

Components detected by headspace-solid phase microextraction in artisanal fresh goat's cheese smoked using dry prickly pear (*Opuntia ficus indica*)

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Abstract – The study of the headspace components of six different samples of hand-made fresh goat's cheese smoked with dry prickly pear (*Opuntia ficus indica*) smoke, protected by the Palmero Denomination of Origin, was carried out. These cheeses were manufactured by six different artisans from the Island of Palma. In spite of this cheese not being a ripened cheese, more than 330 components were detected, by means of solid phase microextraction using a polyacrylate fiber followed by gas chromatography/mass spectrometry. The cheese's exterior region was the richest in components because in addition to the characteristic cheese components it also contained all those adsorbed smoke components which had not reacted with the cheese components. The cheese's interior region was the poorest in components because only some of the smoke components had diffused towards the interior. Branched acids associated with goat's cheese flavor were not detected. In spite of the different smoking degree in the samples studied, homogeneous proportions of the main smoke phenolic derivatives were observed. Likewise, although differences in the absolute concentrations of acids were observed, fairly homogeneous proportions of the main acids were found. The absence of terpenes and sesquiterpenes and the presence of some nitrogen derivatives as well as of syringol derivatives in significant concentrations, together with characteristic proportions of phenolic derivatives, allow one to distinguish this Palmero cheese from that smoked with pine needles.

***Opuntia ficus indica* / smoked fresh goat cheese / volatile component / solid phase microextraction / gas chromatography-mass spectrometry**

Résumé – Composés volatils des fromages de chèvre frais fumés à la fumée de figuier de Barbarie (*Opuntia ficus indica*) détectés par microextraction en phase solide. Six échantillons de fromages de chèvre frais artisanaux protégés par l'Appellation d'Origine de Palmero, fabriqués par six artisans de l'île de Palma et fumés avec de la fumée de figuier de Barbarie (*Opuntia ficus indica*), sont analysés pour leur teneur en composés volatils. Bien que ces fromages ne soient pas affinés, plus de 330 composés volatils sont détectés après microextraction en phase solide sur fibre polyacrylate couplée à de la chromatographie gaz/spectrométrie de masse. La zone externe du fromage est la plus riche en composés, car elle contient tous les composés de fumée adsorbés qui n'ont pas réagi avec les composés spécifiques au fromage, en plus des composés caractéristiques au fromage. La zone interne du fromage est la plus pauvre en composés, en effet seuls quelques composés de

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fumée ont diffusé vers l'intérieur. Les acides gras ramifiés associés à la flaveur fromage de chèvre n'ont pas été détectés. Malgré leur degré variable de fumage, les échantillons étudiés contiennent des proportions analogues en dérivés phénoliques majeurs de la fumée. De même, des proportions voisines en acides gras majoritaires sont trouvées, malgré des différences dans les concentrations absolues en acides gras. L'absence de terpènes et sesquiterpènes, la présence de certains dérivés azotés, ainsi que des concentrations significatives de dérivés du syringol, et des proportions caractéristiques en dérivés phénoliques permettent de distinguer ce fromage de Palmero de ceux fumés avec des aiguilles de pin.

***Opuntia ficus indica* / fromage de chèvre frais fumé / composé volatil / microextraction en phase solide / chromatographie gaz-spectrométrie de masse**

1. INTRODUCTION

Organoleptic properties are very important in food acceptance by consumers and especially in many cheeses often considered as delicacies. These properties are due to the food composition, and specifically food aroma is mostly determined by its headspace composition. For this reason the components of the headspace of many cheeses have been profusely studied using different techniques [1, 17–22, 25, 28]. However, in spite of the existence of many studies on those components responsible for the flavor of cheeses of very different origins and characteristics, the study of the headspace components of smoked cheeses has been rarely undertaken [2, 5, 16], and the same can be said of fresh goat's cheese [6, 7, 9, 23, 27, 30].

In this paper the study of the volatile and less volatile components of the headspace of the fresh smoked artisanal goat's cheese protected by the Palmero Denomination of Origin is carried out. The cheese studied was smoked exclusively with dry prickly pear (*Opuntia ficus indica*) smoke, although other vegetable matters such as almond shells (*Prunus dulcis*), and the wood or needles of canary pine (*Pinus canariensis*) can be used. These cheeses are manufactured using milk from Palmera goats, by the milk producers themselves, only on the Island of Palma (The Canary Islands), following traditional methods passed down from generation to generation.

The study was accomplished by means of the extraction of the static headspace components using solid phase microextraction (SPME) followed by gas chromatography/mass spectrometry. The aim of this study is to establish the components of the headspace of this cheese, and to know the diffusion degree of the smoke components across the cheese matrix.

