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Phenolic profile in the evaluation of commercial quince jellies authenticity

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Abstract

The phenolic profiles of 12 samples of Portuguese commercial and one home-made quince jelly were determined by reversed-phase HPLC/DAD, in order to evaluate their authenticity. Two different extraction methods were needed for the complete definition of quince jelly profile, one of them including an Amberlite XAD-2 cleaning step. These analyses showed that all samples presented a similar profile composed of at least eight identified phenolic compounds. None of the samples were fraudulently adulterated by the addition of pear or apple, since they did not contain arbutin, the characteristic compound of pear, nor phloretin 2′-xylosylglucoside and phloretin 2′-glucoside, considered the chemical markers of apple. All samples exhibited 5-HMF, a sugar derivative, as the major compound.

1. Introduction

Fruit product adulterations are common and frequently practised with the addition of water, sugars, fruits of inferior commercial value, secondary extracts of fruits and colours (Silva, Seabra, Andrade, Oliveira & Ferreira, 1999).

Quince jelly is a product obtained by cooking a mixture of juice and/or aqueous extract of quince (*Cydonia oblonga* Miller, var. *maliformis* or *piriformis*) and sugars, in appropriate amounts, with sufficient jellied consistency (Decreto-Lei no. 97/84, 1984; Jackix, 1988; Portaria 497/92, 1992).

Due to the similar texture and rheological properties of apple (*Malus communis* Lamk) and pear (*Pirus communis* Lin.), quince products are easily adulterated by these fruits. The stronger odour of quince masks the sweet flavours of both fruits, their presence being very difficult to detect by sensory evaluation.

Phenolic compounds are widely distributed in nature and have been successfully used in the determination of the authenticity of some fruit products (Simón, Pérez-Ilzarbe, Hernández & Gómez-Cordovés, 1992; Spanos & Wrolstad, 1990a, 1992; Spanos, Wrolstad & Heatherbell, 1990; Tomás-Barbéran, Garcia-Viguera, Nieto, Ferreres & Tomás-Lorente, 1993; Tomás-Lorente, Garcia-Viguera, Ferreres & Tomás-Barbéran, 1992; Vallés, Victorero, Alonso & Gomis, 1994).

For quince and its derivatives, few studies have been developed. However, recently Andrade, Carvalho, Seabra and Ferreira (1998) reported a method to detect adulterations in quince pulps by the addition of apple and/or pear, using their phenolic profiles. The addition of apple and pear to quince puree can be detected by the presence of their characteristic compounds, phloretin 2′-xylosylglucoside and phloretin 2′-glucoside for apple (Simón et al., 1992; Tomás-Lorente et al., 1992; Vallés et al., 1994) and arbutin for pear (Simón et al., 1992; Spanos & Wrolstad, 1990a, 1990b; Tomás-Lorente et al., 1992).

The work herein represents a contribution to the definition of quince jelly phenolic profile, allowing the determination of its authenticity. For this purpose, several commercially available samples and a home-made one were analysed by HPLC/DAD.

2. Materials and methods

2.1. Chemicals

The standards were from Sigma (St. Louis, MO, USA) and from Extrasynthése (Genay, France). 3- and

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4-*O*-caffeoylquinic acids were not commercially available, so they were prepared by transesterification of 5-*O*-caffeoylquinic acid using tetramethylammonium hydroxide (Clifford, Kellard & Birch, 1989a, 1989b). HPLC-grade methanol and formic acid were obtained from Merck (Darmstadt, Germany). The water was treated in a Milli-Q water purification system (Millipore, Bedford, MA, USA).

2.2. Samples

Quince jellies (three blends of each sample) were purchased in local supermarkets. Home-made quince jelly was provided from one of us.

