Food Chemistry 358 (2021) 129802

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Potential valorization of Cornelian cherry (*Cornus mas* L.) stones: Roasting and extraction of bioactive and volatile compounds

Radosław Spychaj [a,*], Alicja Z. Kucharska [b], Antoni Szumny [c], Dominika Przybylska [b], Ewa Pejcz [a], Narcyz Piórecki [d,e]

[a] *Department of Fermentation and Cereals Technology, Wroclaw University of Environmental and Life Sciences, J. Chełmońskiego 37, 51-630 Wrocław, Poland*
[b] *Department of Fruit, Vegetable and Plant Nutraceutical Technology, Wroclaw University of Environmental and Life Sciences, J. Chełmońskiego 37, 51-630 Wrocław, Poland*
[c] *Department of Chemistry, Wroclaw University of Environmental and Life Sciences, C. K. Norwida 25, 50-375 Wrocław, Poland*
[d] *Arboretum and Institute of Physiography in Bolestraszyce, 37-700 Przemyśl, Poland*
[e] *Institute of Physical Culture Sciences, Medical College, University of Rzeszów, Towarnickiego 3, 35-959 Rzeszow, Poland*

ARTICLE INFO

Keywords:
Cornus mas L.
Stone
Roasting
Antioxidants
Iridoids
Volatile compounds

ABSTRACT

This study aimed to characterize the antioxidant potential, bioactive and volatile compounds of the stones from fruits of *Cornus mas*.

Both fresh and roasted stones show a high antioxidant potential (166.48–509.74 μmol TE/g dw stones), which significantly depends on the cultivars. The roasted stones preserved 43.6% (DPPH; 'Raciborski') to 97.2% (FRAP; 'Alesha') of the antioxidant activity of the non-roasted stones. In the stones, two iridoids and ellagic acid were determined. During roasting, loganic acid remained stable, whereas cornuside was completely degraded. The analyses showed a 30-fold increase in the concentration of ellagic acid and in the formation of two of its derivatives. The major aroma compound of the roasted stones was furfural, but we also identified 18 pyrazine derivatives.

This study is the first attempt to valorize Cornelian cherry stones via roasting. The roasted stones can be a coffee substitute, or aromatic and bioactive additions to cereal coffees.

1. Introduction

Cornelian cherry (*Cornus mas* L.) is a unique plant due to the health-promoting properties of not only its fruits but also leaves, flowers, and bark (Dinda et al., 2016). However, its fruits are often used because of their valuable components, e.g. anthocyanins, flavonols, phenolic acids, iridoids, terpenes, carotenoids, vitamins, and organic acids (Dinda et al., 2016). Contents of individual compounds depend on the cultivar, growing conditions, amount of water in the growing season, or the degree of fruit maturity (Kucharska, Sokół-Łętowska, & Piórecki, 2011, Kucharska, 2012, Kucharska, Szumny, Sokół-Łętowska, Piórecki, & Klymenko, 2015).

The valuable compounds of Cornelian cherry fruits include loganic acid, a representative of iridoids. Various studies have proved its potential to regulate the levels of triglycerides and cholesterol. It has also been shown to lower the levels of total cholesterol (TC) and low-density cholesterol, to increase levels of total triglycerides (TG) and high-density cholesterol (HDL-C), and to exert an anti-inflammatory effect (Dinda et al., 2016, Sozański et al., 2014). Its positive role has also been reported in lowering the internal pressure and increasing the flow in the eyeball when administered into the conjunctival sac (Szumny et al., 2015), which can be crucial in the prevention and treatment of glaucoma. The content of loganic acid in Cornelian cherry fruit flesh ranges from 81.53 to 461.1 mg/100 g (Kucharska, 2012, Kucharska et al., 2015). It is also regarded as the major iridoid of this raw material, accounting for 88–96% of total iridoid compounds (Kucharska, 2012, Perova, Zhogova, Poliakova, Éller, Ramenskaia, & Samylina, 2014). However, there is no information regarding its presence in the stones of Cornelian cherry (*Cornus mas* L.) fruits.

Like the stones of cherries, plums, apricots, olives, and peaches, the stones of Cornelian cherry fruits are very hard. Today, stones of drupe fruits are treated both potentially and practically as a raw material for biochar production (Angın, Altintig, & Köse, 2013). The food industry uses seeds and stones of fruits as sources of oils with predominating

---

* Corresponding author.
E-mail address: radoslaw.spychaj@upwr.edu.pl (R. Spychaj).

https://doi.org/10.1016/j.foodchem.2021.129802
Received 24 November 2020; Received in revised form 31 March 2021; Accepted 15 April 2021
Available online 20 April 2021
0308-8146/© 2021 Elsevier Ltd. All rights reserved.

concentrations of unsaturated fatty acids, represented mainly by oleic and linoleic acids (Özcan, Ünver, & Arslan, 2014). Kernels of apricots or peaches are used as substitutes of marzipan or for nonfood purposes as fuel (Ordoudi, Bakirtzi, & Tsimidou, 2018).

To date, knowledge about the chemical composition of stones of drupe fruits has been very sparse and limited. Zhen and Xiao (2014) proved a high content of polyphenolic compounds in cherry stones. In another paper, Nowicka and Wojdyło (2019) noted the presence of polyphenolic compounds, carotenoids or tetraterpenoids in peach stones and, consequently, confirmed their high antioxidant potential as well as α-amylase- and β-glucosidase-inhibiting activities. Another interesting source of bioactive compounds is the seeds of the date palm fruit, containing phenolic acids, flavonoids, carotenoids, tocopherols, tocotrienols, and phytosterols (Maqsood, Adiamo, Ahmad, & Mudgil, 2020). They are used as an additive in the production of bakery products, meat dishes, yoghurts or snacks, even in amounts of up to 40%. Date plant seeds are a potential raw material for obtaining oil with a unique fatty acid composition (Abdul Afiq, Abdul Rahman, Che Man, AL-Kahtani, & Mansor, 2013). Date seeds are also used to produce infusions and substitutes of natural coffee (Fikry et al., 2019b). Commercial infusions obtained from these seeds are valuable sources of minerals, free radical scavengers and, interestingly, do not contain caffeine (Fikry et al., 2019a). Fikry et al. (2019b) reported that by applying different roasting conditions (temperature and time) of the defatted date seeds it was possible to obtain products used to prepare infusions with different organoleptic characteristics and that their antioxidant potential increased with increasing process temperature and roasting time. In turn, Nowicka, Gładzik, Wojdyło, and Oszmiański (2018) showed that cherry stones could be a source of bioactive compounds (phenolic acids, flavan-3-ols, flavonols), which ensure their antioxidant potential, but also contained undesirable cyanogenic glycosides in amounts even above 300 mg/100 g. Cornelian cherry fruit seeds contain a fatty acid fraction (Kucharska, Szumny, Sokół-Łętowska, & Zając, 2009, Akalin, Tekin, & Karagöz, 2012) and, unlike cherry seeds, they do not contain cyanogenic glycosides (Kucharska, 2012). Akalın et al. (2012) presented the proposed composition of the light and heavy volatile fractions obtained from Cornelian cherry fruit seeds subjected to pyrolysis (200–300 °C).

Literature reports on Cornelian cherry stones concern their utility in diabetes treatment with local methods, their consumption in a ground form (Genc & Ozhatay, 2006), or their use for oil production (Akalın et al., 2012). Stones account for 16% of Cornelian cherry fruit weight on average (Kucharska et al., 2011), and contain from 1.77% to 7.94% of the lipid fraction (Kucharska et al., 2009, Vidrih, Cejic, & Hribar, 2012). They are mainly used to produce oil, whose composition is predominated by linolenic acid (64.8–72.2%) (Kucharska et al., 2009, Akalın et al., 2012, Vidrih et al., 2012).

Many authors have attempted to produce coffee substitutes by the roasting of plant raw materials, such as chicory, sugar beets, rye, barley, wheat germs, soybeans, ginger, acorns, or date seeds (Fadel, Mageed, & Lotfy, 2008, Majcher, Klensporf-Pawlik, Dziadas, & Jeleń, 2013, Švarc-Gajić, Cvetanović, Segura-Carretero, Mašković, & Jakšić, 2017, Fikry, Yusof, Al-Awaadh, & Rahman, 2020). The products obtained were evaluated for their organoleptic traits (Majcher et al., 2013, Švarc-Gajić et al., 2017) and identified for volatile compounds formed during roasting (Fadel et al., 2008, Švarc-Gajić et al., 2017). Their antioxidant properties (Švarc-Gajić et al., 2017) or stability of their aroma profile have hardly ever been studied (Fadel et al., 2008).

Considering recent research reports on the use of fruits of Cornelian cherry (*Cornus mas* L.), (Sokół-Łętowska et al., 2014, Czyżowska, Kucharska, Nowak, Sokół-Łętowska, Motyl, & Piórecki, 2017) and the sparsity of data on the composition and use of active compounds of Cornelian cherry fruit stones, a study was undertaken to determine the composition of active compounds and antioxidant properties of raw and roasted stones from fruits of different Cornelian cherry cultivars. The roasted stones were also analyzed for the composition of their volatile compounds and compared with commercial coffees.

