)
NaCl (% of TS) Main**	1·29 ± 0·24	2·58 ± 0·88 ($p < 0·05$)	2·05 ± 0·67 (n.s.)	2·36 ± 0·25 ($p < 0·01$)	2·29 ± 0·62 ($p < 0·05$)	2·60 ± 1·06 (n.s.)
NaCl (% of TS) Depth***	0·41 ± 0·12	0·82 ± 0·26 ($p < 0·05$)	1·36 ± 0·54 ($p < 0·05$)	1·40 ± 0·26 ($p < 0·001$)	1·37 ± 0·43 ($p < 0·01$)	1·78 ± 0·67 ($p < 0·05$)
Aw Surface*	0·995 ± 0·001	0·983 ± 0·003 ($p < 0·001$)	0·975 ± 0·003 ($p < 0·001$)	0·950 ± 0·007 ($p < 0·001$)	0·923 ± 0·004 ($p < 0·001$)	0·883 ± 0·013 ($p < 0·001$)
Aw Main**	0·997 ± 0·001	0·989 ± 0·004 ($p < 0·05$)	0·981 ± 0·004 ($p < 0·001$)	0·972 ± 0·006 ($p < 0·001$)	0·951 ± 0·005 ($p < 0·001$)	0·930 ± 0·008 ($p < 0·001$)
Aw Depth***	0·998 ± 0·001	0·996 ± 0·001 ($p < 0·05$)	0·991 ± 0·002 ($p < 0·01$)	0·984 ± 0·006 ($p < 0·01$)	0·978 ± 0·003 ($p < 0·001$)	0·966 ± 0·011 ($p < 0·001$)

† The data are averages of the analysis of four batches ± the standard deviation. The figures in brackets correspond to the p value obtained when comparing the present data with that of zero day (curd). (n.s.) = non-significant differences.
Surface (*), Main (**), and Depth (***) portions were obtained as described by Oria (1986).

Table 3. Evolution of lipidic fraction†

Ripening time (days)	0	2	5	10	17	27
Fat*	48·23 ± 2·22	47·30 ± 3·93	46·65 ± 1·33	46·81 ± 2·73	49·32 ± 1·48	48·54 ± 2·10
Acidity index of fat**	0·70 ± 0·15	0·89 ± 0·17 (n.s.)	1·03 ± 0·12 ($p < 0·05$)	1·16 ± 0·10 ($p < 0·001$)	1·39 ± 0·18 ($p < 0·01$)	1·46 ± 0·15 ($p < 0·001$)
T.B.A. number***	0·082 ± 0·01	0·216 ± 0·12 (n.s.)	0·156 ± 0·11 (n.s.)	0·23 ± 0·10 ($p < 0·05$)	0·28 ± 0·09 ($p < 0·01$)	0·33 ± 0·11 ($p < 0·01$)

† The data are mean values of four batches ± standard deviation. The figures in brackets are the *p* values obtained when comparing the present data with that of day zero (curd). (n.s.) = non-significant differences.
* Expressed as % of Total solids.
** Expressed as mg of KOH/g of fat.
*** Expressed as mg of malonaldehyde/1000 g of cheese.

latter method was also used to determine the non-protein nitrogen (NPN) after precipitating the proteins with trichloroacetic acid at 12%. The amino nitrogen (N-NH_2) and the ammonia nitrogen (N-NH_3) were analysed as described by Ordóñez (1974). The free-amino-acid content was measured by HPLC by using the Wiedmeier *et al.* (1982) procedure.

RESULTS

General milk properties

The composition of the goats' milk used in the making of Valdeteja cheese was studied by taking samples from 30 batches. The results obtained are shown in Table 1.

The pH of the milk immediately before adding the rennet was 6·52 (S.D. ± 0·03) and the titratable acidity 0·171 (S.D. ± 0·012) g of lactic acid per 100 g of milk.

Titratable acidity, lactate content, pH, and Aw of Valdeteja cheese

The analysis carried out on 30 samples of cheese prepared for sale gave the following average values: titratable acidity, 1·39 (S.D. ± 0·39) g of lactic acid per 100 g of total solids (TS); L-lactate, 0·91 (S.D. ± 0·35) g per 100 g TS; D-lactate, 0·47 (S.D. ± 0·28) g per 100 g TS; pH, 4·50 (S.D. ± 0·20); Aw, 0·906 (S.D. ± 0·033).

Cheese composition

This was studied in samples of 30 batches of Valdeteja cheese. The results obtained are shown in Table 1.