2.3. Sample preparation via the Amberlite XAD-2 step

Each quince jelly (ca. 40 g) was thoroughly mixed with five parts of water (pH 2 with HCl) until completely fluid and filtered through cottonwood to remove solid particles. The filtrate was then passed through a column (25×2 cm) of Amberlite XAD-2 (Fluka Chemicals: pore size 9 nm, particle size 0.3–1.2 mm), as reported previously (Ferreres, Andrade & Tomás-Barbéran, 1994). Sugars and other polar compounds were eluted with the aqueous solvent. The column was washed with water (pH 2 with HCl, 100 ml) and subsequently with distilled water (ca. 300 ml). The phenolic fraction remained in the column and was then eluted with methanol (ca. 300 ml). The methanolic extract was evaporated to dryness under reduced pressure (40°C), redissolved in methanol (1.5 ml) and 20 μl were analysed by HPLC.

2.4. Sample preparation via the simplified technique

Each quince jelly (ca. 40 g) was thoroughly mixed with methanol until complete dissolution. The extract was then filtered and evaporated to dryness under reduced pressure (40°C), redissolved in methanol (10 ml) and 20 μl were analysed by HPLC.

2.5. HPLC analysis of phenolics from quince jelly

This was achieved as previously reported (Andrade et al., 1998) on a reversed-phase Spherisorb ODS2 (25.0× 0.46 cm; 5 μm, particle size) column, using water-formic acid (19:1) (solvent A) and methanol (solvent B) as solvents. Elution was performed at a solvent flow rate of 0.9 ml/min, starting with 5% methanol and installing a gradient to obtain 15%B at 3 min, 25%B at 13 min, 30%B at 25 min, 35%B at 35 min, 45%B at 39 min, 45%B at 42 min, 50%B at 44 min, 55%B at 47 min, 70%B at 50 min, 75%B at 56 min and 80%B at 61 min. Detection was accomplished with a diode array detector, and chromatograms were recorded at 350 and 280 nm. The retention times for the different phenolics identified are shown in Table 1.

2.6. Phenolic compound identification and quantification

The different phenolic compounds were identified by chromatographic comparisons with authentic standards and UV–vis spectra in the 200–400 nm range. Phenolics quantification was achieved by the absorbance recorded in the chromatograms relative to external standards of phenolic compounds with detection at 350 nm for 3-, 4- and 5-*O*-caffeoylquinic acids, quercetin 3-galactoside, quercetin 3-xyloside, quercetin 3-rhamnoside and rutin, and 280 nm for the others.

3. Results and discussion

All quince jelly samples were submitted to both extraction methods. The samples presented the same chemical profile, composed by seven identified phenolic compounds (3-, 4- and 5-*O*-caffeoylquinic acids, rutin, quercetin 3-galactoside, quercetin 3-xyloside and quercetin 3-rhamnoside), hydroxymethylfurfural (HMF) and a procyanidin, probably procyanidin B3 (Figs. 1 and 2). This latter hypothesis is based on the chromatographic behaviour and UV spectra of a certified standard of procyanidin B3. Despite this, the isolation and identification by NMR and thiolysis studies would be desirable.

With the Amberlite XAD-2 cleaning step (Fig. 2), as a general rule, the extract had a higher amount of each phenolic compound. However, when this extractive method was used, the procyanidin was not detected, which could be due to its polarity, allowing its elution with the sugars and other polar compounds. So, it was necessary to use another extractive technique, which permitted the determination of this compound. In addition, in a previous work, Andrade et al. (1998) demonstrated that the simplified technique is also needed for the quantification of arbutin, in adulterated quince products by pear.

The presence of the characteristic compound of pear, arbutin, and of the chemical markers of apple, phloretin 2′-xylosylglucoside and phloretin 2′-glucoside, was not verified, suggesting that there was no adulteration by addition of these two fruits to quince jellies.

HMF was the major compound in all analysed samples (Table 1). HMF results from sugar decomposition by heat and cooking duration, so its abundance is not strange, indicating that jellies are prepared with high amounts of sugars and that their thermal processing is severe. This compound was quantified in the methanolic extracts, where it appeared separated from other compounds. Also, the extracts obtained via Amberlite XAD-2 presented smaller amounts of HMF due to its solubility in water.

