Original article

Influence of different heat treatments on the content of phenolic acids and their derivatives in selected fruits

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Influence of different heat treatments on the content of phenolic acids and their derivatives in selected fruits.

Abstract – Introduction. A considerable number of positive effects after the consumption of fruits has been pointed out in the past: hypolipidemic action, reduction of blood glucose levels, hepatoprotection and improvement of the antioxidant status as well as, *inter alia*, antioxidant, antiradical, anti-inflammatory, anticancer and anti-adipogenic status. **Materials and methods**. The changes in the levels of phenolic acids and their derivatives in fresh as well as in processed fruits (chokeberry, wild strawberry, apples var. Idared and Champion, cherry, apricot, peach, raspberry, cranberry, and bilberry) were studied using HPLC with UV detection. Dried fruit homogenates and compotes were produced. Also, fruits were fried to simulate jam production. **Results and discussion**. Eleven phenolic acids and their derivatives were identified in tested samples: caffeic, chlorogenic, p-coumaric, ferulic, gallic, ellagic, protocatechuic, p-hydroxybenzoic, gentisic, syringic and vanillic acids. In most cases, the thermal processing of fruits caused a decrease in the levels of phenolic acids. In some preserves, the level of selected individual phenolic compounds was unchanged or was significantly increased. **Conclusion**. It can be concluded that thermal processing can have a differential effect on the levels of phenolic acids in preserves and general conclusions could not be formulated. The fruit composition in which a phenolic acid is present can play a role in this context.

Poland / fruits / canned fruits / jams / compotes / phenolic compounds / phenolic content

Influence de différents traitements thermiques sur la teneur en acides phénoliques de fruits sélectionnés.

Résumé – Introduction. Un grand nombre d'effets positifs de la consommation de fruits a été déjà mis en évidence : action hypolipidémique, réduction du taux de glucose dans le sang, hépatoprotection, amélioration de l'état antioxydant ainsi que, entre autres, effets antioxydant, antiradicalaire, anti-inflammatoire, anti-cancéreux ou anti-adipogénique. **Matériel et méthodes**. Les changements des taux d'acides phénoliques et de leurs dérivés dans certains fruits (aronia, fraise des bois, pommes var. Idared et Champion, cerise, abricot, pêche, framboise, canneberge et myrtille) frais ou transformés ont été étudiés par HPLC et détection UV. Des homogénats de fruits séchés et de compotes ont été effectués. En outre, les fruits ont été cuits pour simuler la production de confitures. **Résultats et discussion**. Onze acides phénoliques et dérivés ont été identifiés dans des échantillons testés : acides caféique, chlorogénique, p-coumarique, férulique, gallique, ellagique, protocatéchique, p-hydroxybenzoïque, gentisique, syringique et vanillique. Dans la plupart des cas, le traitement thermique des fruits a provoqué une diminution des taux d'acides phénoliques. Dans certaines conserves, le taux de composés phénoliques individuels est resté inchangé ou a été considérablement augmenté. **Conclusion**. Le traitement thermique pourrait avoir des effets différentiés sur les taux d'acides phénoliques dans les fruits transformés et il n'est pas possible de généraliser ces effets. Dans ce contexte, la composition des fruits contenant un acide phénolique peut varier.

Pologne / fruits / conserve de fruits / confiture / compote / composé phénolique / teneur en phénols

1. Introduction

Edible fruits exhibit antioxidant and antiradical activities, as has been repeatedly pointed out in the past [1–3]. Other positive effects of fruit consumption include hepatoprotection by chokeberry (*Aronia melanocarpa*) fruit [4] and peach (*Prunus armeniaca*) fruit [5]. Also, chokeberry fruit exhibit hypolipidemic action, reduce blood glucose levels (metabolic syndrome), improve the antioxidant status of experimental rats [6, 7], exert an antiproliferative effect on Caco-2 cancer cells [8], prevent gastric mucosal damage and inhibit the oxidative stress in mucosa [9]. Bilberry (*Vaccinium myrtillus*) and cranberry (*V. macrocarpon*) fruits protect mitochondria by a decrease in the cytochrome c-enhanced oxidation of 6-hydroxydopamine [10]. Cranberry fruit exhibit antiproliferative properties against colon cancer cells [11] and cancer chemopreventive properties by induction of quinone reductase (phase II xenobiotic detoxification enzyme) [12]. Cherry (*Prunus cerasus*) fruit exhibit antioxidant and anti-inflammatory activity in mice [13]. Raspberry (*Rubus idaeus*) fruit, a very rich source of phenolic compounds [14], exert anti-adipogenic [15], antioxidant, anti-inflammatory and anticancer activity (colon, breast, lung and gastric human tumor cells) [15–17]. Also, apples have previously been pointed out as a source of a wide range of different phenolic compounds, including phenolic acids [18].