Changes in Aw value and in the total solids, ash, and sodium chloride contents during ripening

Samples of zero (curd), 2, 5, 10, 17, and 27 days of ripening from four batches of cheese were analysed. The results are shown in Table 2. The total solids content increased almost linearly with time and changed from being about 45% in the curd to an average of 72·4% after 27 days. The ash and the sodium chloride contents, expressed as percentages of total solids, increased very quickly in the first two days as a result of salt penetration and afterwards remained approximately constant. As was expected, the Aw value progressively and constantly decreased throughout the ripening process, from an initial value on the surface of 0·995 to 0·880 on average.

Table 4. Evolution of free fatty acids of short-chain content†

Fatty acid \ Ripening time (days)	0	2	5	10	17	27
Acetic	732 ± 173	975 ± 325 (n.s.)	1 152 ± 325 (n.s.)	838 ± 88 (n.s.)	825 ± 200 (n.s.)	715 ± 225 (n.s.)
Propionic	Trace	Trace	9·9 ± 3·4	7·0 ± 3·0 (n.s.)*	8·0 ± 3·5 (n.s.)*	10·9 ± 5·4 (n.s.)*
Butyric	20·2 ± 2·2	23·9 ± 5·2 (n.s.)	40·8 ± 1·7 ($p < 0·001$)	52·7 ± 5·7 ($p < 0·001$)	68·6 ± 3·4 ($p < 0·001$)	81·6 ± 4·5 ($p < 0·001$)
Isobutyric	(−)	Trace	4·8 ± 6·8	7·0 ± 5·8 (n.s.)*	15·9 ± 10·6 (n.s.)*	10·3 ± 4·8 (n.s.)*
Valeric	(−)	(−)	8·6 ± 9·5	20·1 ± 9·9 (n.s.)*	16·4 ± 8·8 (n.s.)*	13·3 ± 5·8 (n.s.)*
Hexanoic	3·9 ± 0·9	7·8 ± 1·0 ($p < 0·01$)	10·9 ± 1·8 ($p < 0·01$)	13·8 ± 1·5 ($p < 0·001$)	16·6 ± 1·0 ($p < 0·001$)	19·5 ± 1·9 ($p < 0·001$)

† Average values ± standard deviation of the analysis of four batches (μeq/100 g of fat). The figures in brackets correspond to the *p* value obtained when comparing the present data with that of zero day (curd). (n.s.) = non-significant differences.
(−) = Not detected.
* In comparison with value corresponding to day 5.

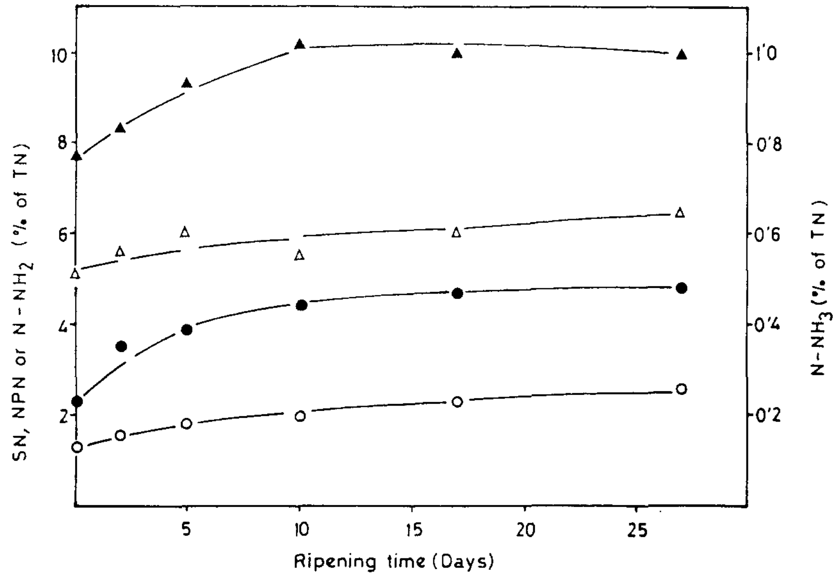

Fig. 2. Evolution of soluble nitrogen (SN, ▲), non-protein nitrogen (NPN, ●), amino nitrogen (N-NH_2, ○), and ammonia nitrogen (N-NH_3, Δ) during ripening. Plotted values, expressed as a percentage of total nitrogen (TN), are the average of those obtained by analyzing samples of four batches of Valdeteja cheese.

Changes in lactose and lactate contents, pH, and titratable acidity

Lactose, which had been considerably hydrolysed in the samples of day zero, continued degrading until disappearing completely after day 17 (Fig. 1). The L-lactic acid content increased rapidly during the first five days and then fell until the end of ripening, whereas the D-lactic acid content continued increasing until day 17 and became stable from that time onwards. An appreciable fall in the pH value and an increase in titratable acidity during the first 5–10 days (Fig. 1) was consequently observed.