2. MATERIALS AND METHODS

2.1. Samples

Artisanal Palmero cheeses, manufactured from fresh untreated milk, by six different artisans of the Palma Island, named T1, T2, T3, T4, T5 and T6, were studied. All of them were smoked using dry prickly pear. The manufacture was carried out following the traditional methods [8]. From each cheese, three different parts were studied separately: the interior of the cheese; the exterior region; and a thin cross-section representative of the entire cheese, containing exterior and interior parts. The samples were chopped, and approximately 1 g of the chopped sample was weighed into a 4-mL amber vial Screw Top (acquired from Supelco, Bellefonte, PA, USA), sealed with a hole cap PTFE/silicone septum, and stored frozen until used for study. The day before the study each sample was transferred to the refrigerator for thawing.

2.2. Generation of the headspace and extraction of its components by SPME

Vials containing 1 g of the cheese sample were introduced into a water bath maintained at 50 °C. After a period of sample equilibration (15 min) the fiber was inserted into the headspace of the sample and was maintained for 60 min. The fiber used was a fiber of Polyacrylate (85 µm film thickness), acquired from Supelco. Previous experiments [11] carried out in our laboratory on the study of the headspace components of other smoked foods using fibers of carboxen/polydimethylsiloxane, polydimethylsiloxane (100 µm film thickness) and polyacrylate (85 µm film thickness) have shown that: carboxen/polydimethylsiloxane fiber basically retained the most volatile components of the headspace, in very high proportions; however, polyacrylate fiber retained components of a broader volatility range; and polydimethylsiloxane fiber had less retention ability of smoke components than polyacrylate fiber.

2.3. Gas chromatography/mass spectrometry study

Fibers with the adsorbed compounds were injected into a Hewlett-Packard gas chromatograph model HP 6890 Series II, equipped with a mass selective detector 5973 and a Hewlett-Packard Vectra XM Series 4 computer operating with the Chemstation program. The column used was a fused-silica capillary column (60 m long × 0.25 mm inner diameter × 0.25 µm film thickness; from Hewlett-Packard, Palo Alto, CA, USA), coated with a non-polar stationary phase (HP-5MS, 5% phenyl methyl siloxane). The operation conditions were the following: the oven temperature was set initially at 45 °C (0.50 min hold), increased to 250 °C at 4 °C·min⁻¹ (20 min hold); the temperatures of the ion source and the quadrupole mass analyzer were kept at 230 and 150 °C, respectively; helium was used as carrier gas at a pressure of

113.76 kPa; injector and detector temperatures were held at 220 and 280 °C, respectively; splitless mode was used for injection with a purge time of 5 min. The fiber was maintained in the injection port for 10 min. Mass spectra were recorded at an ionization energy of 70 eV. After the first desorption, the fiber was routinely desorbed for a second time in order to determine if the first process was complete.

The components were identified by their retention times, by their mass spectra, by comparing their mass spectra with those in a commercial library (Wiley 138L, Mass Spectral Database, Wiley 1990) and by using standards. All those compounds included in Table I were acquired commercially as pure compounds and used as standard for identification; in addition, 4-ethyl-octanoic acid was also used to elucidate its presence or absence in the headspace of this cheese. Due to the overlapping of the signal of many compounds, semi-quantification was based on arbitrary units of the total current ion or of the base specific peak ion counts divided by 10⁵. Tables II and III give the average abundances (A_a) obtained for some main components, as well as the average relative abundances (A_{ra}) expressed as percentages, together with their deviations and the ion used for the quantification in each case.

3. RESULTS AND DISCUSSION

The number of detected compounds was very high, more than 330. However, Table I gives only those compounds, identified by means of standards, found in the headspace of the exterior and/or interior regions of the cheese, as well as in a cross-section which represents the whole cheese sample. These have been grouped according to their nature in acids, alcohols, esters, aldehydes, ketones, hydrocarbons, furan and pyran derivatives, ethers, nitrogen derivatives, phenol, naphthalenol, diphenol, guaiacol and syringol derivatives, and others. The detected compounds showed a broad range of molecular weights and volatilities.

Table I. Detected compounds in different cheese regions together with an indication of their concentration*.