Phenolic acids are well known *in vitro* and *in vivo* antioxidants [19, 20] and are, *inter alia*, anti-inflammatory [21], anticarcinogenic [22] and anti-platelet aggregation [23] agents. It has also been shown that phenolic acids normalize a considerable number of blood parameters [24–30]. The anticancer activity [31] and the protection of hepatocytes by phenolic acids [32, 33] has also been pointed out. Last but not least, the neuroprotection of phenolic acids has been proved in numerous *in vitro* and *in vivo* studies [34–38].

Thermal processing of fruits causes a decrease in the levels of phenolic compounds [39–42]. A limited number of studies have studied the effect of thermal processing on the levels of phenolic acids in preserves made from pears [43], raspberries [44–47], pomegranates [48], strawberries [45, 47, 49], blackberries, blueberries [45], apricots, apples [50], cherries and wild blueberries [47]. However, a considerable number of popular fruits have not yet been studied in this context. Given the numerous health benefits to be derived from the consumption of fruits, our study was designed in order to determine the influence of heat treatment on the levels of individual phenolic acids in selected fruit preserves. It is obvious that the fruits studied in this work contain very differentiated levels of individual phenolic acids. However, our aim was to study how the heat treatment influences the percent loss of phenolic acids, regardless of whether the fruit is a rich or a poor source of these compounds.

2. Materials and methods

2.1. Chemicals and fruits

Phenolic acids (HPLC grade) were purchased from Sigma-Aldrich (Poznań, Poland). Other reagents (HPLC grade) were purchased from P.O.Ch. (Gliwice, Poland).

Black chokeberry (*Aronia melanocarpa*), wild strawberry (*Fragaria vesca*), cherry (*Prunus cerasus*) and raspberry (*Rubus idaeus*) fruits were cultivated on a farm located at 66A Kopernika Street, Bełżyce, Poland (51°10'34" N, 22°16'4" E). Apricot *(Prunus armeniaca)* and peach *(P. persica)* fruits were harvested from a farm located at 1 Dubieckiego Street, Lublin, Poland (51°14'29" N, 22°29'48" E). Apples (*Malus domestica*) var. Idared and Champion, cranberry (*Vaccinium macrocarpon*), and bilberry (*V. myrtillus*) were obtained from the Partnership Wholesale Market S.A. located at 65 Elizówka Street, Ciecierzyn, Poland (51°17'17" N, 22°34'49" E). The identity of fruit samples was authenticated by Prof. Dr Hab. Kazimierz Głowniak from the Department of Pharmacognosy with Medicinal Plants Laboratory, Medical University of Lublin, Chodźki 1, Lublin, Poland.

2.2. Fruit preserves

Compotes were produced by dipping the thawed fruit in boiling water (1:1, w/w) until the moment that the whole sample was boiled. Shortly after the boiling had started, the whole sample was directly placed in jars, which were tightly closed. Before the extraction of phenolic acids, the whole sample was taken out of the jars, homogenized and freeze-dried at –50 °C for 12–24 h (FreeZone 2.5 system, Labconco, USA). Simulation of jam production was performed by the heating of a portion of the thawed fruit (30 g) for 60 min in a kitchen pot with intensive mixing. Every 10 min, an aliquot of the pulp was taken followed by freeze-drying as described above. Dried fruit homogenates were produced by the heating of the homogenized fresh fruits in a conveyor dryer (in the presence of air) in the form of a thin layer (1–3 mm) at (105 ± 2) °C for 12 h [52]. Each preserve was produced in duplicate. HPLC determination of phenolic acids was performed directly after the production of the preserves.

2.3. Determination of the dry mass of samples

The drying was performed by the method of Qian *et al.* [52], with some modifications. The sample was finely ground in a laboratory mortar; a 1-g portion of the fresh fruit was accurately weighed (with a precision of 0.001 g) and dried at (105 ± 2) °C for 24 h. The sample was then weighed and dried again until the change in the weight was less than 0.005 g (1–2 h). The analysis was performed in duplicate.

