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Influence of variety, maturity and processing on phenolic compounds of apricot juices and jams

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Einfluß von Sorte, Reifezustand und Behandlung auf die phenolischen Verbindungen von Aprikosensäften und Konfitüren

Zusammenfassung. Eine HPLC-Technik mit Dioden-Array-Detektion wurde zur Charakterisierung der phenolischen Verbindungen in Früchten, Säften und Konfitüren von Aprikosen benutzt. Chlorogensäure dominierte in allen drei Formen. Quercetin-3-rutenosid war das wichtigste Flavonoid, Kämpferol-3-rutenosid war stets in kleinen Mengen neben anderen Glycosiden vorhanden. Quantitative Unterschiede waren bei 11 Aprikosensorten im Zuge der Reifung zu beobachten, auch bei einigen Produkten. In allen Fällen gab es ein gemeinsames phenolisches Profil. Die Flavonoide kommen hauptsächlich in der Haut der Früchte vor, der Gesamtphenolgehalt ist nicht vom Reifungsverlauf abhängig.

Abstract. High-performance liquid chromatography with diode-array detection was used to characterize the phenolic profile of apricot fruits, juices and jams. Chlorogenic acid was the major phenolic compound present in all samples. Quercetin 3-rutinoside was the main flavonoid and kaempferol 3-rutinoside was present in smaller amounts with traces of other quercetin and kaempferol glycosides. Quantitative differences in phenolics were observed in eleven apricot fruit varieties at three stages of maturity and also in some processed apricot products. A common phenolic profile was observed in all cases. The major portion of the flavonoids occurred in the skin of the fruit and the total phenolic content of apricot fruits had no influence over the softening behaviour observed in some varieties.

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Introduction

The unambiguous characterization of plant-derived food products is important for establishing quality control parameters such as geographical and botanical origin, and for detecting fraudulent mixtures. Flavonoid analysis has been used recently to study the origin of consumables such as wines [1, 2], honey [3, 4] and for the characterization of fruit juices and jams [5–12]. These compounds are very suitable as chemotaxonomic markers, since each plant species has a characteristic and specific flavonoid pattern [13]. However, fruit variety, maturity and processing techniques influence the phenolic composition of some juices [14, 15].

To our knowledge, only a few reports exist concerning apricot fruit phenolics [16] and information is lacking on commercial products such as jams and juices made from these fruits. As part of our research programme studying flavonoids from fruit juices and jams to characterize these products, we have investigated the phenolic profiles of eleven apricot (*Prunus armeniaca* L.) cultivars and derived products to establish flavonoid markers for this fruit. The possible quantitative and qualitative changes in phenolic composition according to variety, fruit maturity and industrial processing treatment are also considered.

Materials and methods

Samples. During 1990 eleven different cultivars of Spanish apricots were harvested at canning maturity from their typical production areas in Murcia. Mauricio, Galtarrocha, Mayero and Valenciano, four early ripening cultivars, were harvested during the third week of May, the others during the second week of June. Seven of the cultivars were collected at three different maturity stages (Table 1).

Five different commercial apricot jams were also studied, made from Búlida cv, by manufacturers located in Murcia (Table 2, samples 1 and 2), Valladolid (samples 3 and 4) and Sevilla (sample 5). Two apricot juices (also Búlida cv, from Murcia) and an apricot purée (from Búlida cv flesh and skin, provided by a canning factory located in Murcia) were also included in this study.

Table 1. Changes in content of phenolic compounds of apricot fruits with maturity

Cultivars	Maturity	Rutin	K-3-rut	Chlor. Ac.
Búlida	M	10.48	0.64	44.84
	SM	12.73	1.42	39.76
	G	26.92	3.36	64.87
Hojaico	M	10.37	0.90	19.69
	SM	13.41	1.75	34.71
	G	6.19	0.72	14.81
Colorao	M	22.67	5.66	41.29
	SM	19.04	0.58	42.70
	G	9.84	4.67	36.01
Pepito	M	5.65	0.10	19.42
	SM	6.77	0.75	19.19
	G	9.42	0.68	29.00
Velázquez fino de agua	M	4.59	1.91	15.79
	SM	10.27	0.61	54.60
	G	7.12	0.38	28.36
Moniquí	M	12.86	0.34	56.68
	SM	8.56	2.39	29.47
	G	9.30	1.53	39.79
Real Fino	M	12.07	1.04	46.39
	SM	13.48	0.93	42.56
	G	26.34	3.57	67.86

