processes

MDPI

Article

Analysis of Selected Physicochemical Properties of Commercial Apple Juices

Leszek Rydzak [1], Zbigniew Kobus [2,*], Rafał Nadulski [3], Kamil Wilczyński [3], Anna Pecyna [2], Francesco Santoro [4], Agnieszka Sagan [1], Agnieszka Starek-Wójcicka [1] and Monika Krzywicka [2]

1. Department of Biological Bases of Food and Feed Technologies, University of Life Sciences, 20-612 Lublin, Poland; leszek.rydzak@up.lublin.pl (L.R.); agnieszka.sagan@up.lublin.pl (A.S.); agnieszka.starek@up.lublin.pl (A.S.-W.)
2. Department of Technology Fundamentals, University of Life Sciences, 20-612 Lublin, Poland; anna.pecyna@up.lublin.pl (A.P.); monika.gruszecka@up.lublin.pl (M.K.)
3. Department of Food Engineering and Machines, University of Life Sciences, 20-612 Lublin, Poland; rafal.nadulski@up.lublin.pl (R.N.); kamilwilczynski100@wp.pl (K.W.)
4. Department of Agro-Environmental Science, University of Bari Aldo Moro, 165/A-70125 Bari, Italy; francesco.santoro@uniba.it

* Correspondence: zbigniew.kobus@up.lublin.pl; Tel.: +48-81-5319-746

Received: 6 November 2020; Accepted: 12 November 2020; Published: 14 November 2020

check for updates

Abstract: The paper presents the comparison of quality of six different commercial apple juices produced in Poland. The apple juices came from two different Polish companies. From each manufacturer three various juices were selected: two cloudy and clarified one produced as a mixture of different apple varieties. The following properties were evaluated: density, soluble solid content, viscosity, total phenolic contents, phenolic acid, and antiradical activity. The obtained results showed that three from fourth cloudy juices (M1Sz, M1A and M2A) differed from clarified juices. The highest differences were noticed for total phenolic contents, phenolic acids, antiradical activity and viscosity. The values of these properties ranged between 60.72–103.6 mg GAE$\cdot$100^{-1} mL^{-1} for phenolic contents, 78.3–90.9% for antiradical activity and 2.68–5.79 mPa$\cdot$s for viscosity. The remaining cloudy juice (M2Sz) was more similar to the clarified ones. The strong correlation between total phenolic content and antiradical activity of apple juices was found. The high correlation coefficient obtained between these features indicates that both producers do not apply excessive amounts of vitamin C during the production of cloudy apple juices. There was also a strong interrelation between the density of juice and solid soluble content. However, no correlation was found between the solid soluble content and the viscosity of the tested juices.

Keywords: commercial apple juice; total phenolic contents; antiradical activity; DPPH; correlation analysis

1. Introduction

Poland is the largest producer and exporter of apples in the European Union. In 2017, production reached 3.08 million tons [1]. Due to overproduction of dessert apple almost 50% of them are processed, mostly into concentrated juice [2].

The main constituent of apple juice is water which accounts for 70-97% of juice [3]. The second largest components are carbohydrates such as glucose, fructose, and sucrose [4]. The content of sugars ranges from 3 to 25%. In 100 mL apple juice contains also fiber (0.77 g), organic fruit acids (0.74 g), protein (0.07 g), potassium (116 mg), phosphorus (7.0 mg), magnesium (6.9 mg), calcium (4.2 mg) and vitamin C (1.4 mg) [5]. Among the most important constituents of apple juice are phenolic compounds, such as: hydroxycinnamic acids, dihydrochalcones, flavonols (quercetin glycosides), catechins and oligomeric procyanidins [6]. Polyphenols increase antioxidant potential of juice, affect lipid metabolism [7] and absorb the cholesterol [8].

The polyphenols content in apples can range widely from 10 mg to 500 mg $100^{-1} \cdot g^{-1}$ of raw material [9,10]. The amount of polyphenols in juices is much smaller. This is mainly due to clarification processes or thermal juice preservation (pasteurization) [11].

One of the quite popular commercial juices found on the Polish market are juices produced from the Antonówka and Szampion varieties. The content of polyphenols in these apples varies from 126.45–190 mg $100^{-1} \cdot g^{-1}$ [12,13] for the Szampion variety to 312.5 mg $100^{-1} \cdot g^{-1}$ [11] for the Antonówka variety. The content of polyphenols in juices obtained from the Szampion variety ranges from 69.8 to 104.4 mg GAE$\cdot 100^{-1}$ mL^{-1} [9], while in the case of the Antonówka lies within the range of 36.34 to 172.2 mg GAE$\cdot 100^{-1}$ mL^{-1} [9,11].

The levels of juice compounds are highly influenced by the production process [14,15]. Apple juice is commonly consumed as a clear juice, but there is a growing market for natural cloudy apple juice [16]. Cloudy juices, as opposed to clear juices have particles of solids distributed in a liquid phase. Such juices are characterized by a large amount of components with health promoting properties (polyphenols, vitamins, and fiber) [17,18].

The nutritional and bioactive quality of juice depends strongly on the apple cultivar used for processing [19,20], method of extraction and further process of juice treatment [21].

The exploration of the physicochemical properties of juices is crucial in analyzing juice nutritional and bioactive quality and can even be used for the authenticity of apple juice. The estimation of juice quality is based on such analysis as: solid soluble content, titratable acidity, ash, pH, proline, density, formal index values, sugars, non-volatile organic acids, minerals, amino acids, phenols, and isotopic carbon ratios [22]. The research results suggest that some physicochemical properties of fruit juices may be strongly related to each other. For example Vieira et al. [23] studied the antioxidant activity with the use of the DPPH reagent, and noted a close correlation with the content of polyphenols. Tsen and King [24] examined physical properties of banana puree, and noticed that density is related to soluble solids concentration and temperature.

The presence or absence of correlations between the individual properties of apple juice may also indicate the addition of enriching substances. Teleszko et al. [13] examined the content of polyphenols in apple juices and found that the addition of ascorbic acid in the amount of 500 mg$\cdot$kg^{-1} for apples affects the final content of polyphenols in juice. The ascorbic acid also changed the correlation between the content of polyphenols and DPPH (2,2-Diphenyl-1-picrylhydrazyl)-scavenging activity. In juices produced without the addition of vitamin C, the content of polyphenols significantly correlated with anti-radical activity (correlation coefficient $r = 0.51$), while in the case of juices enriched with vitamin C there was no such correlation. In the available literature, data on the correlation between the individual physicochemical properties of apple juices are limited.

The aim of the study was to compare selected the physicochemical properties of six different commercial apple juices produced in Poland and to extract additional information regarding the differences between individual juices based on correlation analysis.

2. Materials and Methods

2.1. Materials

The apple juices came from two different Polish companies. From each manufacturer three juices were selected: two cloudy ones produced from varieties Antonówka (*Malus domestica 'Antonówka Zwykła'*) and Szampion (*Malus domestica 'Szampion'*) and clarified one, produced as a mixture of several different varieties. The juices were stored in a refrigerator at a temperature of 4 °C before the experimental stage. The samples were taken for analysis over one week. The following properties were evaluated: density, soluble solid content, viscosity, pH, total phenolic content and antiradical activity. The following abbreviations were used for the different samples of juice:

M1M-manufacturer 1, mixture of varieties, clear juice,
M2M-manufacturer 2, mixture of varieties, clear juice,
M1Sz-manufacturer 1, Szampion variety, cloudy juice,
M2Sz-manufacturer 2, Szampion variety, cloudy juice,
M1A-manufacturer 1, Antonówka variety, cloudy juice,
M2A-manufacturer 2, Antonówka variety, cloudy juice.

Chemical composition of juices according to the producers' declaration is shown in Table 1.

Table 1. Chemical composition of juices according to the producers' specification.