2.4. Hydrolysis and extraction of phenolic acids

The method proposed by Häkkinen *et al.* [51] was used with slight modifications. The accurately weighed freeze-dried sample (0.5 g) was mixed with 15 cm^3 of double ionized water (DDI) water (containing 80 mg of ascorbic acid), 25 cm^3 of 96% (v/v) methanol and 10 cm^3 of 6 $mol{\cdot}dm^{-3}$ HCl. Then, the solution was purged using oxygen-free CO_2 (the gas was also in the headspace of the tube) and the sample was sonicated (Sonics Vibra-Cell, 80% amplitude/50 sec pulses and 50 sec off, total time 2 min). The flask was wrapped in aluminum foil and the solution was gently shaken (100 rpm, 35 °C, 16 h, Infors Minitron shaker, Switzerland). The extract was then filtered (0.45-μm cellulose filters). A volume of 15 cm^3 of the filtrate was evaporated to dryness (35 °C, –0.09 MPa), followed by the addition of 1.5 cm^3 of 99.8% (v/v) methanol. Directly prior to HPLC, the sample was filtered (Acrodisc LC13 PVDF Gelman Sciences M1, 0.45 μm). The levels of phenolic acids were expressed according to the dry mass of the sample. For each sample, hydrolysis and extraction for HPLC were repeated twice.

2.5. HPLC-UV analysis of phenolic acids

The HPLC-UV system consisted of two Smartline 100 pumps, a loop (0.1 cm^3), a dynamic mixer and a Retriever 500 fraction collector (Knauer, Germany). Separations were performed using a Symmetry C18 column (5-μm particles, 4.6 mm × 250 mm) coupled with a Symmetry C18 precolumn (5-μm particles, 8.0 mm × 20 mm) (Waters, Ireland). Signals were recorded at 260 nm, 280 nm, 320 nm or 365 nm using a Linear 200 UV-VIS detector (USA) coupled to an Interface IF-2 (Knauer, Germany). Chromatographic data were analyzed using EuroChrom Basic Edition ver. 3.05 (Knauer). The mobile phase consisted of DDI water + 1% (v/v) of glacial acetic acid (A) and 50% (v/v) acetonitrile in DDI water (B). The gradient (1 $cm^3{\cdot}min^{-1}$) ran in the following manner: 0–5 min 3%→5% B, 5–10 min 5%→8% B, 10–15 min 8%→13% B, 15–19 min 13%→19% B, 19–47 min 19%→40% B, 47–64 min 40%→65% B, 64–65 min 65%→80% B, 65–66 min 80%→98% B, 66–69 min 98% B, 69–72 min 98%→3% B. The laboratory reproducibility of the method for ferulic acid (within-laboratory standard deviation within 1 month of the studies) was in the range of 3.5–7.0%. Intra-day repeatability and reproducibility of the HPLC method, calculated using HPLC standards of

Table I.
Levels of total phenolic acids (ng·g^{-1} dry matter) in fruits and their corresponding preserves.

Fruit	Fresh fruit	Compote	Duration of fruit heating for jams (min)					
			10	20	30	40	50	60
Apple var. Idared	68 ± 4 d	54 ± 9 cd	58 ± 7 bcd	38 ± 6 abcd	33 ± 6 abc	32 ± 5 abc	23 ± 4 ab	20 ± 3 a
Apple var. Champion	51 ± 5 b	18 ± 2 a	25 ± 3 a	27 ± 2.0 a	21 ± 3.0 a	12 ± 4 a	12 ± 4 a	11 ± 2 a
Apricot	31 ± 5 a	35 ± 5 a	27 ± 3 a	34 ± 2 a	32 ± 6 a	26 ± 3 a	17 ± 3 a	24 ± 4 a
Bilberry	87 ± 8 a	56 ± 6 a	57 ± 7 a	58 ± 6 a	55 ± 3 a	66 ± 4 a	68 ± 6 a	70 ± 7 a
Black chokeberry	183 ± 19 c	158 ± 19 bc	108 ± 17 abc	109 ± 8 abc	100 ± 15 ab	104 ± 5 ab	79 ± 8 a	74 ± 8 a
Cherry	92 ± 7 c	73 ± 5 bc	61 ± 3 abc	50 ± 6 a	59 ± 5 ab	55 ± 4.0 ab	48 ± 6 a	36 ± 6 a
Cranberry	9 ± 2 a	8 ± 3 a	7 ± 1 a	6 ± 1 a	6 ± 2 a	6 ± 1 a	4 ± 1 a	4 ± 1 a
Peach	88 ± 6 d	65 ± 8 c	35 ± 3 b	22 ± 2 b	7 ± 2 a	3 ± 1 a	1 ± 0 a	1 ± 0 a
Raspberry	1381 ± 71 c	967 ± 161 bc	784 ± 102 ab	598 ± 54 ab	540 ± 40 ab	437 ± 47 a	473 ± 37 a	455 ± 31 a
Wild strawberry	214 ± 22 c	162 ± 27 bc	119 ± 16 ab	105 ± 10 ab	87 ± 9 ab	98 ± 9 ab	66 ± 10 a	76 ± 8 ab

