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Principal component analysis as tool of characterization of quince (*Cydonia oblonga* Miller) jam

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Abstract

Fifty-one quince jams from several different brands, commercialised in three consecutive years, traditionally prepared and industrially manufactured, were studied. Principal component analysis (PCA) was performed, in order to assess the correlations between the different components of quince jam phenolics, organic acids and free amino acids. Phenolics determination was the most interesting. The differences between phenolic profiles of traditional and industrial quince jams were emphasised during PCA. Two main PC characterise the quince jam phenolic composition (54.4% of all variance): PC1 (37.4%) and PC2 (17.0%). The PC1 describes the differences between the contents of 3-*O*- and 5-*O*-caffeoylquinic acids and all flavonoids and the PC2 relates the contents of 4-*O*- and 5-*O*-caffeoylquinic acids against 3-*O*-caffeoylquinic and 3,5-dicaffeoylquinic acids. The results indicate that many industrial manufacturers usually use unpeeled fruits in the preparation of the jams. The PCA of phenolic compounds enabled clear discrimination between quince jams prepared with peeled and unpeeled fruits.

Keywords: *Cydonia oblonga* Miller; Quince jam; Phenolic compounds; Organic acids; Free amino acids; Principal component analysis

1. Introduction

According to Portuguese Legislation (Decreto-Lei n° 97/84 de 28 de Março), quince jam is the food product of homogeneous and consistent mixture, obtained exclusively by boiling quince (*Cydonia oblonga* Miller) mesocarp with sugar. Because quince is a seasonal fruit, its homemade jam is prepared during September/October, by boiling a mixture composed only of sugar and quince pulp, normally in the proportion of 50:50. The industrially manufactured quince jam is prepared with quince puree, sugar and additives (preservatives such benzoic and sorbic acids, antioxidants such as ascorbic acid, acidity regulators such as citric and tartaric acids, etc).

In the past few years, the chemical constituents of quince fruit and its derivatives have been subject of study by our research group, (Andrade, Carvalho, Seabra, & Ferreira, 1998; Ferreres, Silva, Andrade, Seabra, & Ferreira, 2003; Silva, Andrade, Mendes et al., 2000; Silva, Andrade, Valentão et al., 2000; Silva, Andrade, Seabra, & Ferreira, 2001; Silva, Andrade, Mendes, Seabra, & Ferreira, 2002; Silva, Andrade, Ferreres et al., 2002; Silva et al., 2003; Silva, Casal et al., 2004; Silva, Andrade, Gonçalves et al., 2004; Silva, Andrade, Ferreres et al., 2005; Silva, 2005). Furthermore, past studies have included the evaluation of the antioxidant potential (Silva, Andrade, Valentão et al., 2004). Among the several chemical parameters studied, phenolic profile

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seemed to be the most useful in the evaluation quince product authenticity (Andrade et al., 1998; Silva, Andrade, Mendes et al., 2000; Silva, Andrade, Valentão et al., 2000; Silva et al., 2001; Silva, Andrade, Ferreres et al., 2002; Silva, Andrade, Gonçalves et al., 2004).

As the published results were only from organic acid and free amino acid composition of quince jams commercialised in 2000 (Silva, Andrade, Mendes et al., 2002; Silva, Casal et al., 2004), and considering the possibility of the influence of quince jam brand and the year of commercialisation on the chemical profile, the paper herein reports, for the first time, the organic acid and free amino acid composition of quince jams commercialised in 2001 and 2002. Principal component analysis (PCA) was applied to these data to assess the correlation between the different components of quince jam phenolics, organic acids and free amino acids. PCA was performed separately to each studied chemical parameter and to the global data.

2. Materials and methods

2.1. Samples

Forty-nine commercial quince jam samples were analysed and they included eight traditionally manufactured jams (observations 1–8) and 41 industrially manufactured jams (observations 11–51), randomly purchased on the Portuguese market in the years of 2000–2002 (Table 1). Additionally, a quince jam (observation 9) was prepared in the laboratory by boiling fresh quince pulps with sugar (in the proportion of 50:50), for approximately 90 min. Another quince jam (observation 10) was prepared by the same procedure, but using unpeeled fruits.

