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Food Chemistry 93 (2005) 89–93
Food Chemistry
www.elsevier.com/locate/foodchem

Phenolic compounds in pear juice from different cultivars

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Received 8 June 2004; received in revised form 6 September 2004; accepted 6 September 2004

Abstract

The phenolic contents of pear juice samples obtained from seven different varieties were analyzed by HPLC. The results indicated that chlorogenic acid ranged from 73.1 to 249 mg/l, epicatechin from 11.9 to 81.3 mg/l, caffeic acid from 2.4 to 11.4 mg/l and *p*-coumaric acid from 0.0 and 3.0 mg/l.

Keywords: Phenolic compounds; Pear juice; Chlorogenic acid; Epicatechin; Caffeic acid

1. Introduction

Phenolics, a large group of aromatic phenols are present in more than 4000 different types in plants (Hollman, Hertog, & Katan, 1996). They are involved in enzymatic browning, haze formation, as well as disease prevention and authenticity control. As is well known, the substrate for the enzymatic browning reaction consists of *o*-dihydroxyphenolic compounds. *o*-Dihydroxyphenols are in turn converted to *o*-quinone, trihydroxy-benzene, hydroxyquinone and melanine (Eskin, Henderson, & Townsend, 1976; Mathew & Parpia, 1971; Oleszek, Lee, & Price, 1989) in this reaction. This reaction is catalysed by *o*-diphenoloxidase and diphenoloxidases (Bruchmann, 1976).

Phenolics contribute to the formation of haze in beverages such as fruit juice and wine. Haze occurrence depends on the condensation of the phenolics with each other or complex formation with the proteins (Heatherbell, 1984; Oh & Hoff, 1987). That is why the phenolic content needs to be reduced below a certain level in order to prevent haze formation (Schobinger, Barbic, Dürr, & Waldvogel, 1995). Methods based on the oxidation and removal of phenolics via the laccase enzyme have been developed (Dietrich, Wucherpfennig, & Maier, 1990; Ritter, Maier, Schöplein, & Dietrich, 1992).

Although the complete removal of phenolics is beneficial in terms of haze formation, it has a negative impact in terms of taste because of the fact that phenolics are responsible for the astringency of food (Joslyn & Goldstein, 1964). The concentration of phenolics should be 300–800 mg/l in order to have proper taste in some beverages (Schobinger et al., 1995).

Phenolics have been shown to have antioxidative properties (Ramandthan & Das, 1992; Thumann & Herrmann, 1980). The antimutagenic and anticarcinogenic effects of phenolics have also been demonstrated (Deschner, Rupeto, Wong, & Newmark, 1991; Newmark, 1987; Stich & Rosin, 1984). Phenolics are also known to have protective roles against cancer, cardiovascular diseases and cataract (Hertog, Hollman, & Katan, 1992; Hollman et al., 1996). There is evidence to show that phenolics possess antibacterial (Tomas-Lorente, Garcia-Viguera, Ferreres, & Tomas Barberan, 1992), antifungal (Weidenbörger, Hindorf, Jha, & Tsotsonos, 1990) and enzyme inhibiting effects (Dick,

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0308-8146/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.foodchem.2004.09.009

Williams, Bearne, & Lidster, 1985; Walker & Wilson, 1975).

Since each fruit and vegetable has a specific phenolic profile, phenolic compounds are also very important for the adulteration control of foods (Brause & Raterman, 1982; De Simon, Perez-Ilzarbe, Hernandez, Gomez-Cordoves, & Esterella, 1992; Sontag & Bernwieser, 1994; Tomas-Lorente et al., 1992).

Early studies showed that pear contained chlorogenic acid, cryptochlorogenic acid and neochlorogenic acid (Sondheimer, 1958). According to another study, the main phenolics found in pear are leucocyanidin, catechin, epicatechin, chlorogenic acid, quercitrin and quercetin (Sioud & Luh, 1966).

The presence of arbutin in pear was first reported by Durkee, Johnston, Thivierge, and Poapst (1968). According to the Duggan's (1969) findings, the phenolic content of pear varies from cultivar to cultivar. Wildanger and Herrmann (1973) found that the major flavonol in apple and pear is quercetin and there is also kaempferol in small quantities whereas quince contains more kaempferol than quercetin.

Phenolic content in fruits depends on maturity. For example, the phenolic content in apple and pear increases in the first three months and decreases later (Mosel & Herrmann, 1974). Risch and Herrmann (1988) reported that the amounts of catechin and epicatechin in pear are 0–10 and 5–60 mg/kg, respectively.