2. Materials and methods

2.1. Materials

The research materials were stones of Cornelian cherry fruits (*Cornus mas* L.) from 8 cultivars ('Alesha', 'Elegantnyi', 'Koralovyi', 'Kresowiak', 'Paczoski' I – early harvest, 'Paczoski' II – late harvest, 'Podolski', 'Raciborski', and 'Słowianin') and 1 ecotype (NN). Fruits were harvested in the Arboretum and Institute of Physiography in Bolestraszyce, near Przemyśl, Poland, in 2014. The plant materials were authenticated by Elżbieta Żygała, M.Sc. (Arboretum and Institute of Physiography in Bolestraszyce, Poland) and the adequate voucher specimens ('Alesha' – BDPA 14600; 'Elegantnyi' – BDPA 14132; 'Koralovyi' – BDPA 14136; 'Kresowiak' – BDPA 3946; 'Paczoski' – BDPA 3966; 'Podolski' – BDPA 10462; 'Raciborski' – BDPA 3967; 'Słowianin' – BDPA 3965; NN – BDPA 6774) have been deposited at the Herbariums of Arboretum and Institute of Physiography in Bolestraszyce, Poland. Stones were husked from frozen Cornelian cherry fruits manually, whereas flesh residues were removed with water. They were left to dry under laboratory conditions (temp. 20 °C, humidity 70%, time 168 h) and then roasted at 170 °C for 30 min, cooled, vacuum-packed non-disintegrated, and stored at −18 °C. The roasting conditions of Cornelian cherry stone were established on the basis of a literature review and preliminary laboratory tests. The roasted stones contained from 3.3% ('Alesha') to 5.3% ('Słowianin' and 'Podolski') moisture.

The comparative materials included the commercial cereal coffee Kujawianka (rye 60%, barley 20%, chicory, sugar beet – roasted) and the natural ground coffee Jacobs Krönung (100% Arabica), both from the local retail market. The cereal and natural ground coffee contained 6.3% and 5.5% moisture, respectively.

2.2. Analytical method

2.2.1. Chemicals and reagents

The following reagents were used in this work: 2,2′azynobis(3-etylobenzotiazoline-6-sulfonic acid (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH); 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ), $FeCl_3$, methanol, acetonitrile (gradient grade for HPLC) and formic acid (98–100%) were acquired from Sigma (Germany, Schnelldorf). Iridoids and phenolic acids standards were purchased from Extrasynthese (France, Genay). All reagents were analytical or HPLC grade.

2.2.2. Extraction process

The samples of raw and roasted stones (~20 g) were ground in a WŻ-1 grinder (1000 W, 6000 rpm, ~20 °C, 10 s) (WBZPP, Poland). The ground stone particle size was similar to that of the coffee used as a reference material (ground coffee Jacobs Krönung). Grinding took place immediately before the preparation of water infusions with distilled water having a temperature of ~80 °C (1:10, 10 min) (see e.g. Fikry et al., 2019a). After cooling, the infusions were filtered through paper filters (Whatman filter No. 3) and analyzed.

2.2.3. Antioxidant activity

The antioxidant activity of the water extracts from raw and roasted stones of Cornelian cherry fruits was determined with the ABTS and DPPH methods and by determining ferric ion reduction with the FRAP method according by Przybylska et al. (2020). Results were expressed in μmol of Trolox equivalent (TE) per 1 g of dry weight (μmol TE/g dw) stones. Samples' extinction was read out using a UV–VIS 2401PC spectrophotometer (Shimadzu Corp. Japan). The analyses were run in three replications.

2.2.4. Quantification of compounds by HPLC-PDA

The HPLC-PDA method was previously described by Sokół-Łętowska et al. (2014). The quantification analysis was performed using a Dionex (Germering, Germany) system, equipped with the diode array detector model Ultimate 3000, quaternary pump LPG-3400A, autosampler EWPS-3000SI, thermostated column compartment TCC-3000SD, and controlled by Chromeleon 7.2 software (Thermo Scientific Dionex, Sunnyvale, CA, USA). The Cadenza Imtakt column CD-C18 (75 × 4.6 mm, 5 μm) was used. Loganic acid and cornuside were detected at 245 nm, ellagic acid and its derivatives at 254 nm, derivatives of caffeic acid at 320 nm. Loganic acid and cornuside were expressed as loganic acid, ellagic acid and its derivatives as ellagic acid, and derivatives of caffeic acid as 5-*O*-caffeoylquinic acid. The analyses were run in three replications and the results were expressed as mg per 100 g dry weight (dw) of stones.

2.2.5. Identification of compounds by LC-MS

Identification of compounds was carried out using an Acquity ultra performance liquid chromatography system (UPLC) equipped with a quadrupole-time of flight (Q-TOF) MS instrument (UPLC/Synapt Q-TOF MS, Waters Corp., Milford, MA, USA), with an electrospray ionization (ESI) source in negative mode. Separation was achieved on an Acquity BEH C18 column (100 mm × 2.1 mm i.d., 1.7 μm) at 30 °C. The mobile phase consisted of aqueous 0.1% formic acid (A) and 100% acetonitrile (B). Samples (5 μl) were eluted according to the linear gradient described previously by Przybylska, et al. (2020). The conditions of the mass spectrometer were: a source block temperature of 130 °C, desolvation temperature of 350 °C, capillary voltage of 2.5 kV, cone voltage of 30 V, a desolvation gas (nitrogen) flow rate of 300 dm^3/h, data acquisition range, *m/z* 100–2500 Da.

2.2.6. Solid-phase micro extraction (SPME) analysis

Immediately before the analysis of volatile compounds, roasted Cornelian cherry stones (<5 g) were ground in a WŻ-1 mill (1000 W, 20 °C, 10 s, 6000 rpm) (ZBPP, Poland) and ground in a head space vial, 20 mL which was heated in a water bath (60 °C; 15 min).

Headspace-SPME analyses (30 min exposure to a 20 mm DVB/CAR/PDMS fiber, Supelco, Bellefonte, PA, USA, followed by desorption analysis at 220 °C for 3 min) was performed on Varian CP-3800/Saturn 2000 apparatus (Varian, Walnut Creek, CA, USA) equipped with a Zebron ZB-5 MSI (30 m × 0.25 mm × 0.25 mm) column (Phenomenex, Shim-Pol, Poland). The protocol was based on our modified methodology published previously (Sadowska, Żabiński, Szumny, & Dziadek, 2016). Half a milligram of 2-undecanone (Sigma Aldrich, Saint Louis, MO, USA) in stock solution was used as an internal standard during analysis.

In brief, the separation, identification, and quantification of volatiles adsorbed on the fiber were conducted using gas chromatography (GC) coupled to a mass spectrometry (MS) detector (Saturn 2000 MS Varian Chrompack, Palo Alto, CA, USA) with a ZB-5 (Phenomenex, Torrance, CA, USA) column (30 m × 0.25 μm film × 0.25 mm inside diameter (i.d.)).

The analyses were performed using helium as a carrier gas at a flow rate of 1.0 mL/min, in splitless mode in SPME, and with the following program for the oven temperature: 40 °C (3 min), to 110 °C at rate 5.0 °C then to 270 °C at rate 20.0 °C. Scanning (1 scan/s) was performed from 35 to 350 *m/z* in electronic impact (EI) mode at 70 eV. The injector and manifold temperature were set at 220 and 250 °C respectively. Before the measurements, a blank sample was done on the same day to evaluate the current experiment conditions and the possibility of interference as room air was used during the experiment. Analyses were run in triplicate.

Identification of all volatile constituents obtained by headspace-SPME analyses were based on the comparison of experimentally obtained compound mass spectra with mass spectra available in the NIST17 database. Moreover, the experimentally obtained Kovats retention index (RI) (logarithmic type) values were compared with RI available in the NIST WebBook [https://webbook.nist.gov/] and literature data. The quantification analysis was performed using ACD/Spectrus Processor (Advanced Chemistry Development, Inc., Toronto, ON, Canada) through the integration of the peak area of the chromatograms.

2.2.7. Aroma sensory evaluation

A team consisting of 20 trained staff assessed the aroma of roasted and ground stones of the four cultivars of Cornelian cherry ’Alesha’, ’Paczoski’ I, ’Raciborski’, ’Podolski’ and the cereal coffee Kujawianka. The evaluation of the aroma of roasted and ground stones and cereal coffee was performed using the scalar method on a five-point scale according to the standard ISO 4121 (1998), where 1 corresponds to the lowest, and 5 to the highest rating. In addition, the acceptability of roasted and ground stones was determined with a nine-point hedonic scale (1 – disliked extremely; 2 – disliked very much; 3 – disliked moderately; 4 – disliked slightly; 5 – neither liked nor disliked; 6 – liked slightly; 7 – liked moderately 8 – liked very much, and 9 – liked extremely). The results are shown in Figs. S1 and S2.

2.3. Statistical analysis

One-way analysis of variance (Cornelian cherry cultivar) was used to analyze the data obtained. Differences between mean values were determined using Duncan’s test at $p = 0.95$. Analyses of antioxidant properties were run in three replications. In addition, principal component analysis (PCA) and cluster analysis (CA) were conducted to compare the antioxidant potential of the raw and roasted materials, and the volatile compounds identified. The single-linkage agglomerative method was used, employing the Euclidean measure to determine the distance between the samples. Results are presented as dendrograms with the scale having the form of distances between the objects.