Table 1
Samples characterization

Observation	Brand	Year
1	A	2000
2	A	2001
3	A	2002
4	B	2000
5	B	2001
6	C	2000
7	C	2001
8	D	2000
9	Homemade 1	2002
10	Homemade 2	2002
11	E	2000
12	E	2001
13	E	2002
14	F	2000
15	F	2001
16	F	2002
17	G	2000
18	G	2001
19	G	2002
20	H	2000
21	H	2001
22	I	2000
23	I	2001
24	I	2002
25	J	2000
26	J	2001
27	J	2002
28	K	2000
29	K	2001
30	K	2002
31	L	2000
32	M	2000
33	M	2001
34	M	2002
35	N	2000
36	N	2001
37	N	2002
38	O	2000
39	O	2001
40	O	2002
41	P	2000
42	P	2001
43	P	2002
44	Q	2000
45	Q	2001
46	Q	2002
47	R	2000
48	R	2001
49	R	2002
50	S	2000
51	T	2000

2.2. Standards

The standards were from Sigma (St. Louis, MO, USA) and from Extrasynthése (Genay, France). Methanol, formic and hydrochloric acids were obtained from Merck (Darmstadt, Germany) and sulphuric acid from Pronalab (Lisboa, Portugal). Ethyl chloroformate (ECF) was from Aldrich (Steinheim, Germany) and pyridine from Fluka (Neu-Ulm, Germany). The water was treated in a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.3. Solid-phase extraction columns

ISOLUTE C18 non end-capped (NEC) solid-phase extraction (SPE) columns (50 μm particle size, 60 Å porosity; 10 g sorbent mass/70 ml reservoir volume) were purchased from International Sorbent Technology Ltd (Mid Glamorgan, UK). The benzenesulfonic SCX Spe-ed SPE cartridges (200 mg; 3 ml) were obtained from Applied Separations (Allentown, USA).

2.4. Extraction and HPLC analysis of phenolic compounds

The extraction of phenolics was achieved as previously reported (Silva et al., 2001; Silva, Andrade, Ferreres et al., 2002) and included a C18 NEC SPE cleaning step.

The extracts were analysed on an analytical HPLC unit (Gilson), using a Spherisorb ODS2 (25.0 × 0.46 cm; 5 μm, particle size) column (Silva et al., 2001; Silva, Andrade, Ferreres et al., 2002). Detection was achieved with a Gilson DAD.

Phenolic compounds quantification was achieved by the absorbance recorded in the chromatograms relative to external standards. 3- and 4-*O*-caffeoylquinic, and 3,5-dicaffeoylquinic acids were quantified as 5-*O*-caffeoylquinic acid. Kaempferol glycoside and kaempferol glycosides acylated with *p*-coumaric acid were quantified as kaempferol 3-glucoside. Quercetin glycosides acylated with *p*-coumaric acid were quantified as quercetin 3-galactoside. The other compounds were quantified as themselves.

2.5. Extraction and HPLC analysis of organic acids

The sample preparation was simple, involving only extraction with methanol (40 °C) and filtration through a C18 NEC SPE cartridge, as reported by Silva, Andrade, Mendes et al. (2002).

The separation was carried out as previously reported (Silva, Andrade, Mendes et al., 2002) with an analytical HPLC unit (Gilson), using an ion exclusion Nucleogel® Ion 300 OA (300 × 7.7 mm) column. Detection was performed with an UV detector set at 214 nm.

Organic acids quantification was achieved by the absorbance recorded in the chromatograms relative to external standards. Malic and quinic acids were quantified together and as malic acid. The other acids were quantified as themselves.

2.6. Extraction and GC of free amino acids

According to Silva et al. (2003), the extraction of L-amino acids was simple, including a SCX SPE purification step. The derivatisation of L-amino acids was carried out as reported previously (Silva et al., 2003). The extracts were analysed on a Chrompack CP 9001 instrument (Chrompack, Middelburg, The Netherlands) equipped with a flame ionisation detector (FID), and an automatic liquid sampler (CP-9050, Chrompack) (Silva et al., 2003).

The amino acids were identified by their retention times and chromatographic comparison with authentic standards. Quantification was based on the internal standard method using L-*p*-chlorophenylalanine.

2.7. Statistical analysis

All statistical analyses involving the experimental data were performed using R 1.9.0 for Linux (R-Project, 2004).

A multifactor ANOVA (without replication) was performed to evaluate the effects of the studied factors – quince jam brand, jam type (traditional or industrial) and the year of commercialisation (2000–2002) – on phenolics, organic acids and free amino acids.

The multifactor linear regression model was analysed for residuals normality and skewness to access the validity of the ANOVA analysis. Despicable factor effects were removed from the full linear model to improve the accuracy of the analysis. The ANOVA tables and factor probabilities and their combinations were obtained. The Tukey multicomparison test was used to perform pair-wise comparisons among factor levels means (Neter, Kutner, Natchtsheim, & Wasserman, 1996a).

The Pearson correlation coefficients between phenolics, organic acids and free amino acids were calculated to obtain possible correlation between the different quince jam constituents (Neter, Kutner, Natchtsheim, & Wasserman, 1996b).