N°	RT (min)	Compound (molecular weight)	Exterior	Cross-section	Interior
Acid					
1	5.85	acetic acid (60)	++	++	++
2	9.26	butanoic acid (88)	++	++	++
3	12.65	pentanoic acid (102)	tr	tr	tr
4	17.39	hexanoic acid (116)	+++	+++	+++
5	20.72	heptanoic acid (130)	tr	tr	tr
6	22.48	2-ethyl-hexanoic acid (144)	tr	-	-
7	24.69	benzoic acid (122)	tr	-	-
8	24.88	octanoic acid (144)	+++	+++	+++
9	27.99	nonanoic acid (154)	+	+	tr
10	30.69	4-hydroxy-3-methoxy-benzoic acid (168) (vanillic acid)	tr	-	-
11	31.65	decanoic acid (172)	+++	+++	+++
12	37.54	dodecanoic acid (200)	++	tr	tr
13	43.13	tetradecanoic acid (228)	++	+	-
14	48.27	hexadecanoic acid (256)	+++	tr	-
15	52.34	9-octadecenoic acid (282)	++	-	-
16	52.82	octadecanoic acid (284)	+	tr	-
Alcohols					
17	3.95	ethanol (46)	++	++	++
18	9.78	2,3-butanediol (90)	++	++	++
19	19.29	benzenemethanol (108)	tr	tr	-
Esters					
20	10.13	ethyl butanoate (116)	-	tr	-
21	18.38	ethyl hexanoate (144)	-	tr	tr
22	21.69	methyl benzoate (136)	tr	tr	-
23	25.38	ethyl octanoate (172)	-	-	tr
24	32.10	ethyl decanoate (200)	-	tr	tr
25	36.40	methyl dodecanoate (214)	tr	-	-
26	36.42	methyl 4-hydroxy-3-methoxybenzoate (182) (methyl vanillate)	tr	-	-
27	38.62	ethyl dodecanoate (228)	-	tr	tr
28	42.11	methyl tetradecanoate (242)	tr	-	-
29	44.77	ethyl tetradecanoate (256)	-	tr	tr
Aldehydes					
30	16.14	benzaldehyde (106)	tr	tr	tr
31	19.67	benzeneacetaldehyde (120)	tr	tr	tr
32	21.99	nonanal (142)	tr	tr	tr
Ketones					
aliphatic linear and cyclic ketones and diketones					
33	7.28	3-hydroxy-2-butanone (88)	-	-	tr
34	9.25	cyclopentanone (84)	tr	-	-
35	12.27	1-(acetyloxy)-2-propanone (116)	tr	-	-
36	13.10	2-heptanone (114)	tr	-	tr
37	13.31	cyclohexanone (98)	tr	-	-

Table I. Continued.

N°	RT (min)	Compound (molecular weight)	Exterior	Cross-section	Interior
38	13.88	2-methyl-2-cyclopenten-1-one (96)	tr	tr	-
39	15.00	2,5-hexanedione (114)	tr	-	-
40	16.43	3-methyl-2-cyclopenten-1-one (96)	tr	tr	-
41	17.95	3-methylcyclohexanone (112)	tr	tr	-
42	19.08	3-methyl-1,2-cyclopentanedione (112) (cyclotene)	+	+	tr
43	22.68	3-ethyl-1,2-cyclopentanedione (126) (3-ethylcyclopentenolone)	tr	tr	-
44	29.00	2-undecanone (170)	tr	-	-
45	35.57	2-tridecanone (198)	tr	-	tr
aromatic ketones and related					
46	20.58	1-phenyl-ethanone (120) (acetophenone)	tr	tr	-
47	34.95	2,5-di-tert-butyl-1,4-benzoquinone (220)	tr	-	-
48	35.50	1-(4-hydroxy-3-methoxyphenyl)-ethanone (166) (acetovanillone)	tr	tr	tr
49	35.50	1-(4-hydroxy-3-methoxyphenyl)-2-propanone (180) (propiovanillone)	tr	-	-
50	36.86	1-(4-hydroxy-3,5-dimethoxyphenyl)-ethanone (196) (acetosiringone)	tr	-	-
Hydrocarbons					
aliphatic hydrocarbons					
51	38.60	hexadecane (226)	tr	-	-
52	41.26	heptadecane (240)	+	+	-
53	44.10	octadecane (254)	tr	-	-
54	49.28	eicosene (282)	tr	-	-
55	65.87	squalene (410)	tr	tr	-
polyaromatic hydrocarbons					
56	25.29	naphthalene (128)	tr	tr	-
57	29.32	2-methylnaphthalene (142)	tr	tr	-
58	29.91	1-methylnaphthalene (142)	tr	-	-
59	34.52	acenaphthylene (152)	tr	-	-
60	44.18	phenanthrene (178)	tr	-	-
Furan, pyran derivatives and others					
61	10.80	2-furancarboxaldehyde (96)	tr	-	-
62	11.84	2-furanmethanol (98) (furfuryl alcohol)	tr	tr	tr
63	14.02	1-(2-furanyl)-ethanone (110) (2-acetylfuran)	tr	tr	tr
64	14.48	2(5H)-furanone (84) (γ -crotonolactone)	tr	tr	tr
65	15.51	5-methyl-2(5H)-furanone (98)	tr	-	-
66	16.27	5-methyl-2-furancarboxaldehyde (110)	tr	-	-
67	19.75	3-methyl-2(5H)-furanone (98)	tr	tr	-
68	22.43	3-hydroxy-2-methyl-4H-pyran-4-one (126) (maltol)	+	tr	tr
69	28.86	δ -octalactone (142)	tr	tr	tr
70	34.88	γ -decalactone (170)	-	tr	-
71	35.29	1,6-anhydro- β -D-glucopyranose (162) (levoglucosan)	tr	-	-
72	35.78	δ -decalactone (170)	tr	tr	tr
73	41.09	γ -dodecalactone (198)	tr	tr	tr
74	41.91	4-dodecalactone (198)	tr	tr	-