Changes in the lipids during ripening

Changes in fat content, acidity index of the fat, and T.B.A. index are shown in Table 3. The percentage of fat in the total solids was maintained fairly constant throughout the ripening process. The acidity index of the fat progressively increased. This increase was fairly slight, but it turned out to be statistically significant when the zero-day samples were compared with those of day 5 and the following days. The T.B.A. index significantly increased during ripening with regard to the values corresponding to the curd ($p < 0{\cdot}05$ for samples of the 10th day; $p < 0{\cdot}01$ for those of the 17th and 27th days).

Short-chain free fatty acids were also studied (Table 4). Acetic acid was the most abundant in all cases. This component seemed to increase in the first few days of ripening and later decrease, though the differences observed were not statistically significant. Butyric acid, which increased approximately fourfold in the 27 days

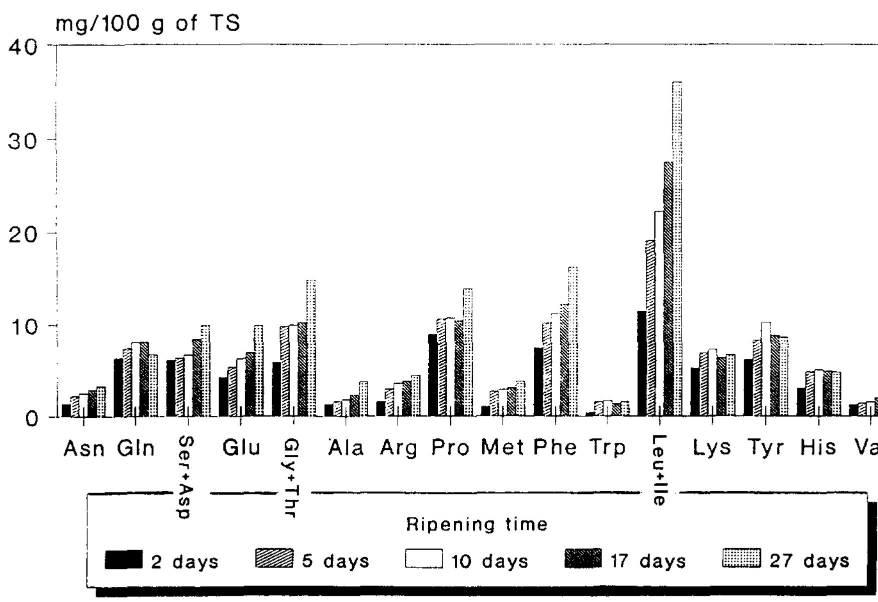

Fig. 3. Evolution of free amino acids: average values of four batches of cheese.

of ripening, was also relatively abundant. The differences in the content of this fatty acid with respect to that corresponding to the curd were significant after day 5. A progressive rise in the hexanoic acid level, significant after day 2, was also observed. With regard to the other compounds analysed, a trend to increase throughout the ripening period was observed, but the differences were not statistically significant.

Changes in nitrogen compounds

Electrophoretical studies of the caseins of 30 samples of Valdeteja cheese at the end of the ripening period gave the following results: β-casein, 58·7% (S.D. ±4·7); α-casein, 29·1% (S.D. ±3·5); γ-casein 6·5% (S.D. ±3·8); pre α-casein, 5·8% (S.D. ±3·6). These figures indicate that Valdeteja cheese undergoes a very slight proteolysis. Data for the different nitrogen fractions during the ripening process confirm this estimation. Soluble nitrogen (SN), non-protein nitrogen (NPN), amino nitrogen ($N\text{-}NH_2$), and ammonia nitrogen ($N\text{-}NH_3$) all increased progressively throughout ripening (Fig. 2). Although the comparison of these data with those corresponding to the curd showed that this increase was significant ($p < 0{\cdot}05$ for SN and $p < 0{\cdot}01$ for NPN, $N\text{-}NH_2$, and $N\text{-}NH_3$), it was not quantitatively important.

The greater part of the free amino acids increased with ripening time (Fig. 3), but this increase was very low when compared with that observed in other similar cheeses. The glutamine, lysine, tyrosine, and histidine contents even seem to decrease towards the end of the ripening period. Nevertheless, the variability in the individual amino-acid contents in the different batches is very large, which is why the differences observed have very little statistical value.

DISCUSSION

The data in Table 1 shows that the goats' milk used for the manufacture of Valdeteja cheese does not exhibit any special characteristics, and its basic composition is fairly common in the Mediterranean area (see Martín Hernández *et al.*, 1984). The cheese shows a low pH and a high content in total solids and fat in comparison with other goats' cheeses (Kalatzopoulos *et al.*, 1983; Martín Hernández *et al.*, 1984; Fontecha *et al.*, 1990).