In each row, different letters denote a significant difference at $p < 0.05$.

vanillic, caffeic, chlorogenic and p-coumaric acids, were below 6.0% and were acceptable for this study.

2.6. Statistical analysis

Mean values with standard deviations were calculated. Tukey's HSD test (STATISTICA 8.0, StatSoft, Inc., USA) was used for the determination of statistical differences with the significance denoted at $p < 0.05$. Each sample was studied in four repeats (each preserve was produced in duplicate, and, from each duplication, hydrolysis and extraction for HPLC were repeated twice).

3. Results and discussion

3.1. Total content of phenolic acids in fruit preserves

The heating of apples (var. Idared and Champion), chokeberry, cherry, peach, raspberry and wild strawberry fruits caused a significant reduction of the total phenolic acid levels in compotes and/or in "jams" (*table I*). The decrease in total phenolic acids in compotes was 0–65%, in comparison with the corresponding fresh-frozen (thawed) fruits. The loss of total phenolic acids in "jams" after 60 min of heating ranged from approximately 20% to 99%, in comparison with the levels in corresponding fresh-frozen (thawed) fruits. In samples produced from apricot, bilberry and cranberry, no significant loss of total phenolic acids was observed, although a decrease in the sum of phenolic acids in absolute terms was seen in the case of these three fruits and corresponding compotes and "jams".

3.2. Content of individual phenolic acids in fruit preserves

It is worth noting that the total level of phenolic acids was significantly decreased at different stages of the heating, depending on the fruit. This phenomenon was most probably caused by differences in the amounts of individual phenolic acids in fruits (the "phenolic acid profile" of fruits). Therefore, the amounts of individual phenolic acids were also analyzed in this project because we suspected that phenolic acids may present differentiated thermostability. Eleven phenolic acids and their derivatives were detected in the test samples: caffeic, chlorogenic, p-coumaric, ferulic, gallic, vanillic, protocatechuic, p-hydroxybenzoic, gentisic, syringic and ellagic acids (*tables II–IV*). In most cases, the thermal processing of fruits caused a decrease in the levels of individual phenolic acids. However, the influence of thermal processing on the amounts of individual phenolic acids was unclear. The most dramatic loss of phenolic acids was predominantly observed in the case of "jams" heated for 60 min, in comparison with the thawed fruit. However, in the case of selected "jam" samples, no significant loss of the following phenolic acids was observed after 60 min of heating: caffeic (cranberry, bilberry), chlorogenic (apricot), p-coumaric (wild strawberry, apricot), ferulic (raspberry, cranberry) gallic (raspberry, apricot), gentisic (raspberry), syringic (chokeberry, apple var. Idared, cherry) and ellagic acids (bilberry) (*tables II–IV*). In the case of cherry "jam", the levels of ellagic acid were significantly increased in samples heated for 30–60 min, in comparison with the fresh cherry fruit (*table IV*). However, the increase in ellagic acid was an exception and, in most cases, a loss of phenolic acids was observed in the "jams" studied in our work. It is known that ellagic acid can be released from ellagitannins and its proportion can be elevated in a preserve in comparison with fresh fruit [46]. Last but not least, a significant ($p < 0.05$) decrease in the levels of the following phenolic acids was observed in dried fruit homogenates in comparison with fresh fruits (*table V*): p-hydroxybenzoic acid (chokeberry); caffeic, chlorogenic and syringic acids (cherry); caffeic, p-coumaric and syringic acids (raspberry). However, the levels of the rest of the phenolic acids detected in dried fruit homogenates were not significantly decreased after drying ($p < 0.05$). The content of ellagic acid in a dried homogenate was increased in comparison with fresh fruit ($p < 0.05$).