Table 1
Phenolic composition of quince jellies (mg phenolic compound/kg jelly) obtained by Amberlite XAD-2 extraction[a]

Samples[b]	HMF[c] (RT 8m31s)	Procyanidin[c,d] (RT 8m51s)	3-*O*-caffeoylquinic acid (RT 9m36s)	4-*O*-caffeoylquinic acid (RT 14m32s)	5-*O*-caffeoylquinic acid (RT 16m01s)	Rutin (RT 41m38s)	Quercetin 3-*O*-galactoside (RT 42m08s)	Quercetin 3-*O*-xyloside (RT 42m55s)	Quercetin 3-*O*-rhamnoside (RT 43m25s)
A1	109 (9.44)	250 (23.39)	4.6 (0.48)	2.4 (0.23)	17.8 (1.48)	0.02 (0.001)	0.2 (0.03)	0.2 (0.04)	0.1 (0.006)
A2	146 (28.31)	43.9 (9.85)	3.7 (0.10)	1.4 (0.08)	19.2 (2.38)	0.07 (0.01)	0.4 (0.04)	0.4 (0.02)	nq
A3	68.2 (1.48)	55.0 (9.94)	6.4 (0.20)	3.4 (0.12)	26.7 (0.81)	0.04 (0.0009)	0.4 (0.009)	0.3 (0.01)	0.1 (0.01)
B1	2012 (44.83)	819 (52.44)	6.8 (0.13)	4.1 (0.41)	12.8 (1.08)	nq	nq	nq	nq
B2	1292 (69.08)	654 (64.41)	1.6 (0.03)	nq[e]	9.0 (0.29)	nq	nq	nq	nq
B3	1357 (30.21)	429 (14.92)	2.7 (0.16)	nq	8.9 (0.40)	0.09 (0.01)	0.3 (0.01)	0.08 (0.005)	0.3 (0.01)
C1	346 (38.98)	67.0 (3.55)	0.1 (0.01)	nq	2.2 (0.13)	nq	1.5 (0.11)	0.3 (0.02)	0.06 (0.007)
C2	369 (28.13)	115 (11.03)	0.3 (0.03)	nq	2.5 (0.06)	nq	nq	nq	nq
C3	289 (15.37)	94.9 (2.16)	0.6 (0.006)	nq	4.4 (0.09)	0.09 (0.009)	0.8 (0.005)	0.3 (0.004)	0.1 (0.005)
D1	222 (97.35)	253 (88.05)	2.5 (0.07)	0.7 (0.06)	6.3 (0.32)	0.2 (0.02)	1.5 (0.03)	0.2 (0.02)	0.2 (0.02)
D2	673 (77.66)	332 (52.73)	2.2 (0.23)	1.0 (0.009)	5.2 (0.61)	nq	3.9 (0.18)	0.3 (0.005)	nq
D3	747 (48.61)	357 (15.05)	nq	nq	4.8 (0.53)	nq	3.5 (0.28)	1.2 (0.10)	0.1 (0.007)
HM	825 (60.36)	349 (7.60)	14.5 (0.17)	13.3 (0.75)	54.2 (4.01)	nq	22.4 (0.63)	0.6 (0.04)	0.4 (0.01)

[a] Values were expressed as mean (standard deviation) of three assays for each sample.
[b] 1, 2, 3 Represent different blends of quince jelly samples from the same manufacture industry.
[c] Probably procyanidin B3.
[d] Determined by the simplified technique. HM, home-made quince jelly.
[e] nq, not quantified.

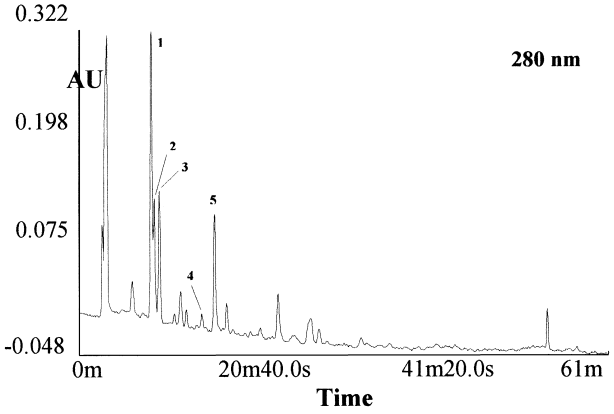

Fig. 1. HPLC profile of quince jelly phenolics obtained by simple extraction with methanol: (1) HMF; (2) probably procyanidin B3; (3) 3-*O*-caffeoylquinic acid; (4) 4-*O*-caffeoylquinic acid and (5) 5-*O*-caffeoylquinic acid.