All statistical computations were performed using the Statistica ver. 13 data analysis software system (Dell Inc., 2016; software.dell.com.)

3. Results and discussion

3.1. Antioxidant activity of raw and roasted stones and of commercial coffee

The antioxidant properties of raw and roasted Cornelian cherry fruit stones and commercial coffees are presented in Fig. 1. The antioxidant potential of the raw stones determined with the ABTS, DPPH, and FRAP methods fell within the following ranges: 301.92–509.74 μmol TE/g dw, 184.88–359.97 μmol TE/g dw, and 166.48–305.44 μmol TE/g dw, respectively, and was higher compared to the commercial coffees (Kujawianka, Jacobs). However, the natural coffee (Jacobs) showed a higher antioxidant activity than cereal coffee (Kujawianka). The antioxidant activity of Cornelian cherry fruit stones was higher than the activity of the whole cherry stones (Nowicka et al., 2018) and lower or comparable to peach kernels (Nowicka & Wojdyło, 2019). The highest antioxidant potential was observed for the extracts from raw stones from fruits of ‘Kresowiak’ and ‘Podolski’ cultivars, whereas the lowest was observed for those from ‘Alesha’ and ‘Paczoski’ II cultivars. Cultivar-dependent differences in the antioxidant potential of stones of, e.g., cherries or peaches, were also observed by other authors (Nowicka & Wojdyło, 2019, Nowicka et al., 2018). The antioxidant potential of raw fruits of Cornelian cherry of Polish cultivars as determined by Kucharska et al. (2011) ranged from 10.85 μmol TE/g fw (DPPH) to 41.08 μmol TE/g fw (FRAP) and was lower than that of the stones.

The roasted stones preserved most of the antioxidant activity of the non-roasted stones. It ranged from 43.6% (DPPH; ‘Raciborski’) to 97.2% (FRAP; ‘Alesha’) (Fig. 1). Like their non-roasted counterparts, the roasted stones from fruits of ‘Kresowiak’ and ‘Podolski’ cultivars showed the highest activity, whereas the roasted stones from fruits of ecotype

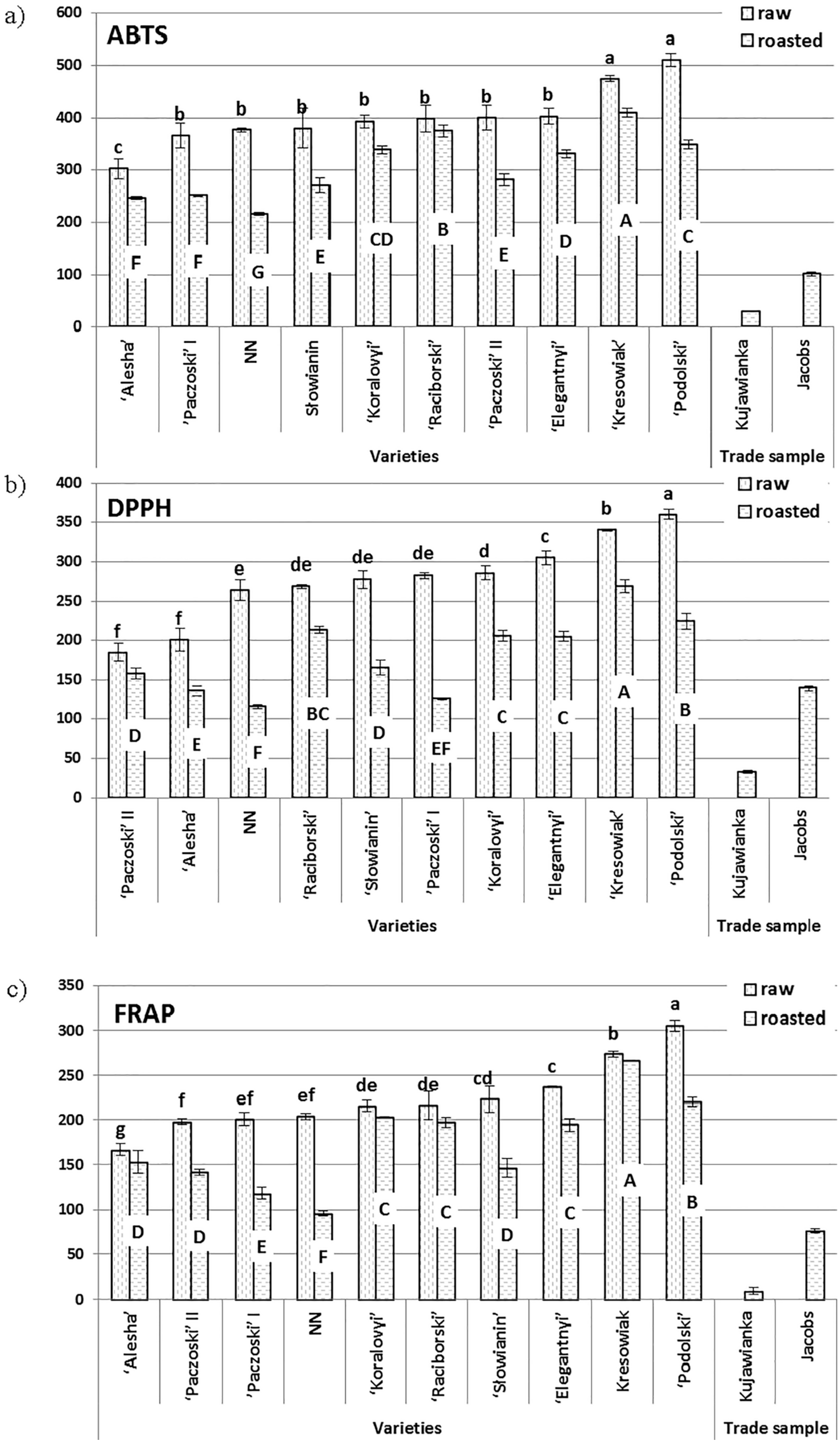

Fig. 1. Antioxidants activity (μmol TE/g dw) by: ABTS (a), DPPH (b) and FRAP (c) of cornelian cherry raw and roasted stone, small letter stand as homogenous group in raw stone, capital letterers stand as homogenous group in roasted stone.

NN and 'Alesha' and 'Paczoski' cultivars showed the lowest activity. The roasting process entails providing energy in the form of temperature, which results in many physical and chemical transformations leading to changes in the color, taste, and aroma of the roasted material (Fareez, Edzuan, Noor Aliah, & Bong, 2015). Duarte, Abreu, Menezes, Santos & Gouvêa (2005) reported that the roasting process contributed to the antioxidant potential reduction. In turn, Samsonowicz, Regulska, Karpowicz and Leśniewska (2019) claimed that, depending on the raw materials used, the antioxidant properties of cereal coffee were attributable to phenolic compounds, including ellagic acid. Finally Zafrilla, Ferreres, and Tomás-Barberán (2001) demonstrated that the heat treatment contributed to changes in the contents of individual ellagic acid derivatives and differences in their antioxidant capabilities.

The presence of ellagic acid derivatives (ellagitannins) in the roasted Cornelian cherry stones increases the bioactive potential of this coffee substitute. Nowicka, Kucharska, Sokół-Łętowska, and Fecka (2019) reported antioxidant capacity in the DPPH and ABTS assays, respectively, as 352.97–1303.25 µmol TE/100 g fw and 849.42–2503.07 µmol TE/100 g fw in a study on strawberry fruit (*Fragaria* × *ananassa* Duch) cultivars. Among the compounds which contribute to this high antioxidant activity, the authors identified ellagitannins (agrimoniin, ellagic acid *O*-pentoside, ellagic acid *O*-deoxyhexoside) and ellagic acid alongside various polyphenols. Okuda (2005) reported potent free radical-scavenging effects (DPPH) of derivatives of ellagic acid, such as tellimagrandins I and II, isoterchebin and geraniin. Al-Sayed et al. (2020) reported that ellagitannins tellimagrandin I, tellimagrandin II, and peduncalagin demonstrate hepatoprotective effects, which may partly be the outcome of their strong antioxidant activity.

The multi-dimensional analysis (Fig. 2a, 2b) showed that the commercial products (Kujawianka and Jacobs) represented a separate cluster, i.e., differed significantly from all Cornelian cherry fruit stones analyzed. Among the raw stones (Fig. 2a), the least similar to the other stones were those from fruits of ‘Alesha’ and ‘Paczoski’ II cultivars, whereas the most similar were the stones from fruits of ‘Słowianin’, ecotype NN, and ‘Paczoski‘ I. The roasting process made the stones of ‘Kresowiak’ the most dissimilar to the other samples. In turn, the most similar roasted stones were those from the fruits of ‘Elegantnyj’, ‘Koralovyj’, and ‘Podolski’ cultivars. It needs to be emphasized that the roasted stones from the fruits of all cultivars were more similar to Jacobs coffee than to cereal coffee Kujawianka and that both commercial products were no longer in a separate cluster (Fig. 3b).