Chemical Composition	**Juice Type**					
	M1M	**M2M**	**M1Sz**	**M2Sz**	**M1A**	**M2A**
Protein	0.0	<0.5	0.1	<0.5	0.2	0.1
Fat	0.0	<0.5	0.1	<0.5	0.2	0.1
Carbohydrates (including sugars)	11.0 11.0	11.0 11.0	10.2 10.2	11.0 11.0	10.5 10.4	11.0 11.0
Vitamin C	6.5 mg	no data	40 mg	12 mg	40 mg	no data

2.2. *Experimental Model*

The experimental chart is presented in Figure 1.

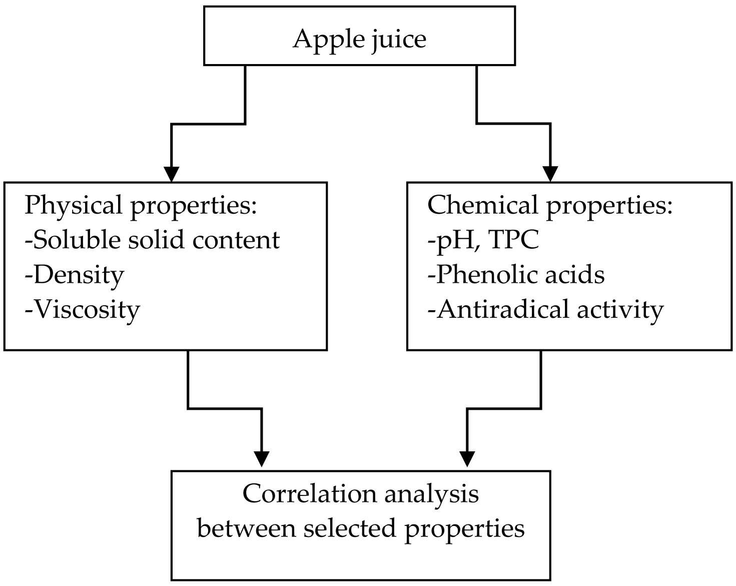

Figure 1. Experimental chart.

2.3. *Physical Properties*

2.3.1. Soluble Solid Content

Soluble solid content (SSC) of apple juice was determined as °Brix at an ambient temperature (20 ± 1 °C). The content of soluble substances in fruit juices was measured by a PAL-1 refractometer (Atago, Tokyo, Japan).

2.3.2. Density

The juice density was determined was calculated as a substance's mass per the volume it occupies using a calibrated density bottle of ISOLAB (Germany) with a volume of 25.657 mL at 20 °C.

2.3.3. Viscosity

Viscosity measurements were made using a Brookfield LVDV-II + PRO viscometer together with the Rheocalc V3.1-1 program. The tests were carried out at a constant temperature of 20 °C using the Brookfield TC-502 water bath. Measurements were made in the ultra low viscosity adapter (ULA) for samples with a volume of 16 mL.

2.4. Chemical Properties

2.4.1. Total Phenolic Content

Total phenolic content (TPC) of apple juice was determined according to the Folin-Ciocalteu (FC) method [25] with slight modification. Gallic acid was used as a standard and methanol gallic acid solution was diluted with methanol to give appropriate concentrations for a standard curve. Sample extract (0.2 mL) was mixed with 2 mL of methanol in a 25 mL volumetric flask. Then Folin-Ciocalteu reagent (2 mL, diluted 1:10) was added and allowed to react for 3 min. Next 2 mL of sodium carbonate (Na_2CO_3) solution was added and the mixture was made up to 25 mL with distilled water. After 30 min at room temperature in dark place the absorbance at 760 nm was measured using a spectrophotometer (UV-1800 Shimadzu, Japan). The results were expressed as mg gallic acid equivalent for 100 mL fresh juice (mg GAE·100^{-1} mL^{-1}).

2.4.2. Antiradical Activity (AA)

The antiradical activity of apple juices was evaluated using DPPH assay. For the analysis, 0.2 mL of apple juice was mixed with an aliquot of 5.8 mL of freshly prepared $6 \cdot 10^{-5}$ M DPPH radical in methanol. After 30 min standing at room temperature absorbance at 516 nm was measured using methanol as a blank. Antioxidant activity was expressed as percentage inhibition of the DPPH radical from following equation [26]:

$$\mathrm{AA}(\%) = \frac{\text{Absorbance of control} - \text{Absorbance of sample}}{\text{Absorbance of control}} \tag{1}$$

2.4.3. Determination of phenolic acids by HPLC

The individual phenolic acids in the apple juices were quantified using a modified version of the HPLC (High Performance Liquid Chromatography) method by Alberti et al. [27] the analysis was conducted using HPLC System S 600 Series equipment (Sykam GmbH, Eresing, Germany) coupled to a photodiode arrangement detector (PDA S 3345, Sykam). Before HPLC analysis, samples of cloudy apple juices were diluted 1:1 (v/v) with methanol and then centrifuged for 15 min at 3130 RCF. This treatment was omitted for samples of clear apple juice. All juices were filtered in a 0.20 µm syringe filter (Nylon, Macherey-Nagel, Düren, Germany), and 20 µL of sample was injected in the system, in triplicate. The separation was carried out using a Bionacom Velocity STR (3.0 mm × 250 mm, 5.0 µm) column at 25 °C. The mobile phases consisted of 25 mL·L^{-1} acetic acid (solvent A) and acetonitrile (solvent B). The system was run with at a flow rate of 1.0 mL·min^{-1} and following gradient program: 3–9% B (0–5 min); 9–11% B (5–15 min) and 11–3% B (15–17 min). The peaks of the compounds were identified and quantified by comparing the retention times and spectra of the samples with calibration curves that had been previously prepared with standards. The runs were monitored at 260 nm.

2.4.4. pH

The pH measurement was carried out at an ambient temperature (20 ± 1 °C) using digital a CP-411 pH-meter (Elmetron, Zabrze, Poland). The meter was calibrated with commercial buffer solutions at pH 6.8 and 4.0. Ten mL apple juice was inserted with a pH electrode and pH was recorded after stabilization.

2.4.5. Repeatability and Reproducibility of TPC and Antiradical Activity

The repeatability was calculated from six repetitions of the analysis of the same sample on the same day and conditions and express as the relative standard deviation (RSD). The reproducibility was calculated from six repetitions of the analysis in different days and daily prepared reagents and also express as the RSD. The repeatability was ranged between 2.4–4.2 for TPC and 2.8–4.0 for antiradical activity. The reproducibility was ranged between 3.9–5.2 for TPC and 3.2–5.8 for antiradical activity.

2.5. Statistical Analysis

Statistical analysis of the data was performed with Statistica software (Statistica 13.1, StatSoft Inc., Tulsa, OK, USA) using one-way and two-way analysis of variance (ANOVA). The significance of differences was tested using Tukey LSD test (p = 0.05). The normality of the distribution was verified by means of the Shapiro–Wilk test. Correlation coefficients (r) were determined by Pearson correlation matrix method. The graphs show mean values and whiskers representing standard deviations. All measurements were made in triplicate.

3. Results

3.1. Soluble Solid Content

The effect of juice kind on the soluble solids content was presented in Figure 2. The soluble solids content in studied juices varied from 10.77 to 12.07 °Brix. The highest content of soluble substances was found in the cloudy juices obtained from the Szampion variety and it amounted to 12.07 °Brix for manufacturer 1 and to 11.2 °Brix for manufacturer 2. Between the other juices there were no statistically significant differences and they were characterized by soluble substances in the range of 10.8–10.9 °Brix. The two-way analysis of variance showed a statistically significant effect of both the apple variety and the producer on soluble solid content in apple juices. The differences in the content of soluble substances result from varietal characteristics and the production method. The Szampion variety is characterized by a sweet taste and contains more soluble substances than the Antonówka variety. As a rule, cloudy juices are also characterized by higher extract content than clear juices. It is worth noting that all tested juices contained the minimum amount of sugars declared by producers on the packaging. In the case of producer 1, the actual values were always higher than those indicated on the packaging. In the case of producer 2, the actual values were almost identical with the values given on the labels.