Total solids progressively increased in the four batches analysed until reaching an average value of 72% on day 27. The ash and NaCl contents quickly grew in the first few days and remained approximately stable until the end of ripening. This resembles the changes observed by Fontecha *et al.* (1990) in Majorero goats' cheese, the composition of which, after a month of ripening, is fairly similar to that of the one we studied. However, the Aw value of Majorero cheese after the first month (Fontecha *et al.*, 1990) is around 0·05 unit lower than that of Valdeteja cheese, which could be explained by its somewhat higher content of NaCl and by its having undergone more severe lipolysis and proteolysis.

The carbohydrates underwent an intense degradation during the ripening of Valdeteja cheese. Almost 65% of lactose was hydrolysed in the curd, around 80% after 10 days, and 100% on day 17. A similar course is observed for this compound in fast-glycolysis cheeses, such as Cheddar cheese (Lin *et al.*, 1979; Choisy *et al.*, 1987). The L-lactate content increases quickly in the first five days and then decreases, while D-lactate reaches a maximum by the third or fourth week. Consequently, the relationship between the D and L isomers of lactic acid changes during the ripening. These changes have been attributed to the action of microbial racemases (Thomas & Crow, 1983), but, in our case, it is obvious that these cannot be responsible for all the effects observed, since the sum of D- and L-lactate contents clearly decreases from day 5 onwards. The final D and L lactic acid content is higher than the figures in the literature for other cheeses (Thomas & Crow, 1983). In agreement with the changes undergone by lactose and lactates, the titratable acidity increases to 1·2–1·4 g/100 g of TS and the pH falls to 4·45–4·5 in the first five to ten days and afterwards both are maintained until the end of ripening.

In contrast to what happens to carbohydrates, the lipids are not degraded much during the ripening of this cheese. Even though our results show that the level of lipolysis is statistically significant, the maximum value that the acidity of the fat reaches is 1·6 mg KOH/g of fat (2·5 mEq of acid/100 g of fat). This figure is very low with respect to those published for other cheeses (Vanbelle *et al.*. 1978; Alonso *et al.*, 1987; Fontecha *et al.*, 1990), especially if it is compared with that of 65–100 mEq of acid/100 g of fat, which some cheeses with very intense lipolysis show (Choisy *et al.*, 1987). Moreover, approximately half of the acidity of the fat of Valdeteja cheese is due to acetic acid (0·5–1·1 mEq/100 g of fat) and, to a less extent, to butyric acid, which, as is well known, could also originate from the metabolism of carbohydrates. Hexanoic acid is only produced by lipolysis. If we take this fatty acid as reference, we can observe that its average content at the end of the ripening is around 20 μEq/100 g of fat. This compound represents around 3 moles/mol of fatty acid in goats' milk (García Olmedo *et al.*, 1979; Sawaya *et al.*, 1984). On the supposition that all the fatty acids are freed by the lipase attack in the same proportion as $C_{6:0}$, it is deduced that hydrolysis of the lipids has produced some 0·7 mEq of free fatty acids/100 g of fat. This low figure may be explained by: (i) the flora of this cheese basically consist of lactic acid bacteria (Gutiérrez *et al.*, 1988), which have a very limited lipolytic activity; (ii) the low pH value, which develops in this cheese from the first moments of ripening, should largely restrain the action of the autochthonous lipases of milk (Deeth & Fitz-Gerald, 1983). The low magnitude of the changes observed in the T.B.A. index shows that the fat of Valdeteja cheese is also scarcely degraded by auto-oxidation reactions.

Like the lipids, nitrogen compounds undergo few changes during the ripening process. This is what indicates the low proportion of γ-caseins and pre-α_s bands in the electrophoretic studies and the changes in the nitrogen fractions throughout the ripening process. SN reaches a maximum value of 10% of TN, NPN of 5%, $N\text{-}NH_2$ of 2·5%, and $N\text{-}NH_3$ of 0·65%. All these figures are very low if they are compared with those reported for other cheeses (Choisy *et al.*, 1987), even in varieties that undergo a moderate-to-low proteolysis (Lenoir, 1963; Choisy *et al.*, 1987; Martín Hernández *et al.*, 1988; Fontecha *et al.*, 1990). The sum of the values reached by individual free amino acids increased only slightly during ripening, which also confirms this conclusion. This can be explained by taking into account the short ripening period of Valdeteja cheese and the very low pHs and high salt/moisture ratios established in it from the beginning, which must intensely hinder the protease activity (Kikuchi *et al.*, 1974; Noomen, 1978; Mulvihill & Fox, 1978; Thomas & Pearce, 1981; Creamer, 1986; Martín Hernández *et al.*, 1988).

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