The determined principal components (PC1: 81.72%, and PC2: 13.17%) strongly distinguished the analyzed stones (Fig. 3a). The PCA demonstrated a significant correlation between the antioxidant properties (ABTS, DPPH, and FRAP) of raw and roasted stones of Cornelian cherry fruits. The most similar antioxidant properties were demonstrated for the stones from fruits of ‘Raciborski‘, ‘Koralovyi’, and ‘Elegantnyi‘ cultivars, whereas the most dissimilar ones were observed for those from ‘Podolski’ and ‘Kresowiak‘ cultivars (Fig. 3b).

3.2. *Quantification of compounds in raw and roasted stones and in commercial coffee*

Table 1 presents the contents of two iridoids (loganic acid and cornuside), ellagic acid and its two derivatives, as well as hydroxycinnamic acids (HCA) in water extracts from raw and roasted stones of Cornelian cherry fruits and in water extracts from cereal coffee and natural coffee.

A difference was observed in the contents of the determined bioactive compounds between raw and roasted Cornelian cherry stones and the commercial products (Kujawianka, Jacobs). The latter contained neither iridoids nor ellagic acid and its derivatives. In turn, the raw and roasted stones of Cornelian cherry fruits did not contain hydroxycinnamic acids. A small amount of these acids was determined in the cereal coffee (0.55 mg/100 g dry weight (DW)), whereas a high content was detected in the natural coffee (197.20 mg/100 g dw).

The content of loganic acid in water extracts of raw stones ranged from 61.07 mg/100 g dw (‘Elegantnyi’) to 106.07 mg/100 g dw (‘Słowianin’), whereas that of cornuside ranged from 3.89 mg/100 g dw (‘Alesha’) to 16.72 mg/100 g dw (‘Kresowiak’) (Table 1). These results point to great differences in the contents of iridoids in the stones depending on the Cornelian cherry cultivar. Likewise, the cultivar harvest date also significantly affected the contents of iridoids in the raw stones. The raw stones of ‘Paczoski’ I had higher contents of both loganic acid (92.72 mg/100 g dw) and cornuside (7.00 mg/100 g dw), compared to the stones of ‘Paczoski’ II fruits picked at the later date (87.78 mg/100 g dw and 5.36 mg/100 g dw, respectively). The roasting of stones from fruits of ‘Alesha’, ‘Paczoski’, and ‘Słowianin’ cultivars and NN ecotype reduced the loganic acid content. An opposite effect, i.e., loganic acid content increase, was observed for the stones from fruits of ‘Elegantnyi’, ‘Koralovyi’, ‘Kresowiak’, ‘Podolski’, and ‘Raciborski’ cultivars. As a complex compound of loganin and gallic acid, cornuside was totally degraded during roasting. The ranges of the total iridoid content before and after stone roasting were comparable and reached 67.07–115.39 mg/100 g dw and 74.76–125.16 mg/100 g dw, respectively. Depending on the Cornelian cherry cultivar, these values were 2 to 5 times lower than in the fruits (Kucharska et al., 2015). The available literature lacks information on the contents of iridoids in stones and seeds of fruits.

As in the case of iridoids, significant differences were also noted in the content of ellagic acid (EA) and its derivatives, depending on the Cornelian cherry cultivar and roasting process. The content of free ellagic acid in raw Cornelian cherry stones was low and ranged from 1.15 mg/100 g dw (‘Raciborski’) to 3.40 mg/100 g dw (‘Podolski’) (Table 1). Ellagic acid content was also determined in seeds and kernels of other fruits. Compared to the other fruit seeds, the content of free ellagic acid in raw Cornelian cherry stones was lower than in water extracts from longan dried seeds (3.15–9.76 mg/g dw) (Rangkadilok et al., 2012) and comparable with that found in peach kernels (0.77–9.42 mg/100 g dw) (Nowicka & Wojdyło 2019). However, ellagic acid content in seeds is mostly dependent on the extraction method and solvent used (Tang et al., 2019). In the case of the roasted Cornelian cherry stones, a rapid 3-fold to 30-fold increase was noted in the

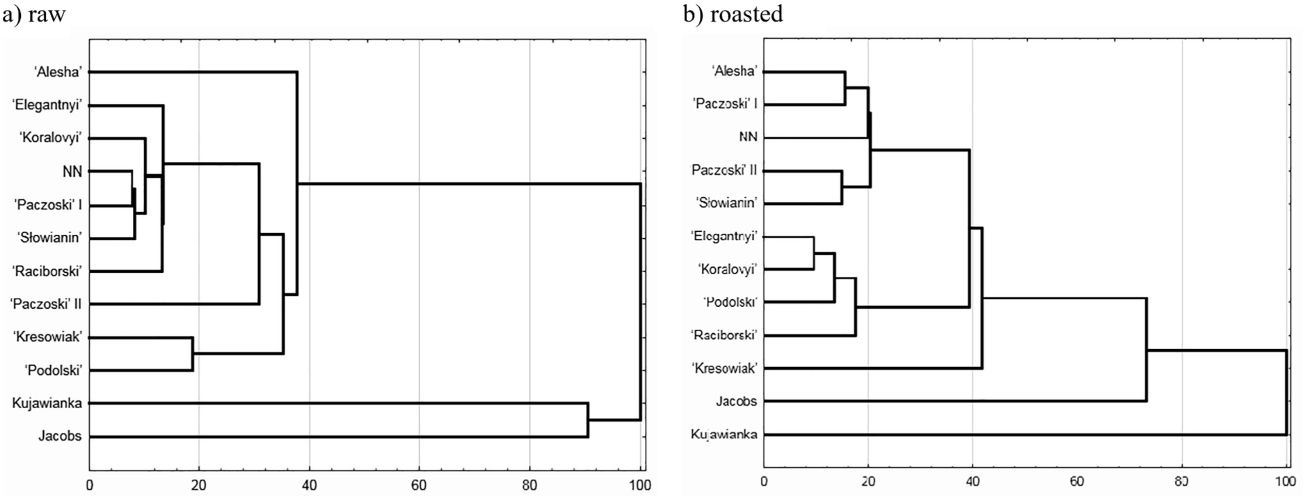

Fig. 2. Comparative analysis of cornelian cherry raw (a) and roasted (b) stone.

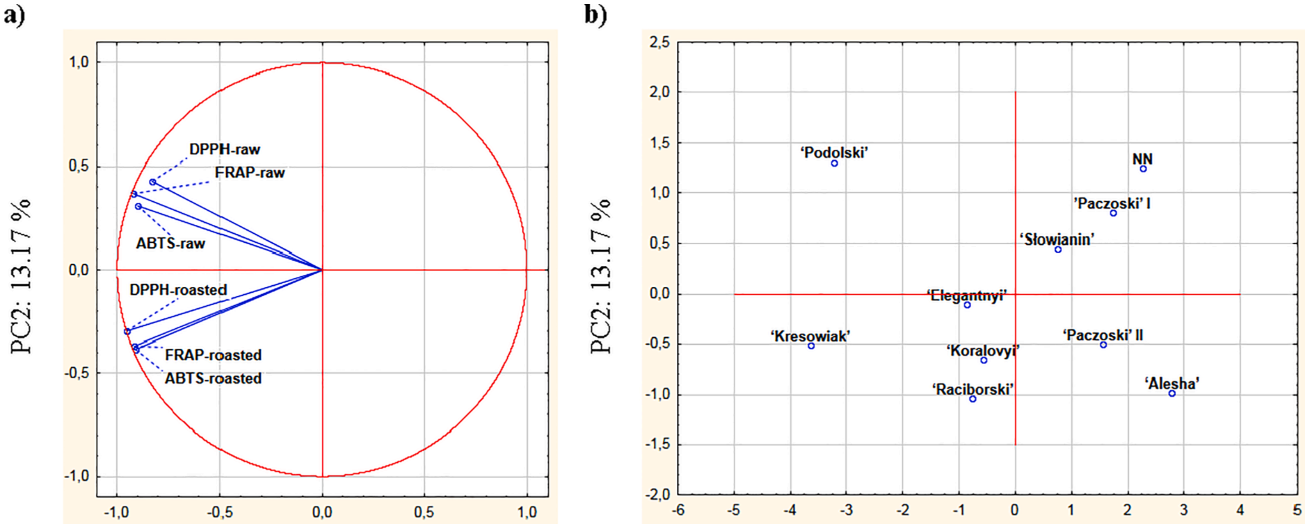

Fig. 3. Principal component analysis antioxidant activity of raw and roasted (a) and varieties (b) cornelian cherry stone.

concentration of free ellagic acid, i.e., from 9.57 mg/100 g dw (ecotype NN) to 48.94 mg/100 g dw (‘Kresowiak’), probably due to its release from high-molecular bonds upon high-temperature treatment during roasting. According to Przybylska et al. (2020), Cornelian cherry fruit stones contain hydrolyzable tannins with molecular weights of 2355 and 2506 Da. In the present study, the roasted stones were additionally found to contain two ellagic acid derivatives (EAd), namely, EAd I, with the content ranging from 0.72 to 7.01 mg/100 g dw, and EAd II, with the content ranging from 1.35 to 7.15 mg/100 g dw. EAd I displayed a deprotonated pseudomolecular ion at m/z = 469 $[M{-}H]^-$, which was identified as valoneic acid dilactone, VDL (MW = 470 Da), and fragment ions at m/z = 425 $[VDL - 44\ (CO_2){-}H]^-$ and m/z = 301 $[EA{-}H]^-$. EAd II showed a deprotonated pseudomolecular ion at m/z = 425 $[M{-}H]^-$, corresponding to the decarboxylated valoneic acid dilactone, DVDL (MW = 426 Da), and a fragment ion at m/z = 301 $[DVDL - 125\ ([gallic\ acid]^- {-}CO_2){-}H]^-$.