The degradation of some phenolic acids can yield other phenolic acids, *e.g.*, the hydrolysis of chlorogenic acid elevates the level of caffeic acid in the product. Spanos and Wrolstad observed an increase in caffeic acid levels due to its release from chlorogenic acid during the thermal processing of fruits [43]. Indeed, there was a statistically confirmed loss of chlorogenic acid in compotes and/or in "jams" produced from apple (var. Idared), cherry, peach and raspberry pulps, whereas in the case of apricot no significant loss of chlorogenic acid was observed (*table II*). However, in our study the loss of caffeic acid due to the heating of the fruit surpassed the *in situ* release of caffeic acid from chlorogenic acid in "jams" produced from apple (var. Idared), cherry and peach.

The changes in the levels of phenolic acids and their derivatives during the heat treatment of fruits studied in our paper were unclear. Other authors have obtained similar results to those presented below. Unfortunately, in many studies the duration of the heating and some other parameters of the production of fruit preserves were not given. In the study by Spanos and Wrolstad [43], a high temperature-short time process (89 °C, 90 s) as well as the pasteurization of pear juice in bottles (85 °C, 2 min) caused an increase in the levels of chlorogenic acid and coumaroylquinic acid, whereas the level of caffeic acid and coumaric acid was either decreased or unchanged. Vacuum concentration (60 °C) caused the hydrolysis of chlorogenic acid and coumaroylquinic acid. Nevertheless, a net loss of coumaric acid was observed in selected samples [43]. Diffusion extraction (at 63 °C) and vacuum evaporation (at 86 °C) caused, respectively, a considerable elevation and the loss of ellagic acid and its derivatives in raspberry juice (in comparison with high-speed centrifugation) [44]. In the study of Zafrilla *et al.*, the levels of ellagic acid, its 4-arabinoside, 4'(4''-acetyl)-arabinoside and 4' (4''-acetyl)-xyloside were not much affected by thermal processing similar to that applied during the industrial production of raspberry jam (78 °C →92 °C →88 °C, filling of the jar) [46]. A higher amount of ellagic acid, ellagic acid glucosides and total ellagic derivatives was observed in pomegranate juice produced after heat treatment in comparison with juice produced from fresh, non-heated fruit or from fruit subjected to freezing at –20 °C [48]. On the other hand, Häkkinen *et al.* highlighted a 20% loss of ellagic acid in strawberry jam (produced by cooking the

Table II.
Levels of cinnamic acid derivatives (ng·g^{-1} dry matter) in fruits and their corresponding preserves.