2.7.1. Principal component analysis

PCA was performed to access the correlations between the different components of quince jam phenolics, organic acids and free amino acids. PCA was performed separately to each studied chemical parameter (phenolic, organic acid and free amino acid profiles), but also to the global data.

Principal components (PC) were analysed for their variance percentage and component coefficients, to access their significance. The Gabriel plot (biplot), using optimal-scaling was performed to gain greater insight of relationships between quince jam components, aiming to interpret the different groups of data (Krazanowski, 1998).

3. Results and discussion

3.1. Experimental design

Quince jams were analysed in terms of phenolics, organic acids and free amino acids. The analysis comprised results from 51 samples, 10 traditionally prepared and 41 industrially manufactured, throughout the commercialisation years of 2000–2002 (Table 1). Although the full factorial design (Box, Hunter, & Hunter, 1978) was initially planned, it was not possible to obtain quince jam samples for every commercialisation year, so the analysis was carried out with the partial factorial design without replication (Montegomery, 1991a, 1991b).

3.2. Phenolic compounds

All quince jams presented a chemical profile composed by at least six identified phenolic compounds: 3-*O*-, 4-*O*- and 5-*O*-caffeoylquinic acids, 3,5-dicaffeoylquinic acid,

Table 2
Phenolic composition of quince jams

	Phenolic compound (%)						
	3-CQA	4-CQA	5-CQA	3,5-diCQA	Q-3-Gal	Q-3-Rut	K-3-Gly
Traditional type quince jams							
Mean	32.8	12.1	44.4	1.97	1.04	6.51	0.11
Maximum	42.3	33.9	54.2	5.57	3.14	15.7	0.39
Minimum	11.9	5.63	31.6	0.20	tr	1.40	nd
SD	11.0	8.75	7.76	1.55	1.25	5.11	0.18
	K-3-Glu	K-3-Rut	Q-Gly-pC1	Q-Gly-pC2	K-Gly-pC1	K-Gly-pC2	$\sum$ (mg/kg)
Mean	0.14	0.34	0.14	0.10	0.07	0.21	176.3
Maximum	0.47	1.50	0.54	0.39	0.39	1.07	275.7
Minimum	nd	nd	nd	nd	nd	nd	112.2
SD	0.19	0.57	0.23	0.15	0.15	0.35	66.5
	3-CQA	4-CQA	5-CQA	3,5-diCQA	Q-3-Gal	Q-3-Rut	K-3-Gly
Industrial type quince jams							
Mean	26.3	9.25	42.7	1.83	3.05	12.9	0.92
Maximum	35.2	19.6	52.9	3.55	5.11	21.1	3.00
Minimum	8.43	4.46	34.4	0.65	tr	5.76	Nd
SD	4.99	3.97	4.36	0.65	1.35	3.23	0.52
	K-3-Glu	K-3-Rut	Q-Gly-pC1	Q-Gly-pC2	K-Gly-pC1	K-Gly-pC2	$\sum$ (mg/kg)
Mean	0.65	1.37	0.39	0.15	0.09	0.37	238.9
Maximum	1.59	3.09	1.38	0.69	0.42	1.05	417.3
Minimum	nd	nd	nd	nd	nd	nd	103.0
SD	0.33	0.56	0.26	0.13	0.12	0.19	81.4

SD, standard deviation; tr – traces; nd, not detected; $\sum$, sum of the determined phenolic compounds; 3-CQA, 3-*O*-caffeoylquinic acid; 4-CQA, 4-*O*-caffeoylquinic acid; 5-CQA, 5-*O*-caffeoylquinic acid; 3,5-CQA, 3,5-dicaffeoylquinic acid; Q-3-Gal, quercetin 3-galactoside; Q-3-Rut, rutin, K-3-Gly-kaempferol 3-glycoside; K-3-Glu, kaempferol 3-glucoside; K-3-Rut, kaempferol 3-rutinoside; Q-Gly-pC1 and Q-Gly-pC2, quercetin glycosides acylated with *p*-coumaric acid; K-Gly-pC1 and K-Gly-pC2, kaempferol glycosides acylated with *p*-coumaric acid.

quercetin 3-galactoside and rutin (Table 2). Although, several samples, especially the industrially manufactured ones, also contained kaempferol 3-glucoside, kaempferol 3-rutinoside, and five not totally identified compounds (one kaempferol glycoside, two quercetin glycosides acylated with *p*-coumaric acid and two kaempferol glycosides acylated with *p*-coumaric acid) (Table 2). The presence of these compounds indicates adulteration of the jams by using unpeeled fruits (Silva, Andrade, Ferreres et al., 2002). Generally, the most abundant phenolic was 5-*O*-caffeoylquinic acid (average value of 43.0% minimum and maximum values of 31.6%, and 54.2% respectively).