As in the case of ellagic acid, also contents of its derivatives were the lowest in the ecotype NN stones. Alternatively, the highest content of valoneic acid dilactone was determined in the stones from fruits of ‘Kresowiak’, and that of decarboxylated valoneic acid dilactone in the stones from fruits of ‘Podolski’. Fruit harvest time had a small but significant effect on ellagic acid content in raw stones from fruits of ‘Paczoski’ I and ‘Paczoski’ II cultivars, whereas the roasting process released similar amounts of ellagic acid in the stones from fruits of all cultivars and caused the formation of EA derivatives.

3.3. *Analysis of volatile compounds in roasted stones and in commercial coffee*

The analysis of the qualitative composition of volatile compounds of the roasted Cornelian cherry fruit stones and commercial products (Jacobs natural coffee and Kujawianka cereal coffee) allowed the detection of 58 compounds, whereas the analysis of degradation products revealed the presence of 51 compounds (Table 2). Depending on the Cornelian cherry variety, the stones contained 40–43 volatile compounds, compared to 26 volatile compounds identified in Kujawianka cereal coffee and to only 11 compounds found in Jacobs coffee. As many as 18 identified compounds were pyrazine derivatives. The lowest number of volatiles was determined in Jacobs coffee (only 11). The major volatile compound of the roasted stones was furfural, with the content ranging from 24.238% (‘Raciborski’) to 44.840% (ecotype NN). Another significant contributor to the analyzed material’s aroma was 2-ethyl-3,5-dimethyl-pyrazine, with its content ranging from 13.427% (ecotype NN) to 27.866% (‘Słowianin’). The compounds predominating in Jacobs coffee aroma included 2-furanmethanol (18.219%), 2–5-methyl-furancarboxaldehyde (16.769%), furfural (9.878%), and 3-methylbutanoatefurfuryl (9.637%). The major compounds of the Kujawianka coffee were three alkanes with contents of 36.290, 32.124, and 15.703%, which were not identified due to dubious degradation products.

The results of the statistical analysis of volatile compounds are presented in Fig. 4. The determined principal components (PC1: 81.90%, and PC2: 8.34%) were highly diverse for the stones analyzed. The results of the statistical analysis indicate that the aroma of the roasted stones from the fruits of all 10 Cornelian cherry cultivars was very similar, but it was significantly different from that of Kujawianka cereal coffee and slightly similar to that of the natural Jacobs coffee.

The volatile compound composition of the Jacobs coffee analyzed in our study seems to be very poor compared to literature data (López-Galilea, Fournier, Cid, & Guichard, 2006). The differences in the qualitative and quantitative composition of volatile compounds of the roasted stones from fruits of various Cornelian cherry cultivars were small (Table 2, Fig. 4). It should also be noted that the major volatiles identified in the roasted stones included pyrazine derivatives and other heterocyclic compounds. According to Cordoba, Fernandez-Alduenda, Moreno, and Ruiz (2020), the major volatile compounds of infusions from coffee grains include pyrazines and furans, accounting for 24% and 20% of total volatiles, respectively, followed by ketones, aldehydes, and pyrroles (15%, 11%, and 8%, respectively). López-Galilea et al. (2006) reported derivatives of furan and pyrazine to predominate among the volatile compounds identified in coffee grains. The pyrazines contributing to the aroma of Cornelian cherry stones in the present study also included compounds described by other authors as those contributing to the aroma of Arabica and Robusta coffees (López-Galilea et al., 2006). The major volatile compound of the roasted stones from Cornelian cherry fruits was furfural. It was also detected in roasted natural coffee grains (Ludwig, Sánchez, De Peña, & Cid, 2014). Furfural is formed upon heat treatment, during which the key roles are ascribed to Maillard reactions and sugar caramelization. As reported by Murkovic and Bornik (2007), it is formed at the initial stage of coffee grain roasting, and its high content is typical of light-roasted products. The temperature and duration of the roasting process applied in our study (170 °C and 0.5 h, respectively) promoted furfural synthesis. According to Majcher et al. (2013), the major aroma compounds of cereal coffee include 2,3-butanedione, 2,3-pentanedione, and 4-hydroxy-2,5-dimethyl-3-(2H)-furanone. These authors also reported that the pyrazine residues 3-isobutyl-2-methoxypyrazine and 2-ethyl-3,5-dimethylpyrazine served the key role in cereal coffee aroma development during its roasting. Also, they emphasized that no 2-ethyl-3,5-dimethylpyrazine was detected in cereal

Table 1

Chemical compounds (mg/100 g DW) in cornelian cherry raw and roasted stone and commercial products (Kujawianka and Jacobs).

Cultivar/ ecotype	Loganic acid 375 [M−H]$^-$ 213 [M−162−H]$^-$ (*m/z*)		Cornuside 541 [M−H]$^-$ 379 [M−162−H]$^-$ (*m/z*)		**Total iridoids**		Valoneic acid dilactone 469 [M−H]$^-$ 425 [M−44−H]$^-$ (*m/z*)		Ellagic acid 301 [M−H]$^-$ (*m/z*)		Decarboxylated valoneic acid dilactone 425 [M−H]$^-$ 301 [M−125−H]$^-$ (*m/z*)		Total ellagic acid derivatives		Total phenolic acids*	
	raw	roasted	raw	roasted	raw	roasted	raw	roasted	raw	roasted	raw	roasted	raw	roasted	raw	roasted
‘Alesha’	76.38 ± 0.56 f**	74.25 ± 0.35 g	3.89 ± 0.08 i	0	80.27 ± 0.48 f	74.25 ± 0.35 g	nd	1.74 ± 0.02 f	2.31 ± 0.10 cd	20.15 ± 0.70 h	nd	2.21 ± 0.14 g	2.31 ± 0.10 cd	24.10 ± 0.87 f	nd	nd
‘Elegantnyi’	61.07 ± 0.25 h	91.46 ± 0.14 d	6.00 ± 0.05 g	0	67.07 ± 0.31 g	91.46 ± 0.14 d	nd	4.70 ± 0.03 d	2.28 ± 0.11 d	34.60 ± 0.37 f	nd	5.28 ± 0.25 c	2.28 ± 0.11 d	44.58 ± 0.59 d	nd	nd
‘Koralovyi’	87.13 ± 0.24 d	96.02 ± 0.16 c	9.20 ± 0.15 e	0	96.33 ± 0.09 d	96.02 ± 0.16 c	nd	6.47 ± 0.10 b	2.52 ± 0.18 c	45.88 ± 0.19 c	nd	5.17 ± 0.06 c	2.52 ± 0.18 c	57.51 ± 0.35 b	nd	nd
‘Kresowiak’	98.54 ± 0.66 b	125.16 ± 1.62 a	16.72 ± 0.38 a	0	115.26 ± 1.04 a	125.16 ± 1.62 a	nd	7.01 ± 0.07 a	2.10 ± 0.02 de	48.94 ± 0.38 a	nd	5.79 ± 0.07 b	2.10 ± 0.02 de	61.74 ± 0.38 a	nd	nd
NN	93.48 ± 0.33 c	88.30 ± 0.92 e	10.80 ± 0.31 c	0	104.28 ± 0.01 b	88.30 ± 0.92 e	nd	0.72 ± 0.04 g	3.18 ± 0.04 b	9.57 ± 0.16 i	nd	1.35 ± 0.04 h	3.18 ± 0.04 b	11.64 ± 0.08 g	nd	nd
‘Paczoski’ I	92.72 ± 0.69 c	74.76 ± 0.85 g	7.00 ± 0.03 f	0	99.72 ± 0.73 c	74.76 ± 0.85 g	nd	3.58 ± 0.14 e	1.98 ± 0.06 e	29.01 ± 0.65 g	nd	2.87 ± 0.11 f	1.98 ± 0.06 e	35.47 ± 0.41 e	nd	nd
‘Paczoski’ II	87.78 ± 0.66 d	80.71 ± 0.39 f	5.36 ± 0.03 h	0	93.13 ± 0.96 e	80.71 ± 0.39 f	nd	3.74 ± 0.08 e	1.63 ± 0.07 f	29.07 ± 0.23 g	nd	3.02 ± 0.05 f	1.63 ± 0.07 f	35.82 ± 0.35 e	nd	nd
‘Podolski’	67.73 ± 0.18 g	95.77 ± 0.58 c	11.32 ± 0.06 b	0	79.05 ± 0.24 f	95.77 ± 0.58 c	nd	6.62 ± 0.21 b	3.40 ± 0.12 a	47.53 ± 0.67 b	nd	7.15 ± 0.05 a	3.40 ± 0.12 a	61.30 ± 0.93 b	nd	nd
‘Raciborski’	82.66 ± 0.78 e	120.45 ± 1.28 b	10.00 ± 0.11 d	0	92.66 ± 0.89 e	120.45 ± 1.28 b	nd	5.07 ± 0.23 c	1.15 ± 0.05 g	37.01 ± 0.28 e	nd	3.50 ± 0.08 e	1.15 ± 0.05 g	45.59 ± 0.60 d	nd	nd
‘Słowianin’	106.07 ± 0.43 a	95.20 ± 0.37 c	9.33 ± 0.33 e	0	115.39 ± 0.76 a	95.20 ± 0.37 c	nd	4.65 ± 0.34 d	3.01 ± 0.09 b	42.46 ± 0.46 d	nd	4.18 ± 0.04 d	3.01 ± 0.09 b	51.29 ± 0.84 c	nd	nd
Kujawianka	nd		nd		nd		nd		nd		nd		nd		0.55 ± 0.01	
Jacobs	nd		nd		nd		nd		nd		nd		nd		197.20 ± 1.41	

*expressed as 5-caffeoylquinic acid derivatives; **- small letter stand as homogenous group; nd—non detected.