Fruit	Fresh fruit	Compote	Duration of fruit heating for jams (min)					
			10	20	30	40	50	60
Caffeic acid								
Wild strawberry	120 ± 15 c	92 ± 15 bc	66 ± 11 ab	51 ± 4 ab	47 ± 7 ab	56 ± 4 ab	35 ± 7 a	43 ± 3 ab
Apple var. Champion	48 ± 5 b	17 ± 2 a	25 ± 3 a	27 ± 2 a	21 ± 3 a	12 ± 3 a	12 ± 4 a	11 ± 2 a
Apple var. Idared	35 ± 2 d	30 ± 4 bcd	31 ± 4 cd	21 ± 3 abcd	22 ± 4 abcd	17 ± 2 abc	14 ± 2 ab	10 ± 2 a
Apricot	10 ± 2 ab	15 ± 2 b	9 ± 1 ab	9 ± 1 ab	9 ± 2 ab	5 ± 1 a	2 ± 1 a	5 ± 1 a
Cherry	17 ± 2 b	17 ± 3 b	15 ± 2 ab	11 ± 2 ab	15 ± 2 ab	13 ± 3 ab	13 ± 2 ab	4 ± 1 a
Peach	36 ± 3 d	29 ± 2 cd	22 ± 1 c	13 ± 1 b	6 ± 2 ab	3 ± 1 a	1 ± 0 a	1 ± 0 a
Raspberry	11 ± 2 b	6 ± 1 ab	4 ± 1 a	7 ± 1 ab	3 ± 0 a	2 ± 0 a	2 ± 0 a	3 ± 0 a
Cranberry	7 ± 2 a	6 ± 2 a	5 ± 1 a	5 ± 1 a	4 ± 2 a	4 ± 1 a	2 ± 1 a	2 ± 1 a
Bilberry	9 ± 1 a	8 ± 1 a	7 ± 0 a	7 ± 1 a	8 ± 1 a	11 ± 1 a	10 ± 2 a	9 ± 1 a
Chlorogenic acid								
Apple var. Idared	6 ± 0 a	7 ± 1 a	6 ± 1 a	–	–	–	–	–
Apricot	5 ± 1 b	2 ± 1 ab	3 ± 1 ab	4 ± 0 ab	2 ± 0 ab	2 ± 0 ab	1 ± 0 a	2 ± 0 ab
Cherry	12 ± 2 b	5 ± 1 a	3 ± 1 a	5 ± 1 a	6 ± 1 ab	3 ± 0 a	4 ± 1 a	4 ± 1 a
Peach	16 ± 2 c	10 ± 1 bc	13 ± 2 bc	9 ± 1 b	1 ± 0 a	–	–	–
Raspberry	43 ± 3 d	27 ± 4 c	26 ± 2 c	23 ± 5 bc	17 ± 1 abc	21 ± 0 bc	5 ± 1 a	8 ± 2 ab
p-Coumaric acid								
Chokeberry	27 ± 2 b	24 ± 1 ab	24 ± 5 ab	20 ± 2 ab	24 ± 2 ab	25 ± 1 ab	13 ± 2 ab	12 ± 3 ab
Wild strawberry	22 ± 3 a	20 ± 5 a	25 ± 1 a	25 ± 3 a	18 ± 1 a	15 ± 1 a	14 ± 2 a	14 ± 2 a
Apple var. Idared	7 ± 1 b	3 ± 0 a	4 ± 0 ab	2 ± 0 a	3 ± 0 a	5 ± 1 ab	3 ± 1 a	2 ± 0 a
Apricot	4 ± 0 ab	4 ± 0 ab	3 ± 0 ab	4 ± 0 ab	5 ±0 ab	3 ± 0 ab	1 ± 0 a	2 ± 0 ab
Cherry	14 ± 2 b	12 ± 0 b	10 ± 0 b	2 ± 1 a	3 ± 0 a	4 ± 0 a	1 ± 0 a	3 ± 0 a
Peach	32 ± 0 a	23 ± 5 a	–	–	–	–	–	–
Raspberry	28 ± 1 d	25 ± 2 cd	17 ± 3 bc	14 ± 2 abc	8 ± 0 ab	10 ± 3 ab	6 ± 1 a	9 ± 1 ab
Ferulic acid								
Apple var. Champion	3 ± 0 a	1 ± 0 a	–	–	–	–	–	–
Apricot	2 ± 0 a	5 ± 1 b	3 ± 0 ab	2 ± 0 a	2 ± 0 a	–	–	–
Cherry	11 ± 0c	7 ± 0 b	2 ± 0 a	2 ± 0 a	1 ± 0 a	2 ± 0 a	–	–
Peach	4 ± 1 a	3 ± 0 a	–	–	–	–	–	–
Raspberry	37 ± 4 a	33 ± 6 a	34 ± 9 a	18 ± 1 a	20 ± 6 a	14 ± 2 a	16 ± 1 a	12 ± 4 a
Cranberry	2 ± 0 a	2 ± 1 a	2 ± 0 a	1 ± 0 a	2 ± 0 a	2 ± 0 a	2 ± 0 a	2 ± 0 a

In each row, different letters denote a significant difference at $p < 0.05$; "–" no phenolic acid detected.

Table III.
Levels of benzoic acid derivatives (ng·g^{-1} dry matter) in fruits and their corresponding preserves.