The multifactor ANOVA analysis described very significant differences between the traditional and industrial quince jams phenolic profile (Table 2 and Fig. 1). It is possible to observe that traditional quince jams were richer in 3-*O*-caffeoylquinic acid ($p < 0$ 01). Industrial quince jams were, generally, richer in terms of flavonoids. Data show that industrial quince jams had higher content than the traditional ones in terms of: quercetin 3-galactoside ($p < 0.001$), rutin ($p < 0.05$), kaempferol glycoside ($p < 0.001$), kaempferol 3-glucoside ($p < 0.01$), kaempferol 3-rutinoside ($p < 0.01$) and quercetin glycosides acylated with *p*-coumaric acid ($p < 0.05$) (Fig. 1). The higher content of flavonoids in industrial quince jams indicates the presence of a higher proportion of quince peel in these jams. Some phenolics content also varied significantly according to the quince jam brand: 4-*O*-caffeoylquinic acid ($p < 0.01$), quercetin 3-galactoside ($p < 0.05$), rutin ($p < 0.001$), kaempferol glycoside ($p < 0.01$), kaempferol 3-glucoside ($p < 0.01$), kaempferol 3-rutinoside ($p < 0.001$) and total content ($p < 0.01$). Other phenolics varied significantly according to the year of commercialisation: quercetin 3-galactoside ($p < 0.01$), rutin ($p < 0.01$) and one of the kaempferol glycosides acylated with *p*-coumaric acid (KGly*p*C2) ($p < 0.05$).

The differences between traditional and industrial quince jams phenolic profiles were emphasised during PCA. Two main PC characterise to the quince jam phenolic composition (54.4% of all variance): PC1 (37.4%) and PC2 (17.0%) (Fig. 2). The PC1 describes the differences between the contents of 3-*O*- and 5-*O*-caffeoylquinic acids and all flavonoids (quercetin 3-galactoside, rutin, kaempferol glycoside, kaempferol 3-glucoside, kaempferol 3-rutinoside, quercetin glycosides acylated with *p*-coumaric acid and kaempferol glycosides acylated with *p*-coumaric acid). The PC2 relates the contents of 4-*O*- and 5-*O*-caffeoylquinic acids against 3-*O*-caffeoylquinic and 3,5-dicaffeoylquinic acids. It is possible to observe, in Fig. 2, a very distinct difference between traditional and industrial quince jams.

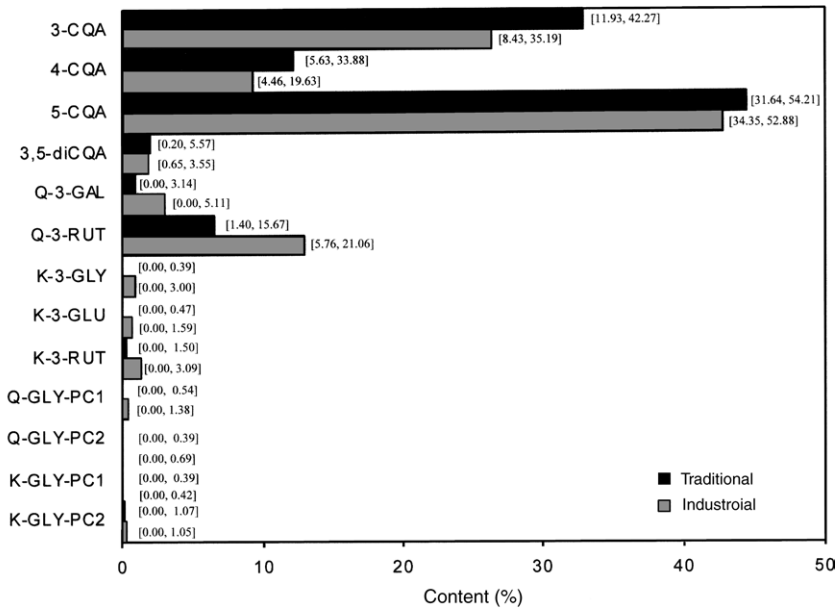

Fig. 1. Quince jam phenolic profile (minimum and maximum values of each compound are presented in brackets). 3-CQA, 3-*O*-caffeoylquinic acid; 4-CQA, 4-*O*-caffeoylquinic acid; 5-CQA, 5-*O*-caffeoylquinic acid; 3,5-diCQA, 3,5-dicaffeoylquinic acid; Q-3-GAL, quercetin 3-galactoside; Q-3-RUT, rutin; K-3-GLY, kaempferol 3-glycoside; K-3-GLU, kaempferol 3-glucoside; K-3-RUT, kaempferol 3-rutinoside; Q-GLY-PC1 and Q-GLY-PC2, quercetin glycosides acylated with *p*-coumaric acid; K-GLY-PC1 and K-GLY-PC2, kaempferol glycosides acylated with *p*-coumaric acid.