According to a study by Kowalczyk [28] the soluble solids content in apple juice extracted in Polish industry is at the level of 11.0 to 12.4 °Brix. For comparison, Eisele and Drake [20] found that the soluble solids content in juices varies from 10.26 to 21.62 °Brix depending on apple variety. Soluble solid content above 10 °Brix is the minimum level for apple juices in accordance with the Polish Standard. According to the European Union standards, minimum extract levels for reconstituted fruit juice and reconstituted fruit purée is 11.2 °Brix [29]. This means that some of the tested juices did not meet these requirements.

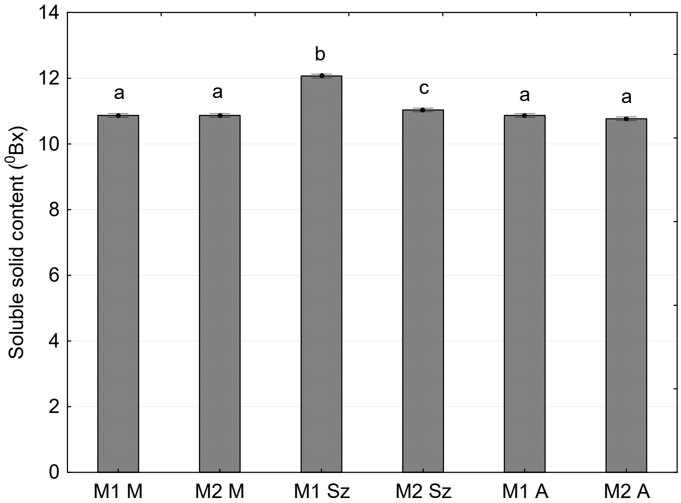

Figure 2. The effect of juice kind on soluble solids content. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

3.2. Density

The influence of provenance on density of apple juice was presented in Figure 3. The largest density (1.078 g·cm^{-3}) was found for the juice produced by manufacturer 1 from the Szampion variety. Lower densities were found in the case of clear juices (M1M and M2M) obtained on the basis of different apple varieties, for which the values were 1.046 and 1.045 g·cm^{-3}, respectively. The lowest densities were obtained for cloudy juices from the Antonówka variety for both manufacturers. There were no statistically significant differences in density values between these juices. The two-way analysis of variance showed a statistically significant only the apple variety density of apple juices. The obtained data correlate well with the results obtained by other authors. Żywica et al. [30] marked the density of apple juices in the range of 1.034–1.051 g·cm^{-3}, Kobus et al. [31] 1.034 to 1.041 g·cm^{-3}, and Nadulski et al. [32] 1.028 to 1.052 g·cm^{-3}. All these data fulfilled the minimum requirements for authentic apple juices given in the Code of Practice of European Fruit Juice Association, which are 1.045 g·cm^{-3} for juice from concentrate and 1.040 g·cm^{-3} for direct juices [33].

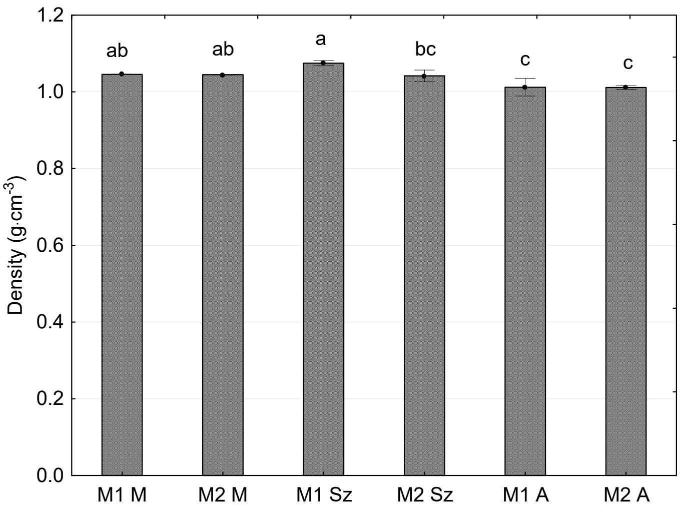

Figure 3. The effect of juice kind on density. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

3.3. Viscosity

The influence of provenance on viscosity of juices was presented in Figure 4. The viscosity of the tested juices was strongly dependent on the producer and variety of apples. The highest viscosity value was found in the case of the Antonówka variety (5.79 mP·s) for manufacturer 2. The second largest viscosity value was marked for juice from variety Antonówka, but produced by manufacturer 2 (3.89 mPa·s). The lowest viscosity was obtained for clear juices of both manufacturers produced on the basis of a mixture of several apple varieties and juice produced by manufacturer 2 from apples of Szampion variety (1.56–1.60 mPa·s). The juice produced by manufacturer 1 from Szampion variety had a significantly higher viscosity of 2.68 mPa·s. The two-way analysis of variance showed a statistically significant effect of both the apple variety and the producer on viscosity of apple juices. According to Will et al. [34] the viscosities of the cloudy apple juices were between 1.74 mPa·s and 2.15 mPa·s. Dynamic viscosity of juices tested by Nadulski et al. [32] ranged from 4.3 mPa·s to 15.1 mPa·s. The main substances responsible for creating the viscosity are pectins that mainly contain esterified 1,4-link α-D-galactosyluronic residues [35].

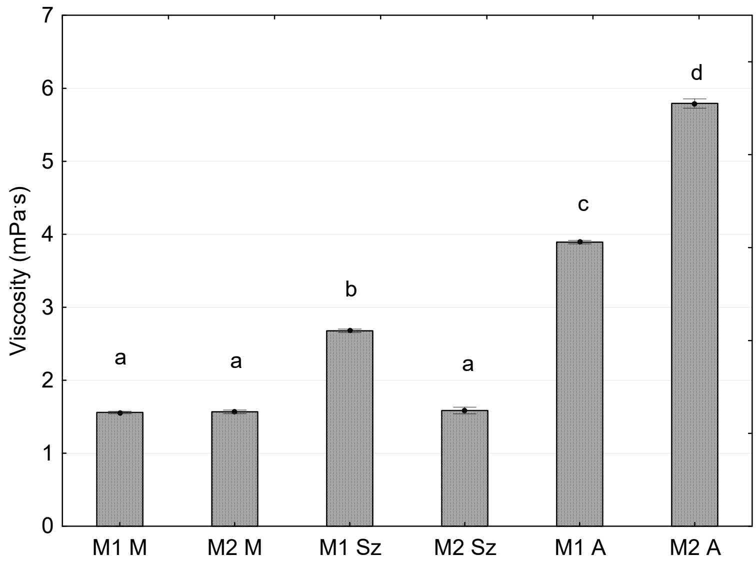

Figure 4. The effect of juice provenance on viscosity. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

3.4. pH

Figure 5 presents the influence of provenance on acidity of apple juices. Despite statistically significant differences in acidity, the extent of difference between all juices was minor and ranged from 3.38 to 3.47. The lowest pH value was obtained for clarified juice produced by manufacturer 1, and the highest was recorded in the case of the juice from Szampion variety produced by the same company. The two-way analysis of variance showed a statistically significant effect of both the apple variety and the producer on pH of apple juices. Similar results were also reported by much previous research. The pH values were determined to range from 3.34 to 3.68 [36] and from 3.39 to 3.77 [18]. The pH value of juices is influenced by the variety, date of apple harvest, the method of obtaining and further processing of juices. Giryn et al. [37] showed that the pH value of raw juices ranged from 3.39–3.77, and that of juices reconstructed from concentrate 2.91–3.29.