Values are expressed as micrograms of phenolic compound per gram of fresh fruit: K-3-rut, kaempferol-3-rutinoside; Chlor. Ac., chlorogenic acid; M, mature; SM, semimature; G, green

Table 2. Phenolic compounds in jams, juices and purée

Sample	Rutin	K-3-rut	Chlor. Ac.
Jams			
1	14.04	2.35	38.84
2	14.07	2.51	48.70
3	21.24	2.75	90.08
4	6.36	1.32	12.23
5	19.76	3.42	18.75
6	10.37	2.12	29.62
Juices			
1	28.27	1.92	30.53
2	15.51	1.19	26.46
Purée	5.14	1.10	10.33

Values are expressed as micrograms of phenolic compound per gram of fresh fruit

Apricot maturity determination. Cultivars Búlida, Hojaico, Colorao, Pepito, Velázquez fino de agua and Moniquí were harvested at three different maturity-stages (green, semimature and mature). Three different parameters were considered in order to assess the degree of maturity: *colour*, the a* parameter in Hunter's Lab System [17], which gives a range of colour between green and red which is the most suitable for apricots according to Delwiche and Baumgardner [18]; *firmness*, performed with a Monet penetrometer [19] and *ethylene production* [20].

Extraction of phenolic compounds. Fruits with stones removed (200 g) were homogenized and exhaustively extracted with 400 ml of methanol-water (4:1) for 18 h at room temperature and filtered. The filtrates were concentrated under reduced pressure to remove methanol and the phenolic compounds were completely extracted from the aqueous residue with *n*-butanol. The same extraction procedure was applied to the jams and purée. Phenolics in the available juices (200 ml) were exhaustively extracted with *n*-butanol (200 ml).

Table 3. Distribution of the main phenolic compounds of apricot fruits at canning maturity

Cultivars	Rutin	K-3-rut	Chlor. Ac.	Total
Mauricio	38.4	10.0	51.6	7.39
Galtarrocha	24.0	4.1	71.9	12.26
Mayero	34.9	9.6	55.5	15.71
Valenciano	41.1	8.0	50.9	5.89
Búlida	18.8	1.1	80.1	55.96
Hojaico	33.5	3.0	63.5	30.96
Colorao	32.6	8.1	59.3	69.62
Pepito	22.5	0.4	77.1	25.17
Velázquez fino de agua	20.6	8.6	70.8	22.29
Moniquí	18.3	0.5	81.2	69.80
Real Fino	20.3	1.7	78.0	59.50

Total values are micrograms of total phenolic compounds analysed per gram of fresh fruit. Rutin, kaempferol-3-rutinoside and chlorogenic acid are expressed as the percentage of total phenolic compounds analysed

Sample preparation. Butanol extracts were dried under reduced pressure, redissolved in dilute HCl (pH 2.0) and passed through a 40 × 2 cm column of Amberlite XAD-2 resin (Fluka), particle size 0.3–1.2 mm, pore diameter 90 Å [21]. The adsorbed phenolic compounds were eluted with methanol and the eluate concentrated to 2 ml under reduced pressure.

HPLC analysis. Phenolic fractions (10 µl) were analysed by HPLC (Merck Hitachi L-6200 pump equipped with a photodiode array detector Merck Hitachi L-3000) using a Lichrochart 100 RP-18 column (12.5 × 0.4 cm, particle size 5 µm) (Merck, Darmstadt, Germany). Solvents used were (A) water-formic acid (95:5 v:v) and (B) methanol at a flow-rate of 1 ml/min. Linear gradient elution was used starting with 5% of B increasing to 30% B at 20 min and then 50% B at 25 min. Chromatograms were recorded at 350 nm.

All HPLC analyses were done in duplicate, the mean values being reported. Reproducibility was approx. ± 6%.

Identification and quantification of phenolic compounds. The phenolic compounds were identified using standard methods [22] including (a) UV spectroscopy in methanol before and after the addition of the classical shift reagents, (b) acid hydrolysis and identification of products and (c) chromatographic comparisons with authentic markers (rutin from Roth, Karlsruhe, Germany; Kaempferol 3-rutinoside isolated and identified previously from *Capparis spinosa* [23]; chlorogenic acid from Fluka, Switzerland). Phenolic compounds were quantified by peak area using authentic standards.