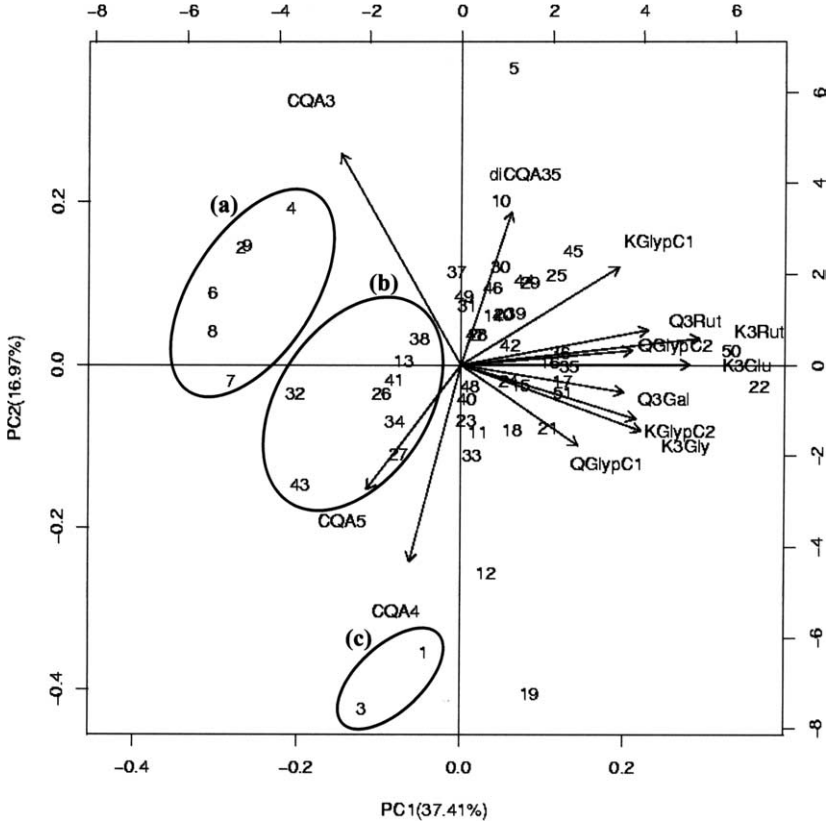

Fig. 2. Principal component analysis of phenolic compounds in quince jam, from 51 independent observations. CQA3, 3-*O*-caffeoylquinic acid; CQA4, 4-*O*-caffeoylquinic acid; CQA5, 5-*O*-caffeoylquinic acid; diCQA35, 3,5-dicaffeoylquinic acid; Q3Gal, quercetin 3-galactoside; Q3Rut, rutin; K3Gly, kaempferol 3-glycoside; K3Glu, kaempferol 3-glucoside; K3Rut, kaempferol 3-rutinoside; QGlypCl and QGlypC2, quercetin glycosides acylated with *p*-coumaric acid; KGlypCl and KGlypC2, kaempferol glycosides acylated with *p*-coumaric acid.

Almost all industrial type jams are localised in the positive axis of PC1, indicating that, according to Portuguese Legislation (Decreto-Lei n° 97/84 de 28 Março), most of the samples were adulterated with quince peel. However, a small group of industrial type jams were prepared with peeled fruits or with a lower proportion of peel (Fig. 2 – group b). Traditional quince jams were, generally, characterised by higher amount of caffeoylquinic acids. It is possible to distinguish two different groups of traditional type jams (Fig. 2): group a – higher content in terms of 3-*O*-caffeoylquinic and 3,5-dicaffeoylquinic acids and group c – higher content of 4-*O*-caffeoylquinic acid. Previous studies on quince fruit composition have revealed that the pulp composition in terms of 4-*O*-caffeoylquinic and 3,5-dicaffeoylquinic acids is antagonistic (Silva, 2005). Generally, pulps with high 4-*O*-caffeoylquinic acid content exhibited low 3,5-dicaffeoylquinic acid and vice-versa (Silva, 2005). Under these circumstances, the difference in composition in terms of 4-*O*-caffeoylquinic acid and 3,5-dicaffeoylquinic acid was expected.