Table I. Continued.

N°	RT (min)	Compound (molecular weight)	Exterior	Cross-section	Interior
Ethers					
75	23.64	1,2-dimethoxybenzene (138)	tr	tr	-
76	24.96	1,4-dimethoxybenzene (138)	tr	tr	-
77	25.22	1,3-dimethoxybenzene (138)	tr	tr	-
Phenolic derivatives					
phenol derivatives					
78	16.95	phenol (94)	++	+	tr
79	19.98	2-methylphenol (108)	++	+	-
80	20.81	4-methylphenol (108) and 3-methylphenol (108)	++	+	-
81	22.15	2,6-dimethylphenol (122)	+	tr	-
82	23.28	2-ethylphenol (122)	+	tr	-
83	23.68	2,4-dimethylphenol (122)	+	tr	-
84	23.73	2,5-dimethylphenol (122)	+	tr	-
85	24.27	4-ethylphenol (122)	+	tr	-
86	24.46	3-ethylphenol (122)	+	tr	-
87	30.65	2-(1,1-dimethylethyl)-4-methyl-phenol (164)	tr	-	-
88	36.11	2,4-bis(1,1-dimethylethyl)-phenol (206)	tr	-	-
89	36.29	2,6-bis(1,1-dimethylethyl)-4-methyl-phenol (220) (BHT)	tr	tr	-
diphenol derivatives					
90	23.57	3-methoxy-1,2-benzenediol (140) (3-methoxyprocatechol)	tr	tr	-
91	25.68	1,2-benzenediol (110) (procatechol)	tr	-	-
92	27.90	3-methyl-1,2-benzenediol (124) (3-methylprocatechol)	tr	-	-
methoxyphenol derivatives					
93	21.49	2-methoxyphenol (guaiacol) (124)	+++	++	tr
94	25.50	4-methyl-2-methoxyphenol (138) (4-methylguaiacol)	++	+	tr
95	28.62	4-ethyl-2-methoxyphenol (152) (4-ethylguaiacol)	++	tr	-
96	29.82	4-vinyl-2-methoxyphenol (150) (4-vinylguaiacol)	++	tr	-
97	31.31	4-(2-propenyl)-2-methoxyphenol (164) (eugenol)	+	tr	-
98	32.06	4-propyl-2-methoxyphenol (166) (4-propylguaiacol)	+	tr	-
99	32.74	4-hydroxy-3-methoxy-benzaldehyde (152) (vanillin)	tr	tr	-
100	32.98	4-(1-propenyl)-2-methoxyphenol (164) (isoeugenol)	+	tr	-
101	34.30	4-(1-propenyl)-2-methoxyphenol (164) (isoeugenol)	+	tr	-
dimethoxyphenol derivatives					
102	31.03	2,6-dimethoxyphenol (154) (syringol)	++	+	-
103	34.17	4-methyl-2,6-dimethoxyphenol (168) (4-methylsyringol)	+	tr	-
104	38.91	4-(2-propenyl)-2,6-dimethoxyphenol (194)	tr	tr	-

* Great number of area counts: +++; medium number of area counts: ++; small number of area counts: +; very low number of area counts: tr; no detected: -. Data in Tables II and III give an approximate idea of the signification of these symbols.