Table 2
Volatile compounds detected in roasted cornelian cherry stone (relative %).

No in group	Compound	Odour type*	Exp. Retention Index	'Alesha'	'Elegantnyi'	'Koralovyi'	'Kresowiak'	NN	'Paczoski' I	'Paczoski' II	'Podolski'	'Raciborski'	'Słowianin'	Kujawianka	Jacobs
Alkanes															
1	Unknown alkane isomer	–	n.d.											1.258	
2	Unknown alkane isomer	–	n.d.											15.703	
3	Unknown alkane isomer	–	n.d.												1.322
4	Unknown alkane isomer	–	n.d.												3.394
5	Unknown alkane isomer	–	n.d.											36.290	
6	Unknown alkane isomer	–	n.d.												2.756
7	Unknown alkane isomer	–	n.d.											32.124	
Total				0	0	0	0	0	0	0	0	0	0	85.375	7.472
Aldehydes															
1	2-metylopropanal	aldehydic, breads	550	0.118	0.087	0.063	0.052	0.081	0.117	0.072	0.137	0.148	0.028		
2	2-methyl-butyraldehyde	coffee, nutty	914	1.302	0.851	0.255	0.575	0.267	0.219	0.675	0.910	1.516			
3	3-methyl-butanal	chocolate, peach	918	1.183	0.751	0.342	0.644	0.297	0.453	0.977	1.065	1.372	1.268		
4	(E)-2-Butenal	flower	1039	0.067	0.059	0.060	0.058	0.061	0.054	0.039	0.086	0.053	0.053		
5	Hexanal	green, fruity	1083	0.237	0.158	0.315	0.241	0.174	0.169	0.348	0.33	0.241	0.288		
6	Benzaldehyde	fruity, sharp, almond	1520	0.263	0.233	0.271	0.376	0.308	0.309	0.286	0.211	0.401	0.343		
Total				3.170	2.139	1.306	1.946	1.188	1.321	2.397	2.739	3.731	1.980	0	0
Ketones															
1	2-pentanone	sweet, fruity	980	0.090	0.074	0.102	0.07	0.118	0.159	0.097	0.111	0.108	0.092		
2	4-hydroxy-4-methyl-2-pentanone	characteristic	1358	0.092	0.907	0.409	0.419	0.024	0.421	1.610	2.942	0.045	1.025		
Total				0.182	0.981	0.511	0.489	0.142	0.580	1.707	3.053	0.153	1.117	0	0
Sulphuric compounds															
1	2-isopropyl-4-methyl-thiazole	fruit tropical	1346	0.031	0.041	0.03	0.063	0.03	0.078	0.047	0.031	0.052	0.016		
2	Dimethyl trisulfide	alliaceous, onion garlic	1377	0.135	0.313	0.098	0.235	0.011	0.125	0.225	0.179	0.150	0.143		
3	2.5-diethyl-4-methylthiazole	green nutty	n.d.	0.099	0.107	0.083	0.120			0.109	0.065	0.081	1.418		
4	2-furanmethanethiol	coffee roasted	1430	0.209	0.223	0.188	0.119	0.310	0.132	0.084	0.136	0.178	0.122	0.631	2.287
5	Disulfide 1-methylethyl 2-propen-1-yl	truffle, garlic, onion	n.d.	0.072	0.068	0.102	0.092	0.054	0.09	0.081	0.054	0.075	0.042		
Total				0.546	0.752	0.501	0.629	0.405	0.425	0.546	0.465	0.536	1.741	0.631	2.287
Pyrazine derivatives															
1	Pyridine	sour, fishy	746												0.800
2	p-pyrazine	nutty, cocoa roasted	1212	0.106	0.087	0.073	0.082	0.081	0.101	0.081	0.079	0.117	0.056		
2	2-methylpyrazine	nutty, roasted chocolate	1266	7.471	5.197	4.286	4.476	6.383	5.989	5.016	3.494	7.192	2.923		3.639
3	2,5-dimethyl-pyrazine	chocolate, cocoa roasted	1320	9.232	6.912	5.005	5.857	7.327	7.279	6.254	4.179	7.891	2.773	0.983	2.336
4	2,6-dimethyl-pyrazine	chocolate, cocoa roasted	1328	6.484	5.261	4.489	4.339	5.474	5.346	5.336	3.549	6.362	3.162		2.152
5	Ethylpyrazine	nutty, roasted chocolate.	1337	2.272	1.816	1.740	1.615	1.035	1.884	1.797	1.329	2.28	1.119		1.633
6	2,3-dimethyl-Pyrazine	nutty skin, caramellic	1343	0.386	0.452	0.278	0.258	0.328	0.349	0.265	0.240	0.375	0.159		0.578
7	2-ethyl-6-methyl-pyrazine	roasted potato	1383	3.479	4.220	3.436	3.215	1.952	2.190	3.501	2.135	3.127	0.028		2.523

(*continued on next page*)

Table 2 (*continued*)

No in group	Compound	Odour type*	Exp. Retention Index	'Alesha'	'Elegantnyi'	'Koralovyi'	'Kresowiak'	NN	'Paczoski' I	'Paczoski' II	'Podolski'	'Raciborski'	'Słowianin'	Kujawianka	Jacobs
8	2-ethyl-5-methyl-pyrazine	coffee, nutty roasted	1387	2.870	3.142	2.312	2.612	1.126	1.273	2.522	1.881	2.543	1.975		1.757
9	2-ethyl-3-methyl-pyrazine	nutty, peanut	1407	4.517	4.504	2.876	3.054	3.374	3.732	3.21	2.319	3.769	1.380		
10	Propylpyrazine	nutty barley roasted	1444												0.105
11	2,6-diethyl-pyrazine	cocoa roasted nutty	1444	0.177	0.200	0.157	0.179	0.154	0.206	0.170	0.104	0.163	0.090		2.920
12	2-ethyl-3.5-dimethyl-pyrazine	burnt, almond, coffee	1456	15.193	17.212	21.949	20.12	13.427	19.948	25.574	24.607	22.863	27.866		
13	2,3-dimethyl-5-ethyl-pyrazine	burnt roasted cocoa	1460												1.467
14	3-ethyl-2,5-dimethyl-pyrazine	cocoa roasted nutty	1462											1.348	0.683
15	2-ethenyl-6-methyl-pyrazine	roasted potato	1490	0.180	0.274	0.155	0.108	0.112	0.188	0.159	0.081	0.154	0.098		
16	3,5-diethyl-2-methyl-pyrazine	nutty, vegetable	1496	0.697	0.844	0.411	0.558	0.514	0.909	0.518	0.341	0.517	0.119		2.504
17	1-(6-methyl-2-pyrazinyl) ethanone	roasted coffee, coffee	1688	1.752	1.369	0.608	0.717	0.695	0.955	0.708	0.387	1.677	0.420		
18	2-(2-pyrazinyl)-2-propanol	coffee, roasted	n.d.	0.043	0.058			0.005				0.047			
19	2-methyl-3-(2-propenyl)-pyrazine	roasted, nutty	1740	0.160	0.093	0.074	0.089	0.125	0.076	0.099	0.023	0.058			
20	1-(2-furanylmethyl)-1H-pyrrole	fruity, coffee vegetable	1824												2.684
Total				55.019	51.641	47.849	47.279	42.112	50.425	55.21	44.748	59.135	42.168	2.331	24.981
Other heterocycle compounds															
1	2-pentyl-furan	fruity green	1231	0.393	0.043	0.178	0.232	0.313	0.163	0.115	0.259	0.230	0.094		
2	Furfura	bready, caramellic	1461	28.283	33.073	39.586	36.618	44.84	34.548	29.046	39.144	24.328	43.326		9.878
3	Acetylfuran	balsamic, cocoa, coffee	1499	2.095	3.092	2.364	2.869	1.246	3.112	2.528	2.380	2.763	1.703	0.833	
4	1-(2-furanyl)-ethanone	sweet balsamic almond	1500												2.191
5	3-methylbutanoatefurfuryl	berry fruity grape ripe	n.d.												9.637
6	5-methyl-2-furancarboxaldehyde	caramellic maple, spicy	1570	3.098	2.93	3.611	4.058	4.45	3.642	3.245	3.662	2.985	4.527	4.869	16.401
7	*N*-methyl-2-formyl pyrrole	roasted nutty	1626	1.366	1.638	0.953	1.544	0.933	1.538	1.173	0.734	1.446	0.237		1.755
8	5-ethyl-2-methyl-pyridin-4-amine	nutty potato roasted	n.d.	1.804	1.364	0.857	1.025	1.105	1.515	1.146	0.504	1.239	0.268		
9	2-furanmethanol	coffee caramellic bready	1660											1.057	17.819
10	Methyl pyrrol-2-yl ketone	nutty, coumarinic bready	1973	0.458	0.294	0.215	0.275	0.261	0.248	0.317	0.176	0.273	0.245		
11	Furaneol	caramellic sweet, candy	2031	2.147	1.007	0.803	1.145	1.540	1.076	1.058	0.585	1.570	0.633		