Spanos and Wrolstad (1990) claim that the phenolic content of pear depends primarily on variety and the level of maturity. Herrmann (1992) indicated that the phenolics found in pear and apple are chlorogenic acid, catechin, epicatechin and procyanidin. These results are supported by the findings of Spanos and Wrolstad (1992) who claim that the phenolics in pear juice are chlorogenic acid, epicatechin, catechin, caffeic acid and coumaroylquinic acid. Pear juice contains arbutin (6.7–16.8 mg/l) and quercetin, as well. Herrmann (1993) reported that the amounts of chlorogenic acid, *p*-coumaroylquinic acid, epicatechin and catechin in pear are 134, 14, 26 and 3 mg/kg, respectively.

Oleszek, Amiot, and Aubert (1994) isolated four hydroxycinnamic acid esters and eight flavonol glucosides in pear. Three of the glucosides were quercetin and the remaining five were isorhamnetin glucosides.

Enzymatic as well as nonenzymatic browning, due to phenolics, take place during the storage of pear juice and concentrate (Beveridge & Harrison, 1984, 1986, 1987; Beveridge, Meheriuk, & Harrison, 1990; Hsu, Heatherbell, & Yorgey, 1990; Petropakis & Montgomery, 1984).

The findings of Amiot, Tacchini, Aubert, and Oleszek (1995) in a way reflect all the information available on this topic. According to Amiot et al. (1995), the main phenolics in pear are chlorogenic acid (2.7–14.1 mg/100 g), and epicatechin (0.6–8.7 mg/100 g); catechin content is ≈0.05 mg/100 g. Phenolic content and browning tendency primarily depend on variety, not on the year of growth or the level of maturity.

There is no information available on the phenolic content in the varieties of pear grown in Turkey.

2. Materials and methods

2.1. Materials

The material for the study involves samples of fruit juice obtained from 7 pear varieties. The pear cultivars, growth regions and dates of processing are summarised in Table 1.

The steps involved in the processing of the raw material are washing, filtering, grinding, pressing (AMOS), filtration, bottling, sealing, pasteurisation (20 min at ~97 °C) and cooling (to 20 °C) in order.

In order to determine the effects of clarification, three of the samples (Ankara, Williams, Starcrimson) were clarified. The samples were exposed to AMYLASE AG 2001 (25 g/h l) and PECTINEX AR (25 g/h l) for 30 min at 50 °C and then filtered after adding gelatin (250 ppm) and bentonite (1000 ppm).

2.2. Methods

The total solubles content of the samples and the total amount of polyphenols in the samples were measured by the refractometric method and Folin-Ciocalteu method (Tanner & Brunner, 1978), respectively. An HPLC method (Karadeniz, 1994; Mazza & Velioğlu, 1992) was used to determine the phenolic compounds. For the analysis of phenolic substances, a Knauer brand HPLC, UV detector (280 nm) and a C18 column (250 × 4.5 μm) were used. The phenolics in the HPLC chromotogram were identified by the time of retention. Retention times were 5.3 min for chlorogenic acid, 6.9 min for caffeic acid, 7.8 min for epicatechin and 12.4 min for *p*-coumaric acid under the conditions of the analysis.

Table 1
The growth regions and processing dates of the pear cultivars

Pear cultivars	Growth region	Processing date
Akça	Ankara	25.07.1995
Şeker	Ankara	03.08.1995
Williams	Ankara	25.08.1995
Santa Maria	Bursa	05.09.1995
Starkrimson	Ankara	08.09.1995
Passa Crassane	Ankara	19.09.1995
Ankara	Ankara	20.09.1995

3. Results and discussion

The total amount of polyphenol of pear juice samples varied between 196 and 457 mg/l. The main phenolics determined in pear juice were chlorogenic acid, epicatechin, caffeic acid and coumaric acid (Table 2).

According to Table 2, the phenolic in highest concentration is chlorogenic acid. The samples which have the highest amounts of chlorogenic acid are those obtained from Akca (248 mg/l), Williams (174 mg/l), Starcrimson (166 mg/l), Ankara (148 mg/l) and Passa Crassane (148 mg/l) in descending order. On the other hand, the samples corresponding to Seker and Santa Maria varietes have relatively lower amounts of chlorogenic acid (95.1 and 73.1 mg/l, respectively).