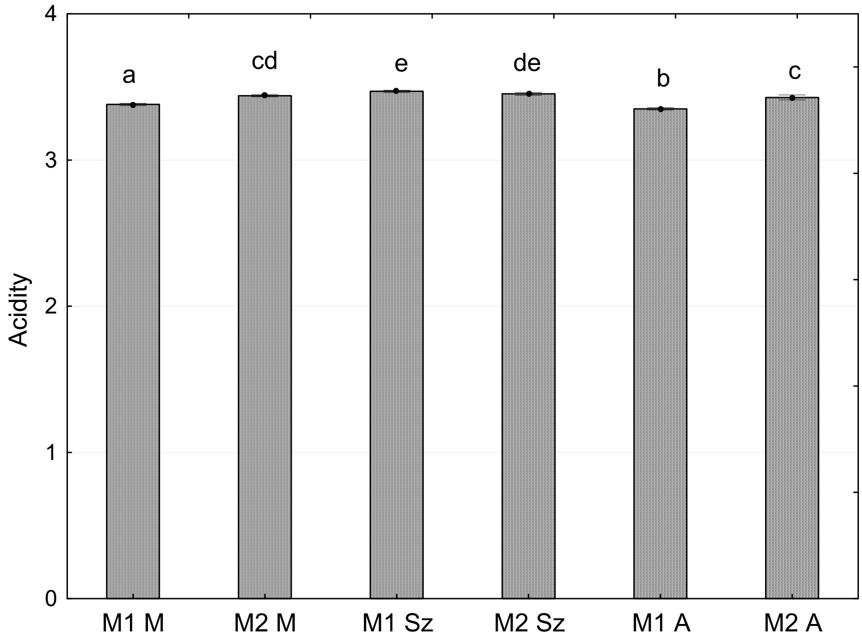

Figure 5. The effect of juice provenance on pH. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

3.5. Total Phenolic Content

The influence of provenance on total phenolic content of apple juice was presented in Figure 6. The highest content of polyphenols was marked for the juice of the Szampion variety produced by manufacturer 1, where the presence of tested compounds was found at 103.55 mg GAE$\cdot$100$^{-1}\cdot$mL^{-1}. The lowest content of polyphenols (40.75 mg GAE$\cdot$100$^{-1}\cdot$mL^{-1}) was obtained for clear juice produced by manufacturer 2. Generally, cloudy juices (except for M2Sz juice) contained much more polyphenols than clear juices, which is consistent with the literature data [38]. The two-way analysis of variance showed a statistically significant effect of both the apple variety and the producer on TPC in apple juices.

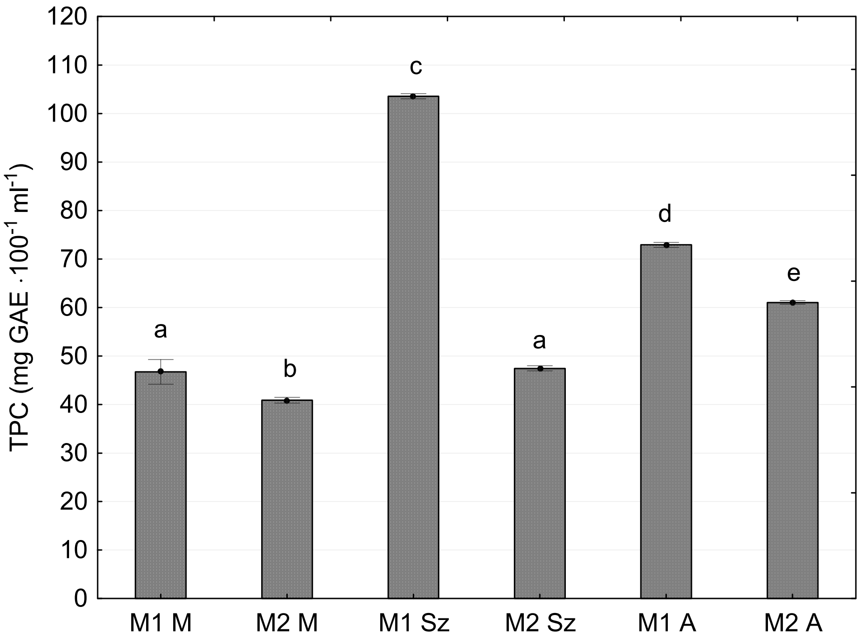

Figure 6. The effect of juice provenance on the total phenolic content. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

The big differences in the concentration of polyphenols can be attributed to raw material variety, cultivation conditions, climate, as well as the methods of juice extraction and processing [18]. The total phenolic content in juices produced in Europe varies within a broad range, from 10 to 500 mg GAE·100^{-1}·mL^{-1} [9,38,39].

An interesting fact is the higher content of polyphenols in all juices produced by the manufacturer M1. This may be due to differences in the juice production process. Czerwonka et al. [11] showed that losses of polyphenols caused by pasteurization ranged from 30 to 35% depending on the variety. An important stage is also the process of grinding apples into a mush. Teleszko et al. [13] showed that in the case of the Szampion variety, the addition of vitamin C during the apple grinding caused an increase in the polyphenol content from 190 to 389.66 mg GAE·100^{-1}·mL^{-1}. The rise in polyphenol content in juices can be explained by the protective effects of vitamin C on these compounds. It is worth noting that the amount of vitamin C in juices produced by the manufacturer M1 is much higher than at the M2 producer.

3.6. Concentration of Phenolic Acids

The concentration of phenolic acids in commercial apple juices under study is presented in Table 2. Differences in the phenolic acids content between cloudy and clear apple juices are obvious. Total phenolic acids amounts in cloudy apple juices varied between 33.07 and 49.69 mg 100^{-1}·mL^{-1} whereas in clear apple juices changed from 9.79 to 16.00 mg 100^{-1}·mL^{-1}. This finding is in good agreement with previously published data [38,40]. The highest content of phenolic acids was marked for the juice of the Szampion variety produced by manufacturer 1, and the lowest for clear juice produced by manufacturer 2. The main phenolic constituent among the tested acids was chlorogenic acid. The content of this acid varied from 30.28 to 48.32 mg 100^{-1}·mL^{-1} in cloudy apple juices, whereas in clear juices ranged from 6.71 to 12.68 mg 100^{-1}·mL^{-1}. The results are in good agreement with literature data where chlorogenic acid is the main polyphenolic substance in apple [41,42]. The cloudy juices also contained more caffeic acid than the clear juices. On the other hand, the content of gallic acid was about three times higher in clear juices as compared to cloudy juices. This is probably due to the fact that clear juices were made from different apple varieties, while cloudy juices were obtained from one specific variety (Szampion or Antonówka). There was only trace amounts of vanillic acid in the analyzed juices.

Table 2. Concentration of phenolic acid in commercial apple juices (mg 100^{-1}·mL^{-1}).

Chemical Composition	Juice Type					
	M1M	M2M	M1Sz	M2Sz	M1A	M2A
Gallic acid	1.45 ± 0.21a	1.62 ± 0.18a	0.57 ± 0.05b	0.42 ± 0.04c	0.48 ± 0.04c	0.33 ± 0.03d
Chlorogenic acid	12.68 ± 0.54a	6.71 ± 0.41b	46.41 ± 0.83c	32.11 ± 0.76d	48.32 ± 0.91c	30.28 ± 0.61d
Caffeic acid	1.88 ± 0.22a	1.46 ± 0.19b	2.72 ± 0.20c	2.17 ± 0.22d	2.72 ± 0.21c	2.47 ± 0.21e
Vanillic acid	TA	TA	TA	TA	TA	TA
Total acids	16.00 ± 0.97a	9.79 ± 0.78b	49.69 ± 1.08c	34.69 ± 1.02d	51.52 ± 1.15c	33.07 ± 0.84d

Average values in the raw marked with the same letter are not statistically significantly different (p < 0.05). TA-trace amounts.

3.7. Antiradical Activity

The antiradical activity is a very important quality characteristic of juices. The most popular method for measurement of antiradical activity of juice is application of stable radicals such as 2,2-diphenyl-1-picrylhydrazyl (DPPH). The influence of variety and manufacturer on the scavenging activity of apple juice was presented in Figure 7.

