Agricultural and Food Science (2024) 33: 237–246 https://doi.org/10.23986/afsci.143844

Polyphenol composition and antioxidant activity of wine raw materials and pomace from hybrid grapes, aronia, and Japanese quince

^{1,2,3}Reelika Rätsep, ²Mariana Maante-Kuljus, ²Kadri Karp, ¹Hedi Kaldmäe, ²Priit Põldma, ²Angela Koort, ²Leila Mainla, and ²Ulvi Moor

¹Polli Horticultural Research Centre, Chair of Horticulture, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Uus 2, 69108, Polli, Estonia

²Chair of Horticulture, Institute of Agricultural and Environmental Sciences, Estonian University of Life Sciences, Fr. R. Kreutzwaldi 5, Tartu, 51006, Estonia

³ERA Chair for Food (By-) Products Valorisation Technologies, Estonian University of Life Sciences, Kreutzwaldi 56/5, 51006, Tartu, Estonia

e-mail: reelika.ratsep@emu.ee

Wine pomace contains high amounts of bioactive compounds, mainly polyphenols, with varying concentrations depending on multiple factors. This research aimed to determine differences in the content of polyphenols and antioxidant activity of the wine raw materials and pomace of Japanese quince ('Rasa'), aronia (seedlings), and grape ('Hasansky Sladky') and between harvest years (2021, 2022), as well as between fruits and pomace. Pomace from aronia and Japanese quince was obtained after maceration for 5 and 7 days, respectively, while grape pomace was collected on the day of harvest. The polyphenol content of fruits and pomace varied significantly between harvest years. Aronia had the highest total polyphenol content in fruits (989 mg GAE 100 g⁻¹) and pomace (1022 mg GAE 100 g⁻¹), followed by Japanese quince (625 and 722 mg GAE 100 g⁻¹) and grapes (390 and 481 mg GAE 100 g⁻¹). Aronia fruits and pomace had higher antioxidant activity. Compared to the fruits, aronia pomace had less chlorogenic acid and neochlorogenic acid. Flavanols were the main polyphenols in the Japanese quince, showing lower content in the pomace when compared to fruits, except catechin content was higher. The content of anthocyanins and flavonols was higher in the rosé wine pomace than in the fruits of grapes.

Key words: Chaenomeles japonica, Aronia melanocarpa, Vitis spp., polyphenols, anthocyanins, flavanols, flavonols

Introduction

In recent years, the number of wine producers in Estonia has significantly increased, with both white and red wines being produced. Since December 2nd, 2021, Estonia has belonged to the northernmost wine-growing zone A of the European Union, allowing the production of wine from grapes under EU requirements and regulations (Maaeluministeerium 2022). There are 15 wine grape cultivars commonly found in commercial vineyards in Estonia, and the white wine cultivar 'Solaris' (*Vitis vinifera*) is the most cultivated. Red and rosé wines are mainly produced from the cultivars 'Rondo', 'Regent', and 'Zilga'. Japanese quince (*Chaenomeles japonica*) and aronia (*Aronia melanocarpa*) have also become very popular as raw materials for fruit wine. However, with the increasing production of fruit and berry wines and grape wines, increased production residues occur. The main residue of wine production is the pomace from the juice pressing. To find adequate and sustainable uses for pomace, it is important to investigate its content of bioactive compounds.

The biochemical content of grapes varies between cultivars, and berries containing higher polyphenols also exhibit increased antioxidant activity (Yang et al. 2009, Maante-Kuljus et al. 2020). Grape berry morphology can be divided into three zones: the peripheral zone (skin of the berry), the intermediate zone (flesh), and the central zone (seed). The chemical composition of tissues in all these zones is variable, influencing the final quality of grapes and products made from grapes. Pomace from the wine industry consists of berry skins and seeds, which serve as potential sources of bioactive polyphenolic compounds (Peixoto et al. 2018). Seeds exhibit the highest content of phenolic compounds and antioxidant activity, while skins contain the highest levels of anthocyanins (Peixoto et al. 2018, Guaita et al. 2023). The presence of these compounds varies depending on the grape cultivar (Negro et al. 2021, Guaita et al. 2023). The phenolic profile differs between white and red cultivars; white grape pomaces show the predominance of flavan-3-ols, while anthocyanins predominate in red pomaces (Abouelenein et al. 2023). In red wine *V. vinifera* cultivars, malvidin-3-O-glucoside is the major anthocyanin, accounting for more than 32% in *V. vinifera* and 22% in hybrid cultivars (Fraige et al. 2014).