In terms of amount of epicatechin, the sample from Starcrimson cultivar comes first (881 mg/l) followed by the samples obtained from Passa Crassane (37.5 mg/l) and Williams (34.9 mg/l) varieties. Similar to comparison of the amount of chlorogenic acid, Santa Maria cultivar has the lowest amount of epicatechin (11.9 mg/l).

The amount of caffeic acid in the sample obtained from the Starcrimson cultivar is 11.4 mg/l. This is followed by the samples from the Ankara (11.0 mg/l) and Passa Crassane (10.1 mg/l) variety. The sample that has the lowest caffeic acid content corresponds to the Akca pear (2.4 mg/l).

The samples from Santa Maria and Seker do not have measurable amounts of *p*-coumaric acid. The amount of *p*-coumaric acid in the other samples is also extremely low (0.46–3.0 mg/l).

The descriptive values of phenolic substances in pear juice that are calculated using the data in Table 2 are given in Table 3. According to Table 3, the primary phenolic in pear juice is chlorogenic acid, averaging 151 mg/l. It is followed by epicatechin (32.4 mg/l). The caffeic acid and *p*-coumaric acid contents in pear juice are 3.9 and 0.8 mg/l, respectively. Phenolic content varies greatly among varieties.

The fact that phloretin-2 glucoside is not one of the major phenolics in pear juice (Herrmann, 1992; Wald & Galensa, 1989) is verified by this study.

Table 3
The descriptive values of major phenolics in pear juice ($N = 7$)[a]

Phenolic compound (mg/l)	Minimum	Maximum	Mean	SD[b]	CV[c] (%)
Chlorogenic acid	73.1	249	151	57.0	37.9
Epicatechin	11.9	81.3	32.4	23.4	72.2
Caffeic acid	2.4	9.2	7.4	3.9	52.7
p-Coumaric acid	0.0	3.0	0.8	1.0	125.0

[a] Number of samples.
[b] Standard deviation.
[c] Coefficient of variance.

According to Amiot et al. (1995) and Herrmann (1993), the primary phenolic in pear juice is chlorogenic acid and the secondary phenolic is epicatechin. Catechin and caffeic acid also exist in pear juice according to the findings of Spanos and Wrolstad (1992). With the exception of catechin, the findings of this research are in accordance with the data presented in the cited references.

There are differences between the findings of this study and other reports of phenolics. The main reason for these differences is probably that the phenol content in pear juice is specifically affected by the fruit variety (Amiot et al., 1995; Hsu et al., 1990).

The effects of clarification on various phenolics are presented in Table 4. As shown,the phenolics decreased by 22.5–39.6% (29.7% average) after clarification. The reduction levels differ from phenolic to phenolic. For instance, the reduction in epicatechin is 62.1% whereas those for caffeic acid and chlorogenic acid are 55.1% and 18.3%, respectively.

Table 4
The effect of clarification on phenolics in pear juice

Pear cultivar	Decreasing rate (%)			
	Chlorogenic acid	Epicatechin	Caffeic acid	Total
Ankara	16.3	45.8	67.3	22.5
Williams	13.9	64.2	56.4	23.7
Starkrimson	24.7	65.4	43.0	39.6
Mean	18.3	62.1	55.1	29.7

Table 2
The amounts of phenol compounds from different cultivars

Pear cultivars	Soluble solids (%)	Chlorogenic acid (mg/l)	Epicatechin (mg/l)	Caffeic acid (mg/l)	Coumaric acid (mg/l)	Total phenolics (mg/l)[a]
Şeker	8.4	95.1	17.6	3.4	–	375
Santa Maria	11.2	73.1	11.9	4.1	–	196
Passa Crassane	10.8	148	37.5	9.1	0.72	417
Akça	13.2	248	21.9	2.4	0.97	455
Ankara	9.6	148	21.4	10.1	0.46	371
Williams	11.4	174	34.9	11.0	0.66	457
Starkrimson	13.6	166	81.3	11.4	3.00	423

[a] Determined by Folin–Ciocalteu method.

According to Ritter et al. (1992) and Karadeniz and Ekşi (2001), the reduction of phenolics in apple juice after clarification, as well differs from compound to compound.

Acknowledgements

Our special thanks go to the ALEXANDER von HUMBOLDT foundation (BONN) for their donation of the HPLC and to Associate Professor Feryal KARADENİZ for her contributions in the analyses.

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