Fruit	Fresh fruit	Compote	Duration of fruit heating for jams (min)					
			10	20	30	40	50	60
Gallic acid								
Apricot	10 ± 2 a	9 ± 1 a	9 ± 1 a	15 ± 1 a	14 ± 4 a	16 ± 2 a	13 ± 2 a	15 ± 3 a
Raspberry	3 ± 1 bc	4 ± 0 cd	5 ± 0 d	2 ± 0 ab	1 ± 0 a	2 ± 0 ab	1 ± 0 a	2 ± 0 ab
Bilberry	41 ± 3 b	26 ± 3 a	17 ± 2 a	28 ± 2 a	21 ± 1 a	19 ± 1 a	27 ± 1 a	22 ± 2 a
Gentisic acid								
Apple var. Idared	6 ± 0 c	2 ± 1 a	4 ± 0 b	1 ± 0 a	1 ± 0 a	1 ± 0 a	1 ± 0 a	1 ± 0 a
Raspberry	93 ± 4 a	90 ± 16 a	87 ± 15 a	83 ± 5 a	78 ± 11 a	60 ± 9 a	58 ± 10 a	53 ± 4 a
p-Hydroxybenzoic acid								
Chokeberry	38 ± 4 d	35 ± 2 cd	17 ± 2 ab	25 ± 2 bcd	26 ± 4 bcd	22 ± 2 abc	9 ± 1 a	–
Wild strawberry	4 ± 0 ab	5 ± 0 b	4 ± 1 ab	5 ± 1b	3 ± 0 ab	2 ± 0 a	2 ± 0 a	2 ± 0 a
Cherry	3 ± 0 a	2 ± 0 a	2 ± 0 a	3 ± 1 a	2 ± 0 a	2 ± 0 a	2 ± 0 a	–
Raspberry	17 ± 2 b	13 ± 2 ab	15 ± 2 ab	18 ± 3 b	13 ± 4 ab	9 ± 3 ab	8 ± 1 ab	3 ± 1 a
Protocatechuic acid								
Chokeberry	11 ± 0 bd	14 ± 2 d	9 ± 1 b	8 ± 0 bc	4 ±0 ac	2 ± 0 a	2 ± 0 a	2 ± 0 a
Wild strawberry	17 ± 0 b	15 ± 3 b	9 ± 2 ab	11 ± 1 ab	6 ±0 a	9 ± 1 ab	9 ± 0 ab	12 ± 2 ab
Cherry	7 ± 0 b	4 ± 0 a	–	–	–	–	–	–
Raspberry	51 ± 4c	53 ± 6c	44 ± 2 bc	31 ± 5 abc	23 ±3 ab	26 ± 4 ab	16 ± 2 a	14 ± 4 a
Syringic acid								
Chokeberry	65 ± 11 a	53 ± 8 a	43 ± 6 a	45 ± 2 a	34 ± 8 a	40 ± 1 a	42 ± 3 a	45 ± 3 a
Apple var. Idared	14 ± 1 a	12 ± 3 a	13 ± 2 a	14 ± 3 a	7 ± 2 a	9 ± 2 a	5 ± 1 a	7 ± 1 a
Cherry	26 ± 1 a	23 ± 1 a	24 ± 0 a	23 ± 1 a	25 ± 1 a	25 ± 0 a	20 ± 2 a	19 ± 3 a
Raspberry	32 ± 4 b	11 ± 1 a	16 ± 3 a	14 ± 2 a	12 ± 2 a	13 ± 3 a	18 ± 3 ab	15 ± 3 a
Vanillic acid								
Raspberry	11 ± 0 b	3 ± 0 a	2 ± 0 a	–	–	–	–	–

In each row, different letters denote a significant difference at $p < 0.05$; "–" no phenolic acid detected.

Table IV.
Levels of ellagic acid (ng·g^{-1} dry matter) in fruits and their corresponding preserves.

Ellagic acid	Fresh fruit	Compote	Duration of fruit heating for jams (min)					
			10	20	30	40	50	60
Chokeberry	42 ± 2 b	32 ± 6 b	15 ± 3 a	11 ± 2 a	12 ± 1 a	15 ± 1 a	13 ± 2 a	15 ± 2 a
Wild strawberry	51 ± 4 c	30 ± 4 b	15 ± 1 a	13 ± 1 a	13 ± 1 a	16 ± 3 a	6 ± 1 a	5 ± 1 a
Cherry	2 ± 0 a	3 ± 0 ab	5 ± 0 abcd	4 ± 0 abc	7 ± 1 cd	6 ± 1 bcd	8 ± 1 d	6 ± 1 bcd
Raspberry	1055 ± 46 c	702 ± 123 b	534 ± 65 ab	388 ± 30 a	365 ± 13 a	280 ± 23 a	343 ± 18 a	326 ± 12 a
Bilberry	37 ± 4 a	22 ± 2 a	33 ± 5 a	23 ± 3 a	26 ± 1 a	36 ± 2 a	31 ± 3 a	39 ± 4 a

In each row, different letters denote a significant difference at $p < 0.05$.

Table V.
Levels of phenolic acids (ng·g^{-1} dry matter) in dried homogenates prepared from fresh fruit.