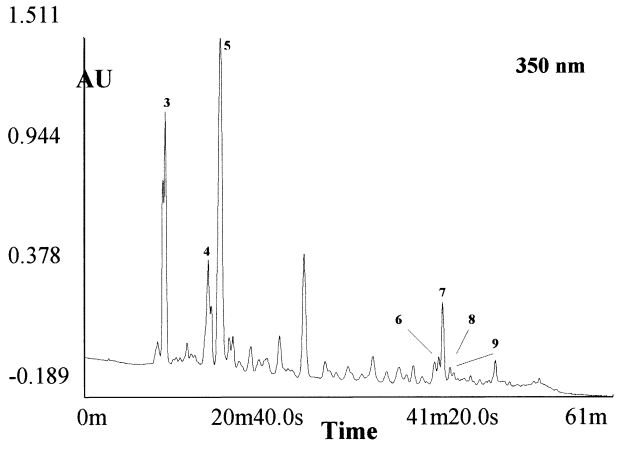

Fig. 2. HPLC profile of quince jelly phenolics obtained by Amberlite XAD-2 extraction: (3) 3-*O*-caffeoylquinic acid; (4) 4-*O*-caffeoylquinic acid; (5) 5-*O*-caffeoylquinic acid; (6) rutin; (7) quercetin 3-*O*-galactoside; (8) quercetin 3-*O*-xyloside and (9) quercetin 3-*O*-rhamnoside.

As with quince jams (Silva, Andrade, Mendes, Valentão, Seabra & Ferreira, in press), in quince jellies the most abundant phenolic acid and flavonol were 5-*O*-caffeoylquinic acid and quercetin 3-galactoside, respectively. In most cases, jellies presented inferior concentrations of the several phenolic compounds in comparison with quince jams, with the exception of the procyanidin. This is not unexpected since the amount of quince required to prepare the same amount of jam is greater (Decreto-Lei no. 97/84, 1984), and also because of the thermal treatment to which the fruit is submitted during the preparation of the jelly, which is more severe. The temperatures employed in its preparation may also be the cause of the high content in procyanidin exhibited by quince jellies, since the glycosidic procyanidin polymers from the quince fruit may be hydrolysed by citric acid, the most common acidity regulator used in its confection, leading to the formation of procyanidin B3. In addition, the presence of sodium benzoate, a popular preservative agent in quince puree (Andrade, Silva, Carvalho, Seabra & Ferreira, 1999) was not detected in the analysed samples, which could be explained by the fact that jellies have a larger amount of sugar than jams that, in turn, may act as preservatives.

Generally, except for procyanidin, rutin and quercetin 3-xyloside, the homemade jelly had higher concentrations of the different phenolic compounds than the industrial ones, perhaps by having a higher quince content. Different lots of the same commercial trade mark presented differences in quantitative terms. This may be due to a deficiency in the control of the manufacturing process of the jelly, particularly concerning time and cooking temperature, since phenolic compounds, especially procyanidins, are quite sensitive to the heat. Moreover, attention must be paid to the inherent natural variability of fruits of the same variety. Other factors, such as the collection date, the geographical origin, the cultural practices, the degree of maturation of the fruit and the storage conditions, may introduce quantitative and qualitative differences in the phenolic profile (Spanos & Wrolstad, 1990a).

In conclusion, this study suggests that the technique presented herein is quite useful for the analysis of the phenolic compounds in quince jelly samples, allowing the determination of its authenticity.

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