Table 3
Organic acid composition of quince jams

	Organic acid (%)						
	Oxalic acid	Citric acid	Ascorbic acid	Malic and quinic acids	Shikimic acid	Fumaric acid	∑ (mg/kg)
Traditional type quince jams							
Mean	0.03	0.57	3.88	95.3	0.18	0.01	4518
Maximum	0.13	1.69	15.7	98.4	0.33	0.03	5894
Minimum	nd	tr	0.75	84.1	0.09	nd	2514
SD	0.04	0.60	4.72	4.66	0.09	0.01	1235
Industrial type quince jams							
Mean	0.06	17.4	2.16	80.2	0.15	0.01	7614
Maximum	1.25	58.9	13.0	97.9	0.69	0.04	12177
Minimum	nd	1.12	tr	32.7	0.02	nd	2988
SD	0.20	14.3	2.34	15.1	0.11	0.01	2629

SD, standard deviation; nd, not detected; tr, traces; ∑, sum of the determined organic acids.

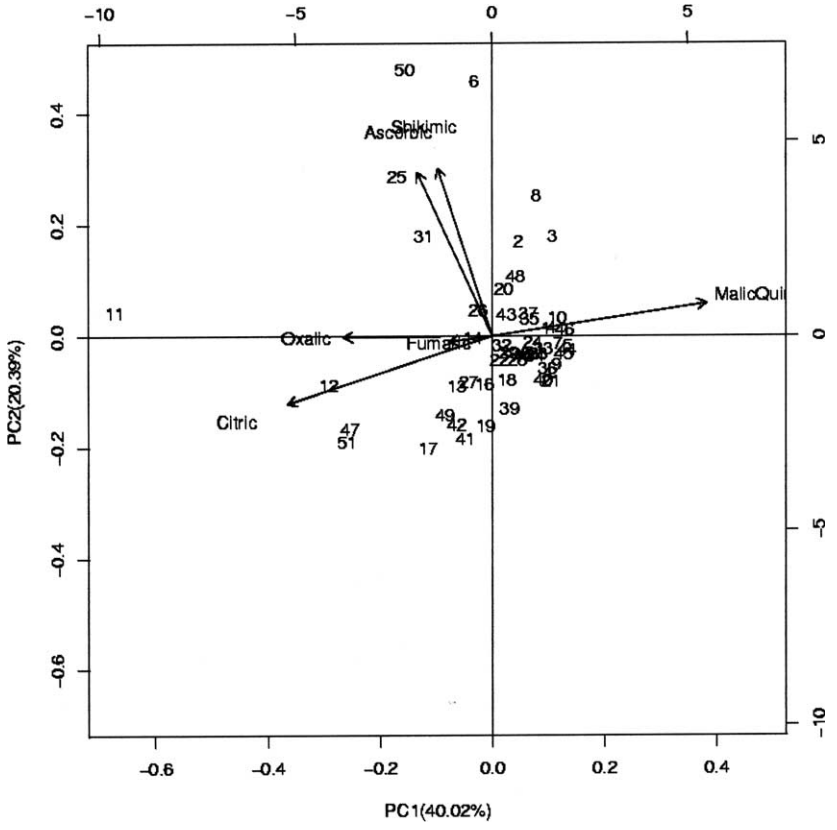

Fig. 3. Principal component analysis of organic acids in quince jam, from 51 independent observations.

One of the traditional jams (observation 10), prepared in the laboratory, by using unpeeled fruits revealed, as expected, a high content of flavonoids, which indicates the use of quince peel during manufacture.

3.3. Organic acids

As previously reported (Silva, Andrade, Mendes et al., 2002), generally, quince jams presented a similar profile composed of seven identified organic acids: oxalic, citric, ascorbic, malic, quinic, shikimic and fumaric acids (Table 3). Usually, quince jam is characterised by large amounts of malic plus quinic acids, containing an average value of 83.2% (with minimum and maximum values of 32.7% and 98.4%, respectively). Generally, citric and ascorbic acids were presented in considerable amounts, with average values of 14.1 and 2.50, respectively.

The multifactor ANOVA analysis described significant differences between the organic acid composition of traditional and industrial quince jams (Table 3), in terms of: citric acid ($p < 0.01$, higher in industrial type quince jams) and malic plus quinic acids of ($p < 0.01$, higher in traditional type quince jams). The contents of some organic acids also varied significantly according to the commercialisation year: ascorbic acid ($p < 0.05$), malic plus quinic acids ($p < 0.05$), fumaric acid ($p < 0.05$) and the total content ($p < 0.01$). Other organic acids varied significantly with quince jam brand: citric acid ($p < 0.05$), ascorbic acid ($p < 0.05$) and the total content ($p < 0.001$).