Acids formed the most important group by concentration, making up nineteen components, present in both the exterior and in the interior region. Most were saturated linear acids, ranging between two and eighteen carbon atoms, with an even or uneven number of carbon atoms, the first in higher concentrations than the second; the origin of these acids can be found in the triglyceride hydrolysis, although other routes are also possible. The importance of hexanoic, octanoic and decanoic acids in goat's cheese flavor has been well known for a long time [3]. Only one branched-chain, 2-ethyl-hexanoic acid, and one unsaturated, 9-octadecenoic acid, were detected. Although 4-methyl- and 4-ethyl-octanoic acids have been considered by different authors as characteristic of goat's cheese [16, 31], these acids were not detected in any of these artisanal Palmero cheese samples studied.

The number of identified alcohols was low. Linear alcohols were present both in the exterior and in the interior region and may be formed by different processes from lactose, aminoacids, or acids [26].

The ester group contained mainly methyl or ethyl ester derivatives. Most of these components come from reactions between acids and alcohols and some of them were detected not only in the exterior but also in the interior region. One should note the presence, in the exterior region, of benzoate as well as of vanillate esters, these latter probably derived from the corresponding acid also detected; although compounds of this nature have not been very often detected in cheese, they contribute not only organoleptic [21] but also preserving properties [29]; it should be noted that methyl vanillate has been included in formulations to reproduce blue cheese flavors [24].

A reduced number of aliphatic and aromatic aldehydes were also identified at very low concentrations. Ketones were very numerous. Some of these, such as 1-(acetyloxy)-2-propanone, the cyclic mono- and di-ketones, and the aromatic ketones are well-known smoke components [12]. Most

of them were only present in the exterior region, except acetovanillone and cyclotene. The diffusion of these latter towards the interior region could be due to different factors such as: their concentration in the exterior region; the size and shape of the compound; or the ability of the compound to establish interactions with the components of the cheese matrix.

In the group of hydrocarbons, aliphatics and aromatics were detected. The main aliphatic hydrocarbon was heptadecane. The origin of the polyaromatic hydrocarbons could be found in the smoke, although those of low molecular weight have also been detected in unsmoked cheese [4, 10, 22]. Most of the detected hydrocarbons were only found in the exterior region.

The furan and pyran derivatives consisted of two different types of components: those from the smoke, covering from 2-furancarboxaldehyde to maltol and related derivatives, and the group of γ - and δ -lactones from the cyclation of hydroxyacids. All these compounds were only detected as trace amounts. Of the components from the smoke, only some, such as 2-furanmethanol, 2-acetylfuran, γ -crotonolactone and maltol, had diffused towards the interior cheese region. Levoglucosan or 1,6-anhydro- β -D-glucopyranose is an anhydrosugar derived from cellulose thermal degradation and is a main smoke component [14]. Lactones were detected mainly in the exterior and only δ -octalactone, δ -decalactone and γ -dodecalactone were detected in the interior region.

The ethers identified were alkyl-aryl ethers and probably come from the smoke, being mainly present in the cheese's exterior region. It is worth noting that a significant group of nitrogenated compounds, basically nitrile, quinoline and indol derivatives, was detected but not included in Table I because their identification was not based on standard compounds.

The most numerous group of components was that of phenolic derivatives, constituted by phenol, diphenol, methoxyphenol (guaiacol)

and dimethoxyphenol (syringol) derivatives. Although some phenol derivatives have been detected in certain unsmoked cheeses, most of these phenolic derivatives come from the smoke. The presence of diphenol derivatives, compounds with well-known antioxidant ability, was significant, as was that of syringol and some of its alkyl derivatives. In spite of the high number of phenolic derivatives detected in the exterior region, only phenol, guaiacol and 4-methyl-guaiacol reached the interior region.

Although the smoke contained higher proportions of compounds from the thermal degradation of wood carbohydrates (aldehydes, ketones, anhydrosugars, acids and furan and pyran derivatives) than from wood lignin (phenolic derivatives) [13], in the headspace of all studied cheeses there were higher proportions of phenolic derivatives than of compounds from carbohydrate pyrolysis. This fact could be: due to these latter being retained more strongly in cheese matrix than the phenolic derivatives; or due to compounds derived from carbohydrate having less affinity to being retained on the fiber than phenolic derivatives; or because they react with cheese components by reactions similar to the Maillard reaction, modifying the texture and the color of the cheese and disappearing from the system.

The headspace of the cheese's exterior region is much richer in components than the headspace of the interior region. This is because the majority of the smoke components present in the exterior region do not diffuse towards the interior of the cheese and because some important reactions which generate volatile compounds, such as esterification and oxidation processes, are probably favored in the exterior region. Smoke components identified in the interior region were cyclotene, acetovanillone, 2-furanmethanol, acetylfuran, γ -crotonolactone, maltol, phenol, guaiacol and 4-methylguaiacol. Although the contribution of each smoke component was not determined since the corresponding threshold

values are unknown, smoke components are likely to influence cheese flavor and this should be taken into account, in particular in the preparation of samples for sensory evaluations.