Aronia, or chokeberry, is known as a rich source of anthocyanins and phenolic acids, and its fruits have long been used as a common raw material for the production of red fruit wines. The chemical composition of its fruits and juice distinguishes it from other berries due to its high content of polyphenols and antioxidant activity compared to raspberry, bramble, and strawberry (Jakobek et al. 2007). The polyphenolic composition of fruits depends on the cultivation area (Denev et al. 2018) and fertilization (Jeppsson 2000). Peels contain the majority of anthocyanins (73% of the total amount in the fruit), while the flesh contains most of the phenolic acids (78%) (Kaloudi et al. 2022). Proanthocyanidins are distributed as follows: 70% are in the flesh, 25% in the skin, and 5% in the seeds (Mayer-Miebach et al. 2012). The main polyphenolic compounds in juices in descending order are: anthocyanins > procyanidin polymers > phenolic acids > flavonols > flavan-3-ols > flavanone (Oszmiański and Lachowicz 2016). At the same time, it was found that the chemical composition of the juice is affected by the previous processing treatment. Pressing previously crushed fruits results in a higher content of polyphenols (70%) in juices compared to pressing whole fruits (30%). Aronia pomace, a by-product of the juice industry, is rich in anthocyanins and other bioactive components. The content of polyphenols and antioxidant activity is higher in the press residue from aronia juice production than in the juice and berries themselves (Oszmiański and Wojdylo 2005). Antioxidant activity, measured in Trolox equivalents showed the results in descending order: pomace > fruit > juice. Four monoglycosylated anthocyanins were identified in aronia pomace extract in the following proportions: cyanidin-3-O-galactoside (62%), cyanidin-3-O-glucoside (4%), cyanidin-3-O-arabinoside (30%), and cyanidin-3-O-xyloside (5%) (Roda-Serrat et al. 2022). The migration of anthocyanins from fruit skin to juice is primarily determined by skin damage. Appropriate crushing before pressing causes damage to cell walls, and thus facilitates the migration of fruit components to the pressed juice. In addition to the above, total anthocyanin levels in pomace were affected by enzyme treatment, followed by maceration temperature (Vagiri and Jensen 2017).

The cultivation of Japanese quince is particularly popular in the Baltic countries, Finland, Sweden, and Poland (Rumpunen 2002, Kaufmane et al. 2021). High acidity and antioxidant capacity are notable features of quince fruits, attributed to their elevated levels of vitamin C and phenolic compounds (Ros-Carcía et al. 2004). On average, cultivars contain 57–90 mg% of vitamin C and 422–550 mg% of phenolic compounds (Kaufmane and Ruisa 2020). Due to the high content of bioactive compounds, fruits, leaves, seeds, and pomace are valuable and have many potential possibilities of use in the food, cosmetic, and pharmaceutical industries (Urbanavičiūtė and Viškelis 2022). The content of bioactive compounds in seeds and pomace is higher than in pulp; therefore, there is also increased interest in using pomace. The oil content, fatty acid profile, and concentration of bioactive compounds in seeds remain stable during the last month of fruit development (Mišina et al. 2020). Winemaking by-product contains up to 42 g 100 g⁻¹ seeds of its dry weight and has a high added value as a source of oil and protein (Ben-Othman et al. 2023). The fruit peel and pulp have been used for the extraction, and such extracts are reported for their antioxidant and antimicrobial activities (Urbanavičiūtė et al. 2020).