The organic acid profile can be described by two PC (Fig. 3), which are responsible to 60.4% of the variance. PC1 (40.0% of the total variation) expresses mainly the ratio malic plus quinic acids against the rest of the organic acids. PC2 (20.4% of the total variation) expresses mainly the citric acid content when compared to the rest of the acids. It is possible to observe, in Fig. 3, that most samples had high malic plus quinic acids ratios. However, samples 12, 47 and 51 exhibited high contents of citric acid and samples 6, 25, 31 and 50 had high ascorbic acid contents. This can be explained by the fact that, frequently, citric and ascorbic acids are added to industrially produced quince jam, as acidity regulator and antioxidant, respectively.

3.4. Free amino acids

Quince jams were richer in terms of aspartic acid (32.1%) and asparagine (30.0%), had medium values of glycine (8.01%), hydroxyproline (6.86%), threonine (3.93%), alanine (3.31%), glutamic acid (3.28%) and cysteine (3.11%), and very small proportions of the other free amino acids (Table 4).

Table 4
Free amino acid composition of quince jams

Amino acid (%)								
Traditional type quince jams								
	Ala	Gly	Val	Leu	Ile	Pro	Thr	Ser
Mean	2.36	4.12	0.74	0.22	0.47	0.51	3.77	1.64
Maximum	4.37	12.16	2.83	0.52	0.94	1.12	11.2	3.04
Minimum	0.90	0.73	0.26	0.07	0.04	0.18	0.15	0.09
SD	1.25	4.08	0.76	0.13	0.30	0.28	3.17	0.92
	Glu	Asn	Asp	Met	Hyp	Phe	Cys	Gln
Mean	2.48	29.9	40.45	0.08	8.12	0.26	2.83	0.42
Maximum	7.61	64.9	68.24	0.29	30.0	0.49	6.28	0.63
Minimum	0.06	9.01	17.13	0.01	0.42	0.07	0.36	0.11
SD	2.43	18.1	19.48	0.09	8.86	0.15	2.22	0.21
	Orn	Lys	His	Tyr	Trp	$\sum$ (μg/kg)		
Mean	0.17	0.56	0.68	0.15	0.07	993		
Maximum	0.51	1.22	1.90	0.30	0.21	2401		
Minimum	0.01	0.13	0.04	0.02	0.01	333		
SD	0.18	0.41	0.62	0.11	0.09	601		
Industrial type quince jams								
	Ala	Gly	Val	Leu	Ile	Pro	Thr	Ser
Mean	3.55	8.96	0.91	0.34	1.43	0.54	3.97	2.18
Maximum	26.5	25.0	3.29	1.16	10.2	1.04	8.81	6.60
Minimum	0.03	0.23	0.21	0.11	0.34	0.19	0.79	0.62
SD	5.03	6.48	0.54	0.23	1.68	0.23	2.14	1.39
	Glu	Asn	Asp	Met	Hyp	Phe	Cys	Gln
Mean	3.47	30.0	30.1	0.06	6.55	0.38	3.18	1.11
Maximum	11.0	62.7	51.1	0.26	30.0	2.16	12.4	2.91
Minimum	0.87	4.51	8.60	0.01	0.69	0.02	0.07	0.04
SD	2.08	15.6	13.0	0.05	7.46	0.40	2.58	0.66
	Orn	Lys	His	Tyr	Trp	$\sum$ (μg/kg)		
Mean	0.20	1.31	1.44	0.16	0.19	698		
Maximum	1.19	4.09	8.73	0.73	1.48	1337		
Minimum	0.02	0.25	0.14	0.02	0.01	309		
SD	0.23	0.83	1.50	0.16	0.25	222		

SD, standard deviation; $\sum$, sum of the determined free amino acids; ala, alanine; gly, glycine; val, valine; leu, leucine; ile, isoleucine; pro, proline; thr, threonine; ser, serine; glu, glutamic acid; asn, asparagine; asp, aspartic acid; met, methionine; hyp, hydroxyproline; phe, phenylalanine; cys, cysteine; gln, glutamine; orn, ornithine; lys, lysine; his, histidine; tyr, tyrosine; trp, tryptophan.

The multifactor ANOVA showed differences in the amino acids composition of traditional and industrial quince jams in terms of: glutamic acid ($p < 0.05$, higher in industrial quince jams), aspartic acid ($p < 0.05$, higher in traditional quince jams), glutamine ($p < 0.05$, higher in industrial quince jams), lysine ($p < 0.01$, higher in industrial quince jams), and total content ($p < 0.01$, higher in traditional quince jams). The content of some free amino acids also varied significantly according to the year of commercialisation: valine ($p < 0.01$), threonine ($p < 0.001$) and glutamic acid ($p < 0.001$). Glutamine content also varied significantly with the quince jam brand.