Figures 1 and 2 show the total current ion chromatograms of the headspace components of the exterior, interior and cross-section of the samples T3 and T4; these cheese samples had the highest concentration in smoke components and in acids, respectively, of all those studied here. It can be observed that in both samples the smoke components' concentration diminished from the exterior towards the interior, whereas the acids' concentration was fairly constant in both cheese regions inside the same sample. So, while in the interior region of both samples (Figs. 1c, 2c), hexanoic, octanoic and decanoic acids predominated, in the exterior region of sample T3 (Fig. 1a) phenolic derivatives predominated, and in the exterior region of sample T4 (Fig. 2a), acids together with phenolic derivatives predominated, showing a great difference in composition between the two regions inside the same cheese sample.

As has been commented on before, these six cheese samples were made by artisans; for this reason, there was a certain variability among the samples. So, T3 was the cheese sample whose headspace had the highest concentrations in smoke components, and the others, T1, T2, T4, T5 and T6, showed lower concentrations of these kinds of components. This variability can be observed in Table II, which gives the cheese's headspace average abundances (A_a) together with the standard deviations (DA_a) of some smoke components in samples T1, T2, T4, T5 and T6. In spite of the different smoking degree undergone by these cheeses, the average relative abundances (A_{ra}) of the smoke components of the six samples, expressed as percentages in relation to the total abundance, given in Table II, reveal that these cheese show a fairly homogeneous aromatic profile of smoke components, mainly made up of

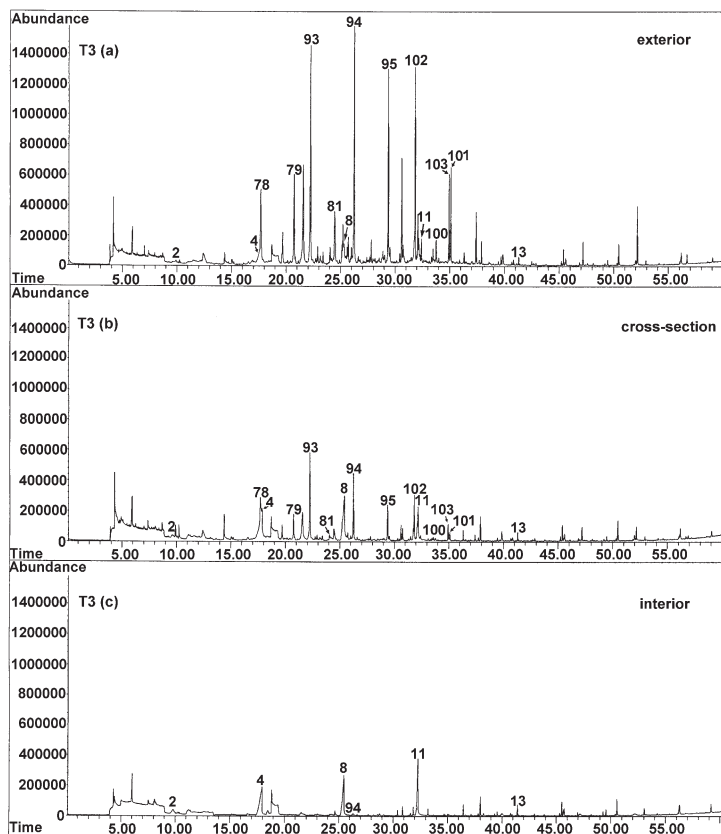


Figure 1. Total ion current chromatogram of the components of the headspace of the exterior (a), cross-section (b) and interior regions (c) of the T3 cheese sample, which contains the highest concentrations in smoke components. The numbers of the components agree with those in Table I.

phenol, guaiacol, 4-methyl- and 4-ethyl-guaiacol, syringol, methyl-phenols and vinyl-guaiacol in quite constant proportions.

Likewise, differences were found between samples in relation to acid concentrations. So, in T1 and T4 headspace samples the concentration of acids is much higher than in the other samples due to an accentuation of the lipolysis process. Table III gives the cheese's headspace average abundances (A_a) of the main acids in samples T2, T3, T5 and T6. These data indicate that there is a great variability in the abundance of acids in the different cheeses, probably due to the

accentuation of the lipolysis process in the manufacture of some samples. In spite of this, the average relative abundance (A_{ra}) of significant acids of the six samples, expressed as percentages in relation to the total abundance, given in Table III, reveal that these cheeses showed a fairly homogeneous aromatic profile of acids, the main ones being hexanoic, octanoic and decanoic, in quite constant proportions.