The highest DPPH-scavenging activity was obtained for juices from the Szampion variety produced by manufacturer 1. The lowest levels of scavenging activity were marked for clear juices. In general, as in the case of polyphenols, cloudy juices were characterized by a much higher ability to scavenge free radicals than clear juices, which is consistent with the literature data [38]. The two-way analysis of variance showed a statistically significant effect of both the apple variety and the producer on scavenging activity of apple juices. The differences in antioxidant activity may result from the different content of phenolic compounds in the tested juices. The chemical composition of the juice and the molecular structure of the main antioxidants affect the ability to convert free radicals. Teleszko et al. [13] showed that the addition of vitamin C significantly influences the antioxidant capacity of apple juices. In juices produced without the addition of an antioxidant, they found significantly lower antioxidant activity compared to samples containing ascorbic acid. It is worth noting that both cloudy apple juices from producer 1 were characterized by significantly higher antioxidant capacity compared to juices from producer 2. This is probably due to the addition of higher doses of ascorbic acid by producer 1 during the juice production process (Table 1).

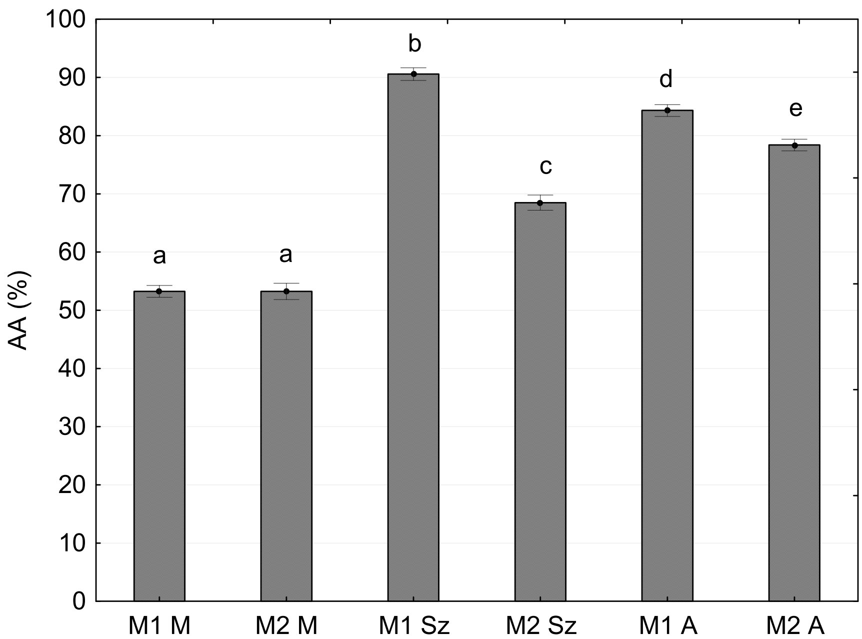

Figure 7. The effect of juice provenance on the antiradical activity. The bars marked with the same letter are not statistically significantly different ($p < 0.05$).

3.8. Correlation Analysis between Selected Properties of Apple Juice

Some of the physical properties such as density and viscosity can be affected by other properties. Figure 8 presents the analysis of the correlation between density and solid soluble content.

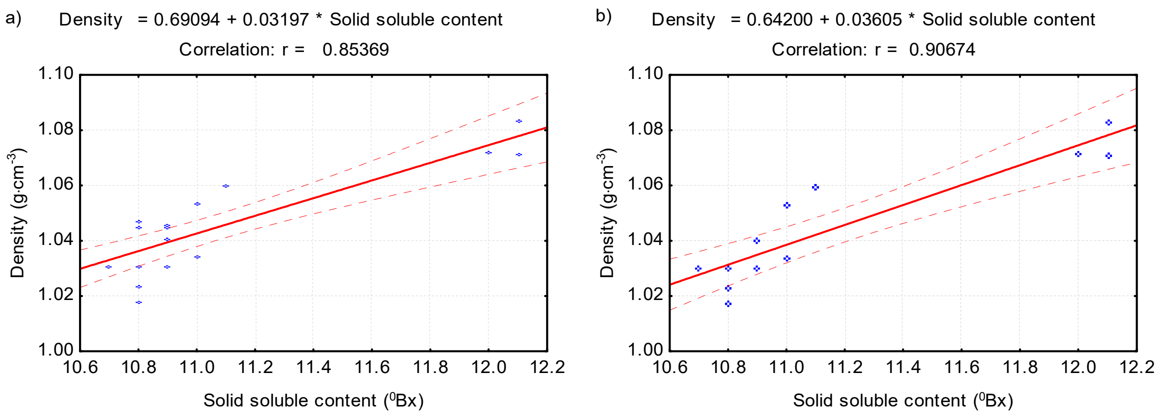

Figure 8. Correlation analysis between solid soluble content and density for: (**a**) all juices and (**b**) cloudy juices.

A strong correlation was found between the two studied features. In the case of the whole examination (all juices), the correlation coefficient was 0.85 and in the case of cloudy juices 0.91, respectively. The correlation between the studied features is easy to explain. In the case of juices, the basic ingredients are sugars, which constitute about 90% of the dry matter content. The increase in the refractive index, which in the case of juices expresses the general sugar content (°Brix) also causes a significant increase in the density of apple juice. By calculating the coefficient of determination (R^2), the variability of density in apple juices can be explained. Based on the determination coefficient, it can be concluded that the density variation is 72% and 83%, respectively, explained by the content of soluble substances, mainly sugars.

The correlations between the analyzed variables were also investigated by other authors [24,43–46]. They obtained significantly higher coefficients of determination between the studied features, but with regard to the same juice. The lower correlation coefficients obtained in this work indicate the existence of components other than sugars such as fiber (mainly pectins), organic acid and fats that affect the density, and also the greater variation in the chemical composition of the tested juices.

The content of soluble substances is an important factor that affects the rheological properties of juice, including viscosity. Figures 9 and 10 present an analysis of the correlation between viscosity and solid soluble content as well between viscosity and density of apple juices tested. In both cases, low negative values of correlation coefficients were obtained. However, these values were statistically insignificant at the level of probability ($p = 0.05$).

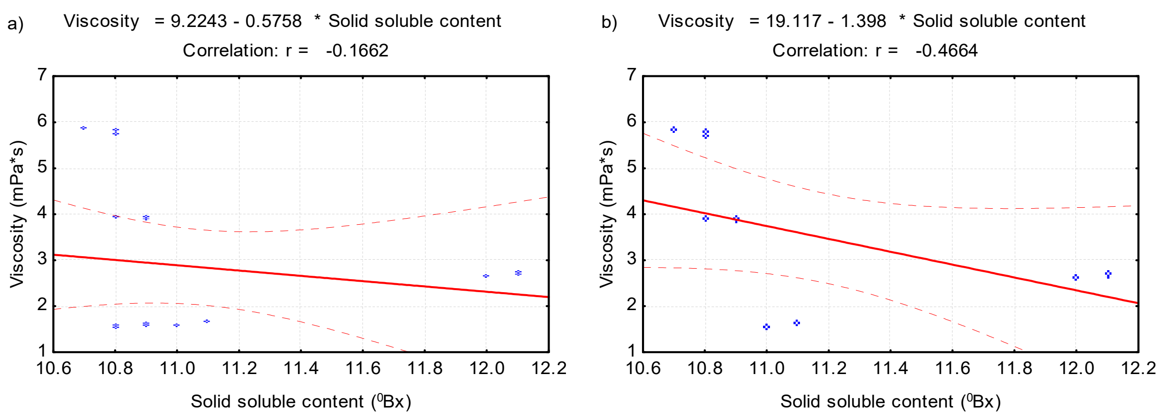

Figure 9. Correlation analysis between solid soluble content and density for: (**a**) all juices and (**b**) cloudy juices.