Two PC describe 38.5% of the total variance: PC1 (24.2%) relates the content of aspartic acid, hydroxyproline and asparagine with the rest of the free amino acids; PC2 (14.3%) relates the proportion of threonine, serine, proline, cysteine, glutamine and aspartic acid against histidine, tryptophan, phenylalanine, hydroxyproline and asparagine. In Fig. 4 (biplot of PC1 vs. PC2), it is possible to observe that most quince jams were rich in terms of

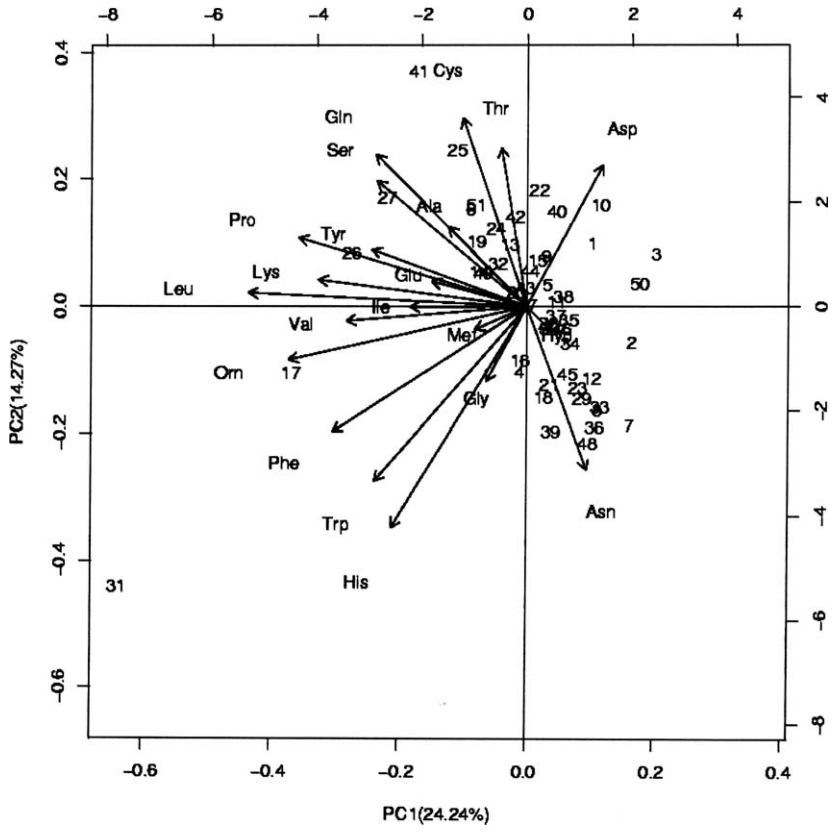

Fig. 4. Principal component analysis of free amino acids in quince jam, from 51 independent observations. Ala, alanine; gly, glycine; val, valine; leu, leucine; ile, isoleucine; pro, proline; thr, threonine; ser, serine; glu, glutamic acid; asn, asparagine; asp, aspartic acid; met, methionine; hyp, hydroxyproline; phe, phenylalanine; cys, cysteine; gln, glutamine; orn, ornithine; lys, lysine; his, histidine; tyr, tyrosine; trp, tryptophan.

aspartic acid and asparagine and the content in terms of the other amino acids is more fluctuating. Quince fruit and quince jam levels of asparagine and aspartic acid exhibited an inverse correlation. Quince fruit composition is higher in asparagine than in aspartic acid, but quince jam has higher aspartic acid than asparagine content. This can probably be explained by the fact that asparagine can be converted into aspartic acid and/or due to hydrolysis of proteins, peptides or other compounds with amino acids in their constitution, which can occur during thermal processing (in acid medium).

3.5. Global analysis

The PCA of all the data reveals that 26.9% of the variation sources can be described by two PCs: PC1 (14.8%) and PC2 (12.2%). Such small percentage of total variance does not suggest substantial differences between quince jams when all the studied parameters are compared. The correlation analysis between quince jam phenolics, organic acids and free amino acids contents leads to the conclusion that no direct correlation exists between the three groups of compounds.

In conclusion, after the analysis of several samples of quince jams from several different brands, traditionally and industrially prepared, commercialised in three consecutive years (2000–2002), the phenolics determination is more interesting than that of organic acids and free amino acids, concerning the discrimination of the two types of manufacture. These results indicate that many industrial manufacturers, usually use unpeeled fruits in the preparation of the jams, which is forbidden by Portuguese Legislation.

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