(*continued on next page*)

Table 2 (*continued*)

No in group	Compound	Odour type*	Exp. Retention Index	'Alesha'	'Elegantnyi'	'Koralovyi'	'Kresowiak'	NN	'Paczoski' I	'Paczoski' II	'Podolski'	'Raciborski'	'Słowianin'	Kujawianka	Jacobs
12	5-methyl-2-formyl-pyrrole	cereal, roasted	2063	0.216	0.104	0.103	0.114	0.200	0.215	0.074	0.010	0.069	0.145		
Total				39.86	43.545	48.67	47.88	54.888	46.057	38.702	47.454	34.903	51.178	6.759	57.681
Other compounds															
1	Unknown	–	n.d.	0.099	0.022	0.100	0.062	0.028	0.031	0.075	0.248	0.155	0.068		
2	Ethyl ester of acetic acid	ethereal/fruity	888	0.090	0.076	0.086	0.04	0.106	0.064	0.090	0.334	0.089	0.376		
3	Cyclotene	caramellic, coffee	1830	0.500	0.343	0.271	0.339	0.463	0.246	0.406	0.224	0.284	0.279		
4	4-methoxy-phenol	caramellic	1845	0.234	0.211	0.211	0.251	0.231	0.178	0.225	0.177	0.215	0.286		
5	2-methoxy-4-vinylphenol	woody roasted, peanut	2188	0.300	0.290	0.495	1.085	0.440	0.673	0.639	0.558	0.799	0.807	4.904	5.147
Total				1.223	0.942	1.163	1.777	1.268	1.192	1.435	1.541	1.542	1.816	4.904	5.147

*_ Example odor described on http://www.thegoodscentscompany.com.

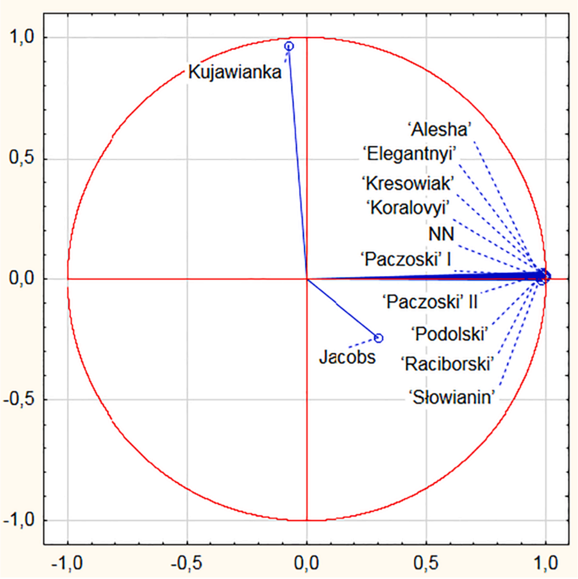

Fig. 4. Principal component analysis of violate compounds of roasted cornelian cherry stone.

coffee, while it was the major compound, next to furfural, in the roasted stones of Cornelian cherry fruits analyzed in our study. The composition of volatile compounds determined in the roasted stones of Cornelian cherry fruits is similar to that determined for coffee beans by other authors (Ludwig et al., 2014). However, noteworthy are the temperature, time, and pressure of the infusion, which result in the extraction of various groups of volatile compounds that determine the organoleptic traits and chemical composition of infusions from coffee grains (Cordoba et al., 2020).

3.4. *Aroma sensory evaluation of roasted stones and of cereal coffee*

Results of sensory evaluation of the aroma of roasted and ground stones of four cultivars of Cornelian cherry 'Alesha', 'Paczoski' I, 'Raciborski', 'Podolski' and cereal coffee Kujawianka on a scale of 1 to 5 points are given in Fig. S1. The aroma of the roasted and ground stones varied depending on the cultivar of Cornelian cherry. The stones of cultivars Raciborski and Podolski were rated the highest, that is, 3.98 and 3.95 points, respectively (on a scale of 1 to 5 points). The commercial grain coffee Kujawianka (3.02 points) and 'Alesha' stones (2.93 points) were evaluated significantly lower than the listed samples. The 'Alesha' seed aroma was described as the most intense and the aroma of cereal coffee as the least perceptible.

In addition, the acceptability of roasted and ground stones was determined with a nine-point hedonic scale. The results are shown in Fig. S2. The flavor of the seeds was positively assessed by 95% of respondents ("liked very much" – 30%, "liked moderately" – 45% and "liked slightly" – 20%). Only 5% of the evaluators indicated "disliked slightly". The results of this evaluation indicate a possible positive perception of the aroma of the roasted stones of Cornelian cherry by consumers.

4. Conclusion

The results of the present study show that both the raw and roasted stones of Cornelian cherry fruits show high antioxidant potential and represent a rich source of bioactive and volatile compounds. The roasting process causes some decrease in the antioxidant potential of Cornelian cherry fruit stones. Despite that, the roasted stones exhibited a higher antioxidant activity than commercial coffees.

The quantitative and qualitative composition of bioactive compounds differed due to the high temperature of the roasting process. The content of loganic acid in the roasted stones either increased or decreased, depending on the cultivar, whereas cornuside was completely degraded. Ellagic acid was released from the high-molecular structures during roasting, which resulted in an almost 30-fold increase in its concentration in the roasted stones. In addition, the high-temperature roasting contributed to the generation of its two derivatives: valoneic acid dilactone and decarboxylated valoneic acid dilactone.

Higher volatile aroma compounds were identified after the roasting of Cornelian cherry fruit stones than in cereal or natural coffees. The major volatile compound of the roasted stones turned out to be furfural. The stones also contained 18 pyrazine derivatives. The volatile compounds formed during the roasting process enable the roasted stones of Cornelian cherry to be used in the form of an additive as a valuable carrier of aroma resembling that of ground coffee.

According to the authors' knowledge, this is the first study focused on the valorization of Cornelian cherry fruit stones. It is based on the antioxidant potential, bioactive composition, volatile compounds, and aroma sensory evaluation of roasted stones. Such stones can be a coffee substitute or constitute an aromatic and bioactive addition to cereal coffees. Current studies of the authors' group are focused on the influence of the conditions of roasting the stones on their phytochemical composition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2021.129802.

References

Abdul Afiq, M. J., Abdul Rahman, R., Che Man, Y. B., AL-Kahtani, H. A. & Mansor, T. S. T. (2013). Date seed and date seed oil. International Food Research Journal 20(5), 2035–2043.

Akalın, M. K., Tekin, K., & Karagöz, S. (2012). Hydrothermal liquefaction of cornelian cherry stones for bio-oil production. *Bioresource Technology, 110*, 682–687.

Al-Sayed, E., Korinek, M., Esmat, A., Chen, G.-Y., Cheng, Y.-B., Hsieh, P.-W., … Hwang, T.-L. (2020). Anti-inflammatory, hepatoprotective and antioxidant activity of ellagitannin isolated from Melaleuca styphelioides. *Phytochemistry, 177*, 112429. https://doi.org/10.1016/j.phytochem.2020.112429.

Angın, D., Altintig, E., & Köse, T. E. (2013). Influence of process parameters on the surface and chemical properties of activated carbon obtained from biochar by chemical activation. *Bioresource Technology, 148*, 542–549.

Cordoba, N., Fernandez-Alduenda, M., Moreno, F. L., & Ruiz, Y. (2020). Coffee extraction: A review of parameters and their influence on the physicochemical characteristics and flavour of coffee brews. *Trends in Food Science and Technology, 96*, 45–60.

Czyżowska, A., Kucharska, A. Z., Nowak, A., Sokół-Łętowska, A., Motyl, I., & Piórecki, N. (2017). Suitability of the probiotic lactic acid bacteria strains as the starter cultures in unripe cornelian cherry (*Cornus mas* L.) fermentation. *Journal of Food Science and Technology, 54*(9), 2936–2946.

Dinda, B., Kyriakopoulos, A. M., Dinda, S., Zoumpourlis, V., Thomaidis, N. S., Velegraki, A., … Dinda, M. (2016). *Cornus mas* L. (cornelian cherry), an important European and Asian traditional food and medicine: Ethnomedicine, phytochemistry and pharmacology for its commercial utilization in drug industry. *Journal of Ethnopharmacology, 193*, 670–690.