Fruit	Caffeic acid	Chlorogenic acid	p-Coumaric acid	Ellagic acid	Gallic acid	p-Hydroxybenzoic acid	Syringic acid
Chokeberry	–	–	–	–	–	13 ± 2	–
Wild strawberry	40 ± 2 b	–	9 ± 1 b	–	–	–	–
Cherry	8 ± 1 a	6 ± 1	1 ± 0 a	5 ± 1	–	–	9 ± 2 a
Raspberry	4 ± 0 a	–	14 ± 2 b	–	–	–	6 ± 2 a

In each column, different letters denote a significant difference at $p < 0.05$.
"–" no phenolic acid detected.

fruit for 30 min) in comparison with fresh fruit [49]. Similarly, Levaj *et al.* demonstrated a considerable loss of ellagic acid in jams produced from sour cherry, strawberry, raspberry and wild blueberry [47]. Amakura *et al.* observed unambiguous results concerning the free and total levels of ellagic acid as well as caffeic acid in blackberry, raspberry, blueberry and strawberry jams in comparison with the corresponding fresh fruits [45]. The results concerning the levels of phenolic acids in raw apricots and apples, their purees, and apricot nectars and jams obtained by Dragovic-Uzelac *et al.* were also not unequivocal [50]. For example, the levels of chlorogenic acid were similar in the three varieties of apricots and in their corresponding purees. However, a significant decrease was observed in the amount of chlorogenic acid during the production of puree from apples (var. Idared). The levels of caffeic acid and p-coumaric acids decreased in apples (var. Idared) puree and in selected apricot purees (but not in all). The levels of ferulic acid were reduced in all apricot purees in comparison with the corresponding fruits. In the same study it was shown that the levels of chlorogenic acid, caffeic acid, p-coumaric acid and ferulic acid were reduced in apricot nectars and jams in comparison with the corresponding fruits. Also, Levaj *et al.* observed a considerable loss of phenolic acids (chlorogenic, caffeic, gallic and p-hydroxybenzoic acids) in jams in comparison with fresh sour cherry, strawberry, raspberry and blueberry fruits [47].

4. Conclusions

Our results showed that elevated temperature caused changes (predominantly a decrease) in the levels of individual phenolic acids but only in selected products. The content of some phenolic acids was not changed or was elevated. The level of the individual phenolic acid in some products was significantly decreased, whereas in other preserves, the level of the same phenolic acid was not changed. Therefore, it can be concluded that the loss of phenolic acids is ambiguous and the evolution of the levels of these compounds during the thermal processing of different fruits cannot be subject to a single explanation. The results we obtained were probably influenced by the composition of the fruit as well as by the processing procedure (water content, temperature of the process, the oxygen access during the intensive mixing of a fruit, etc.). Therefore, compote and jam production should be thoroughly studied taking into consideration these factors.

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Influencia de diferentes tratamientos térmicos en el contenido de ácidos fenólicos en frutos seleccionados.

Resumen – **Introducción**. Ya se resaltó un gran número de efectos positivos en el consumo de frutos : acción hipolipidémica, reducción del índice de glucosa en la sangre, hepatoprotección, mejora del estado antioxidante, así como, entre otros, los efectos antioxidante, antirradicalario, antiinflamatorio, anticancerígeno o antiadipogénico. **Material y métodos**. Se estudiaron por HPLC o detección UV los cambios de los índices de ácidos fenólicos y de sus derivados en ciertos frutos (aronia, frutilla silvestre, manzanas var. Idared y Champion, cereza, albaricoque, melocotón, frambuesa, arándano rojo y arándano) frescos o transformados. Se realizaron homogenados de frutos secados y de compotas. Asimismo, se cocieron los frutos para estimular la producción de mermeladas. **Resultados y discusión**. Se identificaron once ácidos fenólicos y derivados en las muestras testeadas: ácidos cafeico, clorogénico, p-cumárico, ferúlico, gálico, elágico, protocatéquico, p-hidroxibenzoico, gentísico, siríngico y vanílico. En la mayoría de los casos, el tratamiento térmico de los frutos provocó una disminución de los índices de ácidos fenólicos. En ciertas conservas, el índice de compuestos fenólicos individuales permaneció intacto o aumentó considerablemente. **Conclusión**. El tratamiento térmico podría tener efectos diferenciados en los índices de ácidos fenólicos en los frutos transformados, y no es posible generalizar estos efectos. En este contexto, la composición de los frutos con contenido de ácido fenólico puede variar.

Polonia / frutas / frutas en conserva / mermeladas / compotas / compuestos fenólicos / contenido fenólico