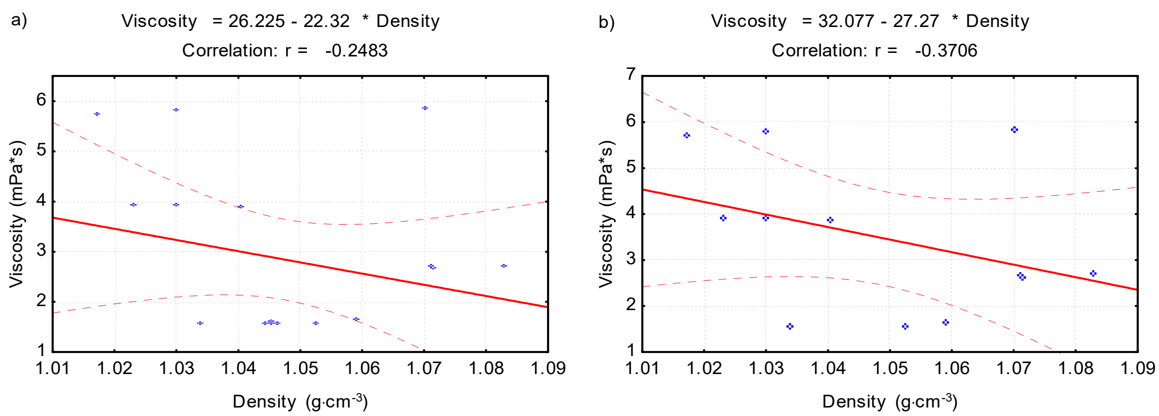

Figure 10. Correlation analysis between viscosity and density for: (**a**) all juices and (**b**) cloudy juices.

The correlation between the content of soluble substances and the viscosity of juices is a well-known issue. There are equations in the literature describing the exponential effect of concentration on the apparent viscosity of fruit juices [47–50]. However, these works are based on the same juice that together with the change in concentration increases its viscosity. The increase in viscosity of juices with increasing concentration is related to the presence of simple sugars and disaccharides, which at higher concentration have much higher viscosity values.

The lack of significant correlation between total soluble content and juice viscosity indicates the presence of components other than simple sugars, which significantly affect the viscosity of the juice. The substances that significantly affect the viscosity of fruit juices include polysaccharides (pectin, cellulose, hemicelluloses, starch) and proteins. Clarification and enzymatic treatment allows reducing juice viscosity by up to 60% [51]. The cloudy juices that are not clarified are characterized by a significantly higher level of viscosity. Thus, probably the higher presence of pectin compounds, especially in juices from the Antonówka variety, contributed to the lack of correlation between the content of soluble substances and viscosity.

Figure 11 presents the correlation analysis between antiradical activity and polyphenol content in apple juices tested.

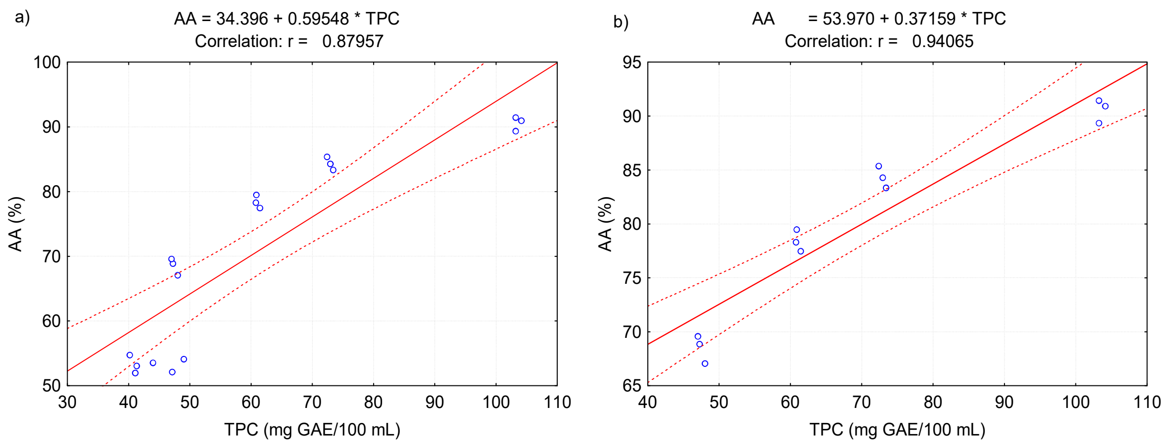

Figure 11. Correlation analysis between total phenolic content and antiradical activity for: (**a**) all juices and (**b**) cloudy juices.

A strong positive correlation coefficient was obtained for the examined features, amounting to 0.88 for the whole sample (all juices) and 0.94 for cloudy juices, respectively. It can therefore be concluded that the antiradical activity of tested apple juices can be explained appropriately for all juices in 77% and for cloudy juices in 88% presence of polyphenols. Generally higher content of polyphenols should also result in higher antiradical activity of juices. Strong correlations between the studied features at the level of 0.939 for the skin and 0.716 for the flesh of apple, respectively, were noted by Vieira et al. [23] and by Chinnici et al. [52] during examining of peels and pulps from cv. Golden Delicious apple. On the other hand, Wolfe et al. [53] did not find any correlation between the total phenolic content and the antioxidant activity of apple tissues.

The reason for the weak correlation between antioxidant activity and total phenolic can be explained by several factors, including the presence of different active compounds in the juice, the synergistic effects of different compounds, the methods used for antioxidant reactions and experimental conditions [54].

Lu and Foo [55] showed that the DPPH-scavenging activity of polyphenols contained in apples decreased in the following order: quercetin glycosides > procyanidins >> chlorogenic acid >> phloridzin. All the polyphenols with the exception of phloridzin, demonstrated 2–3 times better DPPH-scavenging activities then vitamin C and E.

The study found a strong correlation between the phenolic acid content and the antiradical activity of apple juices. The best correlation was found for the chlorogenic acid content (r = 0.95). Total phenolic acid by HPLC correlated with antioxidant activity with similar level r = 0.94. This is in a good agreement with research of Miller and Rice-Evans [56], who stated that chlorogenic acid is important antioxidant in apple juices. In turn, in studies conducted by Schempp et al. [57] with using the ABTS test (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid)) revealed a secondary role in the effect of chlorogenic acid on the antioxidant activity of apple juices. The authors showed that the substance most strongly contributed to the antioxidant potential of the tested apple juices was flavan-3-ols. Thus, the system used to assess the antioxidant activity significantly influences the obtained results.

A common practice in the production of cloudy apple juice is the addition of ascorbic acid. Teleszko et al. [13] showed that a large addition of ascorbic acid resulted in the lack of the correlation between the DPPH-scavenging activities and the content of polyphenols in apple juice. The high coefficient of correlation between free radical scavenging activity and polyphenol content indicates that both manufacturers do not apply excessive amounts of vitamin C during the production of cloudy apple juice.

4. Conclusions

This study shows that the cloudy juices were of better nutritional and bioactive quality than clarified ones for both producers. The highest differences were marked in total phenolic content, antiradical activity and viscosity. The values of these properties ranged between 60.72–103.6 mg GAE $100^{-1}\cdot mL^{-1}$ for phenolic contents, 78.3–90.9% for antiradical activity and 2.68–5.79 mPa·s for viscosity.

Statistical analysis of the tests results showed the strong correlation between total phenolic content and antiradical activity of apple juices. The high correlation coefficient (0.88 for all tested juices and 0.94 for cloudy juices) obtained between these features indicates that both producers do not apply excessive amounts of vitamin C during the production of cloudy apple juices. There was also a high interrelation between the density of juice and solid soluble content. However, no correlation was found between the solid soluble content and the viscosity of the tested juices. This finding suggests that tested juices contained different amounts of polysaccharides (pectin, cellulose, hemicelluloses, starch) and proteins. Thus, probably, the higher presence of pectin compounds are in Antonówka variety apples, resulting in a higher viscosity of the juices produced from it.

In general, juices from producer 1 were characterized by a higher content of polyphenols and antiradical activity. The probable reason was that the manufacturer 1 used higher doses of vitamin C during the grinding of apples, which correlates well with the higher content of vitamin C given on the juice packaging.