The headspace of Palermo cheeses smoked with dry prickly pear shows some differences in relation to the headspace of Palermo cheeses smoked with pine needles [15].

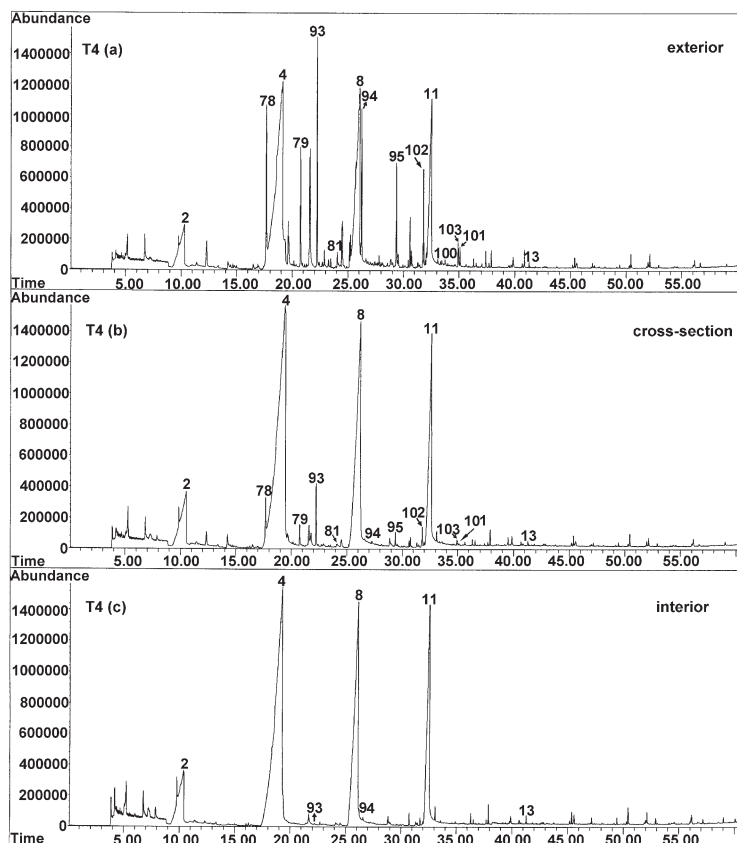


Figure 2. Total ion current chromatogram of the components of the headspace of the exterior (a), cross-section (b) and interior regions (c) of the T4 cheese sample, which contains the highest concentrations in acids. The numbers of the components agree with those in Table I.

In general, the average concentrations of smoke components in the headspace of all samples of cheese smoked with dry prickly pear, and their standard deviations, were lower than in those of cheese smoked with pine needles; this fact indicates that both the smoking degree reached and the variability among samples is lower in the case of dry prickly pear. As the manufacture and smoking process of this cheese is artisanal, both facts mentioned are related to the influence of the vegetable matter on the performance of the pyrolytic process for obtaining

smoke with homogeneous composition and concentration. As previously commented, there are also differences in relation to the presence or absence of components derived from the smoke. So, the absence of terpene and sesquiterpene compounds in the headspace of cheese smoked with dry prickly pear is noteworthy, as is the presence of biphenol derivatives, as well as a more accentuated presence of nitrogen and syringol derivatives than in the headspace of cheese smoked with pine leaves. Differences in the headspace of Palmero cheese smoked with

Table II. Average abundances, A_a , and average relative abundances, A_{ra} of some components derived from the smoke, in the headspace of the exterior cheese region, calculated from data of five (T1, T2, T4, T5, T6) and of six samples, respectively, expressed in area counts of the ion used for the quantification (I) multiplied by 10^{-5} , and as percentages, respectively, together with their standard deviations, DA_a and DA_{ra} .