Duarte, S. M. D. S., Abreu, C. M. P. D., Menezes, H. C. D., Santos, M. H. D., & Gouvêa, C. M. C. P. (2005). Effect of processing and roasting on the antioxidant activity of coffee brews. *Food Science and Technology, 25*(2), 387–393.

Fadel, H. H. M., Mageed, M. A., & Lotfy, S. N. (2008). Quality and flavour stability of coffee substitute prepared by extrusion of wheat germ and chicory roots. Amino Acids, 34(2), 307–314.

Fareez Edzuan, A. M., Noor Aliah, A. M., & Bong, H. L. (2015). Physical and chemical property changes of coffee beans during roasting. *American Journal of Chemistry, 5* (3A), 56–60.

Fikry, M., Yusof, Y. A., Al-Awaadh, A. M., Rahman, R. A., Chin, N. L., Mousa, E., & Lee Sin Chang, L. S. (2019a). Effect of the roasting conditions on the physicochemical, quality and sensory attributes of coffee-like powder and brew from defatted palm date seeds, Foods, 8, 61, 1–19.

Fikry, M., Yusof, Y. A., Al-Awaadh, A. M., Rahman, R. A., & Chin, N. L. (2020). Prediction of the shelf-life of date seeds brew by integration of acceptability and quality indices. *Journal of Food Measurement and Characterization, 14*(3), 1158–1171. https://doi.org/10.1007/s11694-019-00365-4.

Fikry, M., Yusof, Y. A., Al-Awaadh, A. M., Abdul Rahman, R., Chin, N. L., & Ghazali, H. M. (2019b). Antioxidative and quality properties of full-fat date seeds brew as influenced by the roasting conditions. *Antioxidants, 8*(7), 226. https://doi.org/10.3390/antiox8070226.

Genc, G. E., & Ozhatay, N. (2006). An ethnobotanical study in Catalca (European part of Istanbul) II. Turkish. *Journal of Pharmaceutical Sciences, 3*, 73–89.

Kucharska, A. Z. (2012). Active Compounds of Cornelian Cherry Fruit (Cornus mas L.). Wydawnictwo Uniwersytet Przyrodniczy Wrocław, (148) [in Polish].

Kucharska, A. Z., Szumny, A., Sokół-Łętowska, A., Piórecki, N., & Klymenko, S. V. (2015). Iridoids and anthocyanins in cornelian cherry (*Cornus mas* L.) cultivars. *Journal of Food Composition and Analysis, 40*, 95–102.

Kucharska, A. Z., Sokół-Łętowska, A., & Piórecki, N., (2011). Morfologiczna, fizykochemiczna i przeciwutleniająca charakterystyka owoców polskich odmian derenia właściwego (Cornus mas L.). Żywność. Nauka. Technologia. Jakość., 3 (76), 78–89. [in Polish].

Kucharska, A. Z., Szumny, A., Sokół-Łętowska, A., & Zając, K. (2009). Fatty acid compositions of seed oils of cornelian cherry (*Cornus mas* L.). *Acta Biochimica Polonica, 56 Suppl.*(2), 21–22.

López-Galilea, I., Fournier, N., Cid, C., & Guichard, E. (2006). Changes in headspace volatile concentrations of coffee brews caused by the roasting process and the brewing procedure. *Journal of Agricultural and Food Chemistry, 54*(22), 8560–8566.

Ludwig, I. A., Sánchez, L., De Peña, M. P., & Cid, C. (2014). Contribution of volatile compounds to the antioxidant capacity of coffee. *Food Research International, 61*, 67–74.

Majcher, M. A., Klensporf-Pawlik, D., Dziadas, M., & Jeleń, H. H. (2013). Identification of aroma active compounds of cereal coffee brew and its roasted ingredients. Journal of Agricultural and Food Chemistry, 20, 61(11), 2648–54.

Maqsood, S., Adiamo, O., Ahmad, M., & Mudgil, P. (2020). Bioactive compounds from date fruit and seed as potential nutraceutical and functional food ingredients. *Food Chemistry, 308*, 125522. https://doi.org/10.1016/j.foodchem.2019.125522.

Murkovic, M., & Bornik, M.-A. (2007). Formation of 5-hydroxymethyl-2-furfural (HMF) and 5-hydroxymethyl-2-furoic acid during roasting of coffee. *Molecular Nutrition & Food Research, 51*(4), 390–394.

Nowicka P., Gładzik, M., Wojdyło, A., & Oszmiański, J. (2018). Pestka z wiśni – surowiec odpadowy o wysokim potencjale prozdrowotnym. Składniki bioaktywne surowców i produktów roślinnych., ISBN 978-83-946796-1-3, 154–165 [in Polish].

Nowicka, P., & Wojdyło, A. (2019). Content of bioactive compounds in the peach kernels and their antioxidant, anti-hyperglycemic, anti-aging properties. *European Food Research and Technology, 245*(5), 1123–1136.

Nowicka, A., Kucharska, A. Z., Sokół-Łętowska, A., & Fecka, I. (2019). Comparison of polyphenol content and antioxidant capacity of strawberry fruit from 90 cultivars of *Fragaria × ananassa*. Duch. *Food Chemistry, 270*, 32–46.

Okuda, T. (2005). Systematics and health effects of chemically distinct tannins in medicinal plants. *Phytochemistry, 66*(17), 2012–2031.

Ordoudi, S. A., Bakirtzi, C., & Tsimidou, M. Z. (2018). The potential of tree fruit stone and seed wastes in Greece as sources of bioactive ingredients. *Recycling, 3*(1), 9.

Özcan, M. M., Ünver, A., & Arslan, D. (2014). A research on evaluation of some fruit kernels and/or seeds as a raw material of vegetable oil industry. *Quality Assurance and Safety of Crops & Foods, 7*(2), 187–191.

Perova, I. B., Zhogova, A. A., Poliakova, A. V., Éller, K. I., Ramenskaia, G. V., & Samylina, I. A. (2014). Biologically active substances of cornelian cherry fruits (*Cornus mas L.). Voprosy Pitaniia, 83*(5), 86–94.

Przybylska, D., Kucharska, A. Z., Cybulska, I., Sozański, T., Piórecki, N., & Fecka, I. (2020). *Cornus mas* L. stones: A valuable by-product as an ellagitannin source with high antioxidant potential. *Molecules, 25*, 4646.

Rangkadilok, N., Tongchusak, S., Boonhok, R., Chaiyaroj, S. C., Junyaprasert, V. B., Buajeeb, W., … Satayavivad, J. (2012). In vitro antifungal activities of longan *(Dimocarpus longa*n Lour.) seed extract. *Fitoterapia, 83*(3), 545–553.

Sadowska, U., Żabiński, A., Szumny, A., & Dziadek, K. (2016). An effect of peppermint herb (*Mentha piperita* L.) pressing on physico-chemical parameters of the resulting product. *Industrial Crops and Products, 94*, 909–919.

Samsonowicz, M., Regulska, E., Karpowicz, D., & Leśniewska, B. (2019). Antioxidant properties of coffee substitutes rich in polyphenols and minerals. *Food Chemistry, 278*, 101–109.

Sokół-Łętowska, A., Kucharska, A. Z., Wińska, K., Szumny, A., Nawirska-Olszańska, A., Mizgier, P., & Wyspiańska, D. (2014). Composition and antioxidant activity of red fruit liqueurs. *Food Chemistry, 157*, 533–539.

Sozański, T., Kucharska, A. Z., Szumny, A., Magdalan, J., Bielska, K., Merwid-Ląd, A., … Trocha, M. (2014). The protective effect of the *Cornus mas* fruits (cornelian cherry) on hypertriglyceridemia and atherosclerosis through PPARα activation in hypercholesterolemic rabbits. *Phytomedicine, 21*(13), 1774–1784.

Švarc-Gajić, J., Cvetanović, A., Segura-Carretero, A., Mašković, P., & Jakšić, A. (2017). Functional coffee substitute prepared from ginger by subcritical water. *The Journal of Supercritical Fluids, 128*, 32–38.

Szumny, D., Sozański, T., Kucharska, A. Z., Dziewiszek, W., Piórecki, N., Magdalan, J., … Szumny, A. (2015). Application of cornelian cherry iridoid-polyphenolic fraction and loganic acid to reduce intraocular pressure. *Evidence-Based Complementary and Alternative Medicine, 2015*, 1–8.

Tang, Y. Y., He, X. M., Sun, J., Li, C. B., Li, L., Sheng, J. F., & Li, J. M. (2019). Polyphenols and alkaloids in byproducts of Longan fruits (*Dimocarpus Longan* Lour.) and their bioactivities. *Molecules, 24*(6), 1186.

Vidrih, R., Cejic, Ž., & Hribar, J. (2012). Content of certain food components in flesh and stones of the cornelian cherry (*Cornus mas* L.) genotypes. *Croatian. Journal of Food Science and Technology, 4*(1), 64–70.

Zafrilla, P., Ferreres, F., & Tomás-Barberán, F. A. (2001). Effect of processing and storage on the antioxidant ellagic acid derivatives and flavonoids of red raspberry (*Rubus idaeus*) jams. *Journal of Agricultural and Food Chemistry, 49*(8), 3651–3655.

Zhen, T. Y., & Xiao, J. X. (2014). Major components and antioxidant capability analysis of cherry stone. *Food Research and Development, 35*, 112–114.