The exploration of the physicochemical properties of juices is crucial in analyzing juice nutritional and bioactive quality which is of great importance for the sustainability of food processing processes. The study indicates that analysis of correlation coefficients between the selected physicochemical properties can be an important element in extracting additional information about apple juices. High correlation coefficients explain the variability of one feature relative to another. Lower correlation coefficients indicate the presence of additional factors (for example, chemical substances) that influence the variability of the examined feature. Therefore, lower correlation coefficients are a premise for undertaking in-depth analyses of the studied variables.

Author Contributions: Conceptualization, Z.K. and R.N.; Methodology, Z.K., L.R. and A.P.; Formal analysis, Z.K. and F.S.; Investigation, K.W., R.N., Z.K., A.S.-W., M.K., A.S., Data curation, A.P.; Writing—original draft preparation, Z.K. and L.R.; Writing—review and editing, Z.K., L.R.; Visualization, F.S.; Supervision, Z.K. and L.R.; Project administration, Z.K. and F.S.; Funding acquisition, Z.K. and L.R. All authors have read and agreed to the published version of the manuscript.

Funding: Funded from the 'Excellent science' program of the Ministry of Science and Higher Education as a part of the contract no. DNK/SP/465641/2020 "The role of the agricultural engineering and environmental engineering in the sustainable agriculture development".

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Concise Statistical Yearbook of Poland. Warsaw. 2020. Available online: https://stat.gov.pl/obszary-tematyczne/roczniki-statystyczne/roczniki-statystyczne/maly-rocznik-statystyczny-polski-2020,1,22.html (accessed on 30 August 2020).
2. Płocharski, W.; Mieszczakowska-Frąc, M.; Rutkowski, K.; Konopacka, D. Tradycyjne i Innowacyjne Kierunki Zagospodarowania Jabłek w Polsce. Skierniewice. 2019. Available online: http://www.inhort.pl/files/program_wieloletni/PW_2015_2020_IO/spr_2019/Broszura_Plocharski_2019_Tradycyjne_zad.3.5.pdf (accessed on 30 August 2020).
3. Awolu, O.O.; Aderinola, T.A.; Adebayo, I.A. Physicochemical and rheological behaviour of African star apple (*Chrysophyllum albidium*) juice as affected by concentration and temperature variation. *J. Food Process Technol.* **2013**, *4*, 229–234.
4. Adou, M.; Tetchi, F.A.; Gbané, M.; Kouassi, K.N.; Amani, N.G.G. Physico-chemical characterization of cashew apple juice (*Anacardium occidentale*) from Yamoussoukro (Côte d'Ivoire). *Innov. Rom. Food Biotechnol.* **2012**, *11*, 32–43.
5. Souci, S.W.; Fachmann, W.; Kraut, H. *Food Composition and Nutrition Tables*, 6th ed.; Medpharm GmbH Scientific Publishers: Stuttgart, Germany, 2005.
6. Gerhauser, C. Cancer chemopreventive potential of apples, apple juice, and apple components. *Planta Med.* **2008**, *74*, 1608–1624. [CrossRef] [PubMed]
7. Akazone, Y. Characteristic and physiological functions of polyphenols from apple. *Biofactors* **2004**, *22*, 311–314. [CrossRef] [PubMed]
8. Aprikian, O.; Levrat-verny, M.A.; Besson, C.; Busserolles, J.; Remesy, C.; Demigne, C. Apple favorably affect parameters of cholesterol metabolism and of anti-oxidative protection in cholesterol feed rats. *Food Chem.* **2001**, *75*, 445–452. [CrossRef]
9. Oszmianski, J.; Wojdylo, A. Soki naturalnie mętne—Dobry kierunek w przetwórstwie jabłek. *Przem. Ferm. Owoc.-War.* **2006**, *2*, 20–22.
10. Wilczyński, K.; Kobus, Z.; Dziki, D. Effect of press construction on yield and quality of apple juice. *Sustainability* **2019**, *11*, 3630. [CrossRef]
11. Czerwonka, M.; Waszkiewicz-Robak, B. Wpływ procesu technologicznego na zawartość związków polifenolowych i aktywność przeciwutleniającą jabłek i przetworów jabłkowych. *Postępy Tech. Przetw. Spoż.* **2009**, *2*, 61–64.
12. Wojdyło, A.; Oszmiański, J.; Bielecki, P. Chemical composition, phenolic compounds and antioxidant activity of three varieties of apple from organic and conventional farming. *J. Res. Appl. Agric. Eng.* **2010**, *55*, 173–177.
13. Teleszko, M.; Kolniak, J.; Wojdyło, A.; Oszmiański, J. Wpływ odmiany jabłek na zawartość polifenoli i aktywność przeciwutleniającą w sokach mętnych. *Przem. Ferm. Owoc.-War.* **2010**, *7–8*, 40–42.
14. Kadakal, C.; Nas, S. Effect of heat treatment and evaporation on patulin and some other properties of apple juice. *J. Sci. Food Agric.* **2003**, *83*, 987–990. [CrossRef]
15. Suárez-Jacobo, A.; Rüfer, C.E.; Gervilla, R.; Guamis, B.; Roig-Sagués, A.X.; Saldo, J. Influence of ultra-high pressure homogenization on antioxidant capacity, polyphenol and vitamin content of clear apple juice. *Food Chem.* **2011**, *127*, 447–454. [CrossRef] [PubMed]
16. Braun, G. World market(s) for apple juice concentrate 2003—Missing apples? *Fruit Proc.* **2003**, *13*, 422–425.
17. Oszmiański, J.; Wolniak, M.; Wojdylo, A.; Wawer, I. Comparative study of polyphenolic content and antiradical activity of cloudy and clear apple juices. *J. Sci. Food Agric.* **2007**, *87*, 573–579. [CrossRef]
18. Nadulski, R.; Kobus, Z.; Wilczyński, K.; Zawiślak, K.; Grochowicz, J.; Guz, T. Application of freezing and thawing in apple *(Malus domestica)* juice extraction. *J. Food Sci.* **2016**, *81*, E2718–E2725. [CrossRef]
19. Cliff, M.; Dever, M.C.; Gayton, R. Juice extraction process and apple cultivar influences on juice properties. *J. Food Sci.* **1991**, *56*, 1614–1617. [CrossRef]
20. Eisele, T.A.; Drake, S.R. The partial compositional characteristics of apple juice from 175 apple varieties. *J. Food Compos. Anal.* **2005**, *18*, 213–221. [CrossRef]
21. Wilczyński, K.; Kobus, Z.; Nadulski, R.; Szmigielski, M. Assessment of the usefulness of the twin-screw press in terms of the pressing efficiency and antioxidant properties of apple juice. *Processes* **2020**, *8*, 101. [CrossRef]
22. Lee, S.H.; Wrolstad, R.E. Stable isotopic carbon composition of apples and their subfractions—Juice, seeds, sugars, and nonvolatile acids. *J. Assoc. Off. Anal. Chem.* **1988**, *71*, 795–797. [CrossRef]