Results and discussion

Apricot phenolics and their distribution in different cultivars

The main flavonoid in the apricot cultivars, collected at canning maturity, was quercetin 3-rutinoside; additionally, all cultivars contained smaller amounts of a quercetin glycoside (tentatively identified as quercetin 3-glucoside) and kaempferol derivatives, of these, only kaempferol 3-rutinoside was present in sufficient amount to be quantified (Table 3). These results agree with previously reported data for other apricot cultivars [16] but differ from results published on American canned apricots where no kaemp-

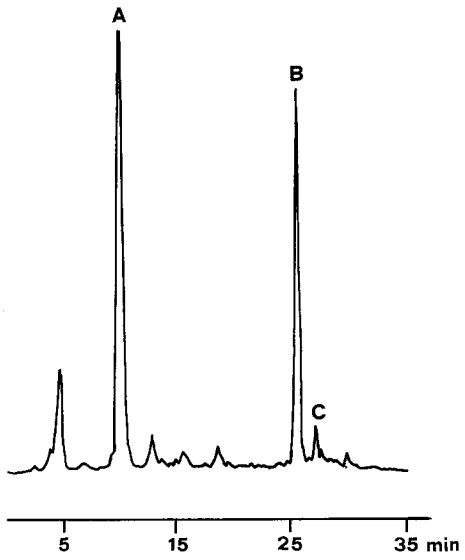

Fig. 1. HPLC profile of phenolic compounds in apricot Búlida cv at full maturity: *A*, chlorogenic acid; *B*, quercetin-3-rutinoside; *C*, kaempferol-3-rutinoside

Table 4. Distribution of phenolic compounds in apricot fruits

Cultivars	Skin	Rutin	K-3-rut	Chlor. Ac	Total
Mauricio	S(+)	38.4	10.0	51.6	7.39
	S(–)	28.1	–	71.9	0.64
Galtarrocha	S(+)	24.0	4.1	71.9	12.26
	S(–)	2.1	–	97.9	3.37
Mayero	S(+)	34.9	9.6	55.5	15.71
	S(–)	1.5	–	98.5	6.09
Valenciano	S(+)	41.1	8.0	50.9	5.89
	S(–)	21.3	–	78.7	1.03

As Table 3: S(+), fruit with skin; S(–), fruit without skin; –, trace amounts

ferol derivatives were detected [24]. Chlorogenic acid was found in all the samples, in agreement with previous findings [25].

The total amount of phenolic compounds analysed showed a twelvefold variation according to cultivar (Table 3). The four early fruiting cultivars contained less than 16 μg phenolics per gram of fresh fruit, whereas the remaining cultivars contained 22 μg or more phenolics per gram of fresh fruit; the cultivars Colorao and Moniquí had the highest phenolic levels. In all samples, chlorogenic acid was responsible for at least 50% of the total phenolics cosidered, quercetin 3-rutinoside contributed 18% or more, while kaempferol-3-rutinoside accounted for less than 10% of the total phenolics studied. The quantity of phenolic compounds in the fruit varied according to maturity stage but it was not possible to establish a correlation between the flavonoid content and the degree of maturity (Table 1). However, the qualitative phenolic HPLC profile was always the same regardless of fruit maturity.

In the industrial treatment of apricot fruits to produce juices, jams or fruit halves, apricots are sometimes peeled while in other cases the whole fruit is processed. For this reason, it is important to evaluate the distribution of phenolics between the peel and the flesh. The results in Table 4 show that the major portion of the flavonoids reside in the skin; in contrast, however, chlorogenic acid is mostly located in the flesh.

All the results indicate that quantitative differences in the phenolic content of apricots depend on the cultivar, maturity stage of the fruit and the part of the fruit used. However, one common qualitative phenolic HPLC profile was detected in all cases (Fig. 1).

Changes in phenolic composition with processing

HPLC analyses of the phenolic compounds from processed apricot products (Table 2) were identical to those observed in fresh fruits, and again showed chlorogenic acid and rutin as the main compounds and kaempferol-3-rutinoside in much smaller amounts. No differences were found between the HPLC phenolic profiles of the commercial juices and the commercial jams available, indicating that the processing treatment, including clarification, did not affect the qualitative phenolic composition (Fig. 1). The only factor affecting quantitative differences was whether the peeled fruit or whole fruit was used in the process.