Research hypothesis: the content of phenolic compounds and antioxidant activity of aronia, grape, and Japanese quince wine raw materials and pomace depends on the species and harvest year. This research aimed to determine differences in the content of polyphenols and antioxidant activity between the wine raw materials and between the wine pomace of Japanese quince (cv. 'Rasa'), aronia (seedlings), and grape (cv. 'Hasansky Sladky') and between the harvest years (2021, 2022). Additionally, differences were examined between fruits and their respective pomace.

Material and methods

Fruit and pomace samples

Fruit samples for analysis were collected in 2021 and 2022 on the day of harvest in three replicates, with each replicate weighing 400 g. Grape samples were collected from different parts of the basal clusters. Aronia and Japanese quince samples were taken from both sides of the bush. Before the analyses, the seeds of grapes and Japanese quince were separated from the fruits manually.

'Hasansky Sladky' is a hybrid wine grape cultivar that was bred by crossing the cultivar 'Dalnevostochnyi Tikhonova' (*Vitis vinifera* × *Vitis amurensis*) with *Vitis amurensis*. The berries are dark-skinned. The fruits of 'Hasansky Sladky' were de-stemmed with a destemmer, and the juice was immediately pressed. On the harvest day in both years, the soluble solids content of the juice was 20 °Brix. The yeast Bioferm Aromatic (*Saccharomyces cerevisiae var. cerevisiae*, Brouwland, Bewerlo, Belgium) was used (dose 2–3 g 10 l⁻¹), which can reduce the malic acid content by 30%. When making wine from the harvest of aronia seedlings, the stems were separated from the fruits and crushed with a destemmer. Wine yeast (*S. cerevisiae*, EnartisFerm Red Fruit, Enartis S.r.l., San Martino, Italy) was added (dose 20–40 g hl⁻¹), and left to ferment for five days, then the juice was pressed. On the harvesting day, the soluble solids content of the juice was 16 °Brix in both years.

The fruits of the Japanese quince cultivar 'Rasa' were crushed (centrifugal mill RM1.5, Voran Maschinen GMBH, Austria), and pectolytic enzyme (EnartisZym 1000 S, Enartis S.r.l., San Martino, Italy) and yeast (*S. cerevisiae*, EnartisFerm Aroma White, Enartis S.r.l., San Martino, Italy) were added (dose 20–40 g hl⁻¹). The soluble solids content of the juice was 6 °Brix in both years. The mixture was macerated for seven days before pressing. For all wines, fermentation took place at a temperature of 18 to 20 °C, with stirring several times every day.

All treatments were pressed with a 20 l stainless water pressure press. Wine pomace of aronia and Japanese quince were obtained after the end of maceration and grape pomace was collected during the harvest day after pressing. Pomaces were collected in three replicates and one replicate contained 500 g of pomace. Samples were stored at -18 °C in vacuum packages until further processing. Before the analyses, the seeds of grape and Japanese quince pomaces were separated manually.

Chemical analyses

The total phenolic content (TPC) was determined by applying the Folin-Ciocalteu (FC) phenol reagent method (Song et al. 2010). Briefly, the following concentrations of the gallic acid (GA) standards were prepared: 50, 150, 250, 350, and 400 μ g ml⁻¹. For the calibration, 0.4 ml of each standard was pipetted into a 4 ml spectrophotometer cuvette, to which 2.0 ml of FC reagent (0.2 N) was added, and after 5 min 1.6 ml of Na₂CO₃ (75 g l⁻¹) was added and the samples were incubated for 60 min in the dark at room temperature. The measurement procedure for the samples was the same as for the standard calibration described previously. The absorbance values of the samples were measured at 760 nm using a spectrophotometer (UV-1800, Shimadzu, Kyoto, Japan). The results were expressed in mg of gallic acid equivalents per 100 g of fresh weight (mg GAE 100 g⁻¹ FW). All chemicals used were of laboratory grade and purchased from Sigma (Steinheim am Albuch, Germany).