23. Vieira, F.G.K.; Borges, G.D.S.C.; Copetti, C.; Pietro, P.F.D.; Nuens, E.D.C.; Fett, R. Phenolic compounds and antioxidant activity of the apple flesh and peel of eleven cultivars grown in Brazil. *Sci. Hortic.* **2011**, *128*, 261–266. [CrossRef]
24. Tsen, J.-H.; King, V.A.-E. Density of banana puree as a function of soluble solids concentration and temperature. *J. Food Eng.* **2002**, *55*, 305–308. [CrossRef]
25. Singleton, V.L.; Orthofer, R.; Lamuela-Raventos, R.M. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent. *Methods Enzymol.* **1999**, *299*, 152–178.
26. Sharma, S.; Kori, S.; Parmar, A. Surfactant mediated extraction of total phenolic content (TPC) and antioxidants from fruits juices. *Food Chem.* **2015**, *185*, 284–288. [CrossRef] [PubMed]
27. Alberti, A.; Zielinski, A.A.F.; Zardo, D.M.; Demiate, I.M.; Nogueira, A.; Mafra, L.I. Optimisation of the extraction of phenolic compounds from apples using response surface methodology. *Food Chem.* **2014**, *149*, 151–158. [CrossRef] [PubMed]
28. Kowalczyk, R. Wydajność tłoczenia i wskaźnik zużycia jabłek w procesie wytwarzania zagęszczonego soku jabłkowego. *Probl. Inż. Spoż.* **2004**, *12*, 20–30.
29. Directive 2012/12/EU of the European Parliament and of the Council of 19 April 2012 Amending Council Directive 2001/112/EC Relating to Fruit Juices and Certain Similar Products Intended for Human Consumption. Available online: https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2012:115:0001:0011:EN:PDF (accessed on 30 August 2020).
30. Żywica, R.; Banach, J.K. Mathematical correlations between selected quality attributes and electrical parameters of apple juice. *J. Food Process. Preserv.* **2019**, *43*, e14107. [CrossRef]
31. Kobus, Z.; Nadulski, R.; Anifantis, A.; Santoro, F. Effect of press construction on yield of pressing and selected quality characteristics of apple juice. In Proceedings of the Engineering for Rural Development, Jelgava, Latvia, 23–25 May 2018; Available online: https://www.researchgate.net/publication/325386311_Effect_of_press_construction_on_yield_of_pressing_and_selected_quality_characteristics_of_apple_juice (accessed on 24 January 2019).
32. Nadulski, R.; Kobus, Z.; Guz, T.; Strzałkowska, K.; Kosik, D. Usefulness of the selected apple cultivars for pressing in farm conditions. *Agric. Eng.* **2014**, *1*, 147–154.
33. AIJN Code of Practice for the Evaluation of Fruit and Vegetable Juice. Latest Amendments. 2007. Available online: http://www.aijn.org (accessed on 30 August 2020).
34. Will, F.; Roth, M.; Olk, M.; Ludwig, M.; Dietrich, H. Processing and analytical characterization of pulp-enriched cloudy apple juices. *LWT-Food Sci. Technol.* **2008**, *41*, 2057–2063. [CrossRef]
35. Rao, M.A.; Cooley, H.J. Rheology of tomato pastes in steady dynamic shear. *J. Texture Stud.* **1992**, *12*, 521–538. [CrossRef]
36. Karaman, K.; Sagdic, O.; Yilmaz, M.T. Potential of natamycin to control growth of *Zygosaccharomyces* spp. in apple juice during storage. *Int. J. Food Microbiol.* **2020**, *332*, 108771. [CrossRef]
37. Giryn, H.; Szteke, B.; Szymczyk, K. Wpływ procesu technologicznego i przechowywania na zawartość kwasów organicznych w zagęszczonych sokach jabłkowych. *Żywn-Nauk.Technol. Jakość* **2004**, *2*, 92–107.
38. Markowski, J.; Baron, A.; Mieszczakowska, M.; Plocharski, W. Chemical composition of french and polish cloudy apple juices. *J. Hortic. Sci. Biotechnol. Isafruit Spec. Issue* **2009**, *84*, 68–74. [CrossRef]
39. Gökmen, V.; Artik, N.; Acar, J.; Kahraman, N.; Poyrazoglu, E. Effects of various clarification treatments on patulin, phenolic compound and organic acid compositions of apple juice. *Eur. Food Res. Technol.* **2001**, *213*, 194–199. [CrossRef]
40. Escarpa, A.; Gonzalez, M.C. High-performance liquid chromatography with diode-array detection for the determination of phenolic compounds in peel and pulp from different apple varieties. *J. Chromatogr. A* **1998**, *823*, 331–337. [CrossRef]
41. Alonso-Salces, R.M.; Ndjoko, K.; Queiroz, E.F.; Ioset, J.R.; Hostettmann, K.; Berrueta, L.A.; Gallo, B.; Vicente, F. On-line characterization of apple polyphenols by liquid chromatography coupled with mass spectrometry and ultraviolet absorbance detection. *J. Chromatogr. A* **2004**, *1046*, 89–100. [CrossRef] [PubMed]
42. Kahle, K.; Kraus, M.; Richling, E. Polyphenol profiles of apple juices. *Mol. Nutr. Food Res.* **2005**, *49*, 796–806. [CrossRef] [PubMed]
43. Choi, Y.; Okos, M.R. The thermal properties of tomato juice concentrates. *Trans. ASAE* **1983**, *26*, 305–311. [CrossRef]

44. Bayindirli, L. Density and viscosity of grape juice as a function of concentration and temperature. *J. Food Process. Preserv.* **1993**, *17*, 147–151. [CrossRef]
45. Ramos, A.M.; Ibarz, A. Density of juice and fruit puree as a function of soluble solids content and temperature. *J. Food Eng.* **1998**, *35*, 57–63. [CrossRef]
46. Telis-Romero, J.; Telis, V.R.N.; Gabas, A.L.; Yamashita, F. Thermophysical properties of Brazilian orange juice as affected by temperature and water content. *J. Food Eng.* **1998**, *38*, 27–40. [CrossRef]
47. Ibarz, A.; Barbosa-Cánovas, G.V. *Unit Operations in Food Engineering*; CRC Press: Boca Raton, FL, USA, 2003.
48. Rao, M.A. Rheological behaviour of processed fluid and semisolid foods. In *Rheology of Fluid and Semisolid Foods*; Aspen Publishers Inc.: Gaithersburg, MD, USA, 1999; pp. 221–223.
49. Kobus, Z.; Nadulski, R.; Guz, T.; Mazur, J.; Panasiewicz, M. Effect of pasteurization on rheological properties of white carrot juice. *Agric. Agric. Sci. Procedia* **2015**, *7*, 99–102. [CrossRef]
50. Wilczyński, K.; Kobus, Z.; Nadulski, R.; Panasiewicz, M.; Kusz, A. The effect of ultrasound on the rheological properties of apple juice. In Proceedings of the IX International Scientific Symposium Farm Machinery and Processes Management in Sustainable Agriculture, Lublin, Poland, 22–24 November 2017; pp. 422–425.
51. Alvarez, S.; Alvarez, R.; Riera, F.A.; Coca, J. Influence of depectinization on apple juice ultrafiltration. *Colloid Surf. A Physicochem. Eng. Asp.* **1998**, *138*, 377–382. [CrossRef]
52. Chinnici, F.; Bendini, A.; Gaiani, A.; Riponi, C. Radical scavenging activities of peels and pulps from cv. Golden Delicious apples as related to their phenolic composition. *J. Agric. Food Chem.* **2004**, *52*, 4684–4689. [CrossRef] [PubMed]
53. Wolfe, K.; Wu, X.; Liu, R.H. Antioxidant activity of apple peels. *J. Agric. Food Chem.* **2003**, *51*, 609–614. [CrossRef] [PubMed]
54. Jayaprakasha, G.K.; Patil, B.S. In vitro evaluation of the antioxidant activities in fruit extracts from citron and blood orange. *Food Chem.* **2007**, *101*, 410–418. [CrossRef]
55. Lu, Y.; Foo, L.Y. Antioxidant and radical scavenging activities of polyphenols from apple pomace. *Food Chem.* **2000**, *68*, 81–85. [CrossRef]
56. Miller, N.J.; Rice-Evans, C.A. The relative contributions of ascorbic acid and phenolic antioxidants to the total antioxidant activity of orange and apple fruit juices and blackcurrant drink. *Food Chem.* **1997**, *60*, 331–337. [CrossRef]
57. Schempp, H.; Christof, S.; Mayr, U.; Treutter, D. Phenolic compounds in juices of apple cultivars and their relation to antioxidant activity. *J. Appl. Bot. Food Qual.* **2016**, *89*, 11–20.