The search for significant quantitative and qualitative differences in the phenolic patterns of the cultivars studied is of additional interest. The role of phenolic compounds as inhibitors of enzymes responsible of fruit softening has been reported [26–29], for this reason the study of the total phenolic content of the different varieties is of special interest. There are well-known differences in the fruit-softening behaviour of the two main apricot cultivars used by the Spanish industries. Thus, cultivar Búlida is the most important apricot used in the Spanish canning industry (90%) for apricot juice and jam production because of its flavour, texture and price. However, this cultivar is not suitable for processing as halves in sucrose syrup, as it suffers softening. On the other hand, cv Real Fino is used without softening problems for canned halves in syrup or water, but its flavour, colour and price make it unsuitable for juice and jam production.

The present study revealed no significant differences in the phenolic composition of either cultivar. Thus it would appear that phenolic composition is not responsible for the differences found in softening behaviour of these two cultivars and other possible causative factors need to be investigated in order to explain this phenomenon.

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References

1. Étievant P, Schlich P, Bertrand A, Symonds P, Bouvier JC (1988) J Sci Food Agric 42: 39–54
2. Tomás-Lorente F, García-Viguera C, Ferreres F, Tomás-Barberán FA, Navarro G (1989) Rev Agroquim Tecnol Aliment 29: 399–406

3. Amiot MJ, Aubert S, Gonnet M, Tacchini M (1989) Apidologie 20: 115–125
4. Ferreres F, Ortiz A, Silva C, García-Viguera C, Tomás-Barberán FA, Tomás-Lorente F (1992) Z Lebensm Unters Forsch 194: 139–143
5. Fernández de Simón B, Pérez-Ilzarbe J, Hernández T, Gómez-Cordovés C, Estrella E (1992) J Agric Food Chem 40: 1531–1535
6. Galensa R (1989) GIT [Suppl 4] 88: 18–25
7. Tomás-Lorente F, García-Viguera C, Ferreres F, Tomás-Barberán FA (1992) Agric Food Chem 40: 1800–1804
8. Wilson EL (1981) J Sci Food Agric 32: 257–264
9. Rousseff RL (1988) J Assoc Off Anal Chem 71: 798–802
10. Sendra JM, Navarro JL, Izquierdo L (1988) J Chromatogr Sci 26: 443–448
11. Singleton VL, Trousdale EK (1983) Am J Enol Vitic 34: 27–34
12. Salagoity-Auguste MH, Bertrand A (1984) J Sci Food Agric 35: 1241–1247
13. Harborne JB, Turner BC (1984) Plant Chemosystematics. Academic Press, London
14. Spanos GA, Wrolstad RE (1990) J Agric Food Chem 38: 817–824
15. Spanos GA, Wrolstad RE, Heatherbell DA (1990) J Agric Food Chem 38: 1572–1579
16. Henning W, Herrman K (1980) Z Lebensm Unters Forsch 171: 183–188
17. Hunter RS (1975) The measurement of appearance. Wiley, New York
18. Delwiche MJ, Baumgardner RA (1985) J Am Soc Hort Sci 110: 53–57
19. Monet R (1978) A. F. nº 293/294, 23
20. Mansour R, Latché A, Pech JC (1982) Fruits 37: 785–791
21. Tomás-Barberán FA, Blazquez A, García-Viguera C, Ferreres F, Tomás-Lorente F (1992) Phytochem Anal 3: 178–181
22. Mabry TJ, Markham KR, Thomas MB (1970) The systematic identification of flavonoids. Springer, Berlin
23. Tomás F, Ferreres F (1976) Rev Agroquim Tecnol Aliment 16: 568–571
24. El-Sayed AS, Luh BS (1965) J Food Sci 30: 1016–1020
25. Möller B, Herrmann K (1983) Phytochemistry 22: 477–481
26. Lidster PD, Dick AJ, Demarco A, McRae KB (1986) J Am Soc Hort Sci 111: 892–896
27. Dick AJ, Williams R, Bearne SL, Lidstar PD (1985) J Agric Food Chem 33: 798–800
28. Dick AJ, Bearne SL (1988) J Food Biochem 12: 97–108
29. Dick AJ, Smith KC (1990) J Agric Food Chem 38: 923–926