Compounds	I	A_a	DA_a	A_{ra}	DA_{ra}
2-Furanmethanol (furfuryl alcohol)	98	14.6	± 4.9	1.8	± 1.0
3-Methyl-1,2-cyclopentanedione (cyclotene)	112	6.1	± 1.5	0.9	± 0.4
3-Hydroxy-2-methyl-4H-pyran-4-one (maltol)	126	4.0	± 1.3	0.6	± 0.2
Phenol	94	154.0	± 61.1	16.9	± 4.1
2-Methylphenol	108	48.3	± 14.3	5.8	± 0.5
4-Methylphenol and 3-Methylphenol	107	100.8	± 29.6	11.7	± 2.1
2,6-Dimethylphenol	122	5.7	± 1.7	0.7	± 0.1
2-Ethylphenol	107	5.5	± 1.3	0.7	± 0.1
2,4-Dimethylphenol and 2,5-Dimethylphenol	107	32.0	± 7.9	4.0	± 0.4
2,3-Dimethylphenol	107	5.7	± 1.3	0.7	± 0.1
2,6-Bis(1,1-dimethylethyl)-4-methyl-phenol (BHT)	205	2.7	± 1.3	0.3	± 0.2
2-Methoxyphenol (guaiacol)	109	113.4	± 28.2	13.9	± 1.5
4-Methyl-2-methoxyphenol (4-methylguaiacol)	138	78.9	± 24.9	9.9	± 1.6
4-Ethyl-2-methoxyphenol (4-ethylguaiacol)	137	96.3	± 28.5	12.2	± 1.4
4-Vinyl-2-methoxyphenol (4-vinylguaiacol)	150	47.3	± 21.2	5.6	± 1.4
4-(2-Propenyl)-2-methoxyphenol (eugenol)	164	8.3	± 3.2	1.1	± 0.3
4-Propyl-2-methoxyphenol (4-propylguaiacol)	137	13.1	± 4.7	1.7	± 0.4
4-(1-Propenyl)-2-methoxyphenol (isoeugenol)	164	4.3	± 1.7	0.6	± 0.2
4-(1-Propenyl)-2-methoxyphenol (isoeugenol isomer)	164	16.1	± 6.2	2.2	± 0.8
2,6-Dimethoxyphenol (syringol)	154	38.5	± 9.0	5.8	± 2.7
4-Methyl-2,6-dimethoxyphenol (4-methylsyringol)	168	13.9	± 2.1	2.2	± 1.0
4-(2-Propenyl)-2,6-dimethoxyphenol	194	1.0	± 0.3	0.2	± 0.1
Naphthalene	128	3.9	± 1.3	0.4	± 0.1
2-Methylnaphthalene	142	0.8	± 0.3	0.1	± 0.0
Acenaphthylene	152	0.6	± 0.4	0.1	± 0.0

dry prickly pear and pine needles can also be found in the proportions of some phenolic derivatives such as 2-methylphenol in relation to phenol, 4-methylguaiacol and 4-ethylguaiacol in relation to guaiacol, and 4-methylsyringol in relation to syringol, due to the differences in the lignin composition of the vegetable matters used for the smoking. In relation to typical headspace cheese

components such as acids, it can be said that their number, their average concentrations and their standard deviations, which represent the variability among samples, are also smaller in cheeses smoked with dry prickly pear than in those smoked with pine leaves.

In conclusion, in the headspace of this cheese typical cheese components and typical smoke components were identified.

Table III. Average abundances, A_a , and average relative abundances, A_{ra} of the acids in the headspace of the exterior cheese region, calculated from data of four (T2, T3, T5, T6) and of six samples, respectively, expressed in area counts of the ion used for the quantification (I) multiplied by 10^{-5} and as percentages, respectively, together with their standard deviations, DA_a and DA_{ra} .

Compounds	I	A_a	DA_a	A_{ra}	DA_{ra}
Pentanoic acid	60	6.1	± 4.7	1.4	± 1.5
Hexanoic acid	60	91.5	± 27.6	37.3	± 9.8
Octanoic acid	60	94.6	± 22.2	30.4	± 4.1
Nonanoic acid	60	2.3	± 0.9	0.6	± 0.3
Decanoic acid	60	89.7	± 19.3	27.7	± 5.9
Dodecanoic acid	73	7.6	± 2.2	2.5	± 1.4

Among the first group of components only some of them are homogeneously distributed in the different cheese regions, the exterior region being generally richer in components than the interior. Most of the components of the second group are present only in the exterior region; however, some of them have diffused towards the interior region. It must be pointed out that although phenolic derivatives are not the main smoke components, nevertheless, in the headspace exterior region these compounds were the smoke components detected in the highest proportions. In spite of the differences found in the headspace component concentrations of the exterior region of the several samples, there is a certain homogeneity shown by similar proportions not only of the smoke components but also of the main acids. The most significant differences in the headspace composition of Palmero cheese smoked with prickly pear and with pine leaves are that the first contains a higher number of syringol and nitrogenated derivatives than the second, and this latter contains terpene derivatives absent in the first. These differences in composition between Palmero cheese smoked with pine leaves and with dry prickly pear allows one to distinguish between the two kinds of cheeses.

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