The antioxidant activity (AA) measurements were performed in triplicate using a 2.2-diphenyl-picrylhydrazyl (DPPH) assay with slight modifications (Brand-Williams et al. 1995). In brief, the following concentrations of the ascorbic acid standard were prepared: 0.125, 0.100, 0.0625, 0.050, and 0.025 mg ml⁻¹. For the measurement, 0.1 ml of each standard was pipetted into a 4 ml spectrophotometer cuvette, to which 3.7 ml of DPPH radical was added. The samples were incubated for 60 min in the dark at room temperature. The procedure for analysis of the sample extracts was the same as for the standard calibration described previously. The absorbance values of the samples were measured at 515 nm using a spectrophotometer (UV-1800, Shimadzu, Japan). The results were expressed in mg of ascorbic acid equivalent (AAE) per 100 g of fresh weight (mg AAE 100 g⁻¹ FW). All chemicals used were of laboratory grade and purchased from Sigma (Steinheim am Albuch, Germany).

The determination of the most abundant polyphenols and polyphenol profiling was performed using Shimadzu Nexera X2 UHPLC coupled with mass spectrometer LCMS 8040 (Shimadzu Scientific Instruments, Kyoto, Japan), as described in Ben-Othman et al. (2021). Individual phenolic compounds were identified by comparing the retention times, UV spectra, and parent and daughter ion masses with those of the standard compounds. The standard compounds of chlorogenic acid, neochlorogenic acid, cyanidin-3-galactoside, cyanidin-3-glucoside, delphinidin-3-glucoside, malvidin, malvidin-3-glucoside, peonidin-3-glucoside, catechin, epicatechin, procyanidin B2, procyanidin C1, kaempferol-3-glucoside, quercetin, quercetin-3-galactoside, quercetin-3-glucoside, and rutin were laboratory grade and purchased from Sigma (Steinheim am Albuch, Germany). The results were expressed in mg per 100 g of fresh weight (mg 100 g⁻¹ FW).

Weather conditions

According to the Heliothermal Index, Estonia is located in a very cool, and in some years, it is considered a cool region (Maante-Kuljus et al. 2019). In both experimental years, the cooler months were May and September, during which night frosts also occurred (Fig. 1). The summer months differed in terms of temperature and rainfall in both experimental years. In 2021, the warmest months were June and July, with average air temperatures of 20 °C and 22 °C, respectively. In 2022, the warmest month was August, with a monthly average air temperature of 20 °C. In 2021, May and August were rainy months, but there was very little precipitation in June and July (Fig. 2). The following year, precipitation was more evenly distributed, with September being the driest month.

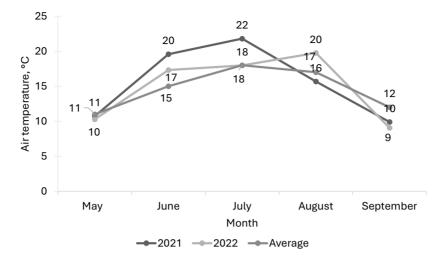
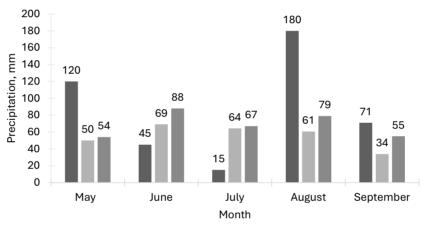


Fig. 1. Monthly average air temperature (°C) compared to the average of many years (1991–2020) from May to September 2021 and 2022 in South Estonia.



■ 2021 ■ 2022 ■ Average

Fig. 2. Monthly total precipitation (mm) and many years average (1991–2020) from May to September in 2021 and 2022 in South Estonia.

Statistical analysis

The results in the figures and the table were represented as the means of three replicates. Analysis of variance (ANOVA) was performed to evaluate the existence of differences between harvest years (2021, 2022) and species (aronia, Japanese quince, grape), as well as between fruits and pomace. Results between the two years (in Figs. 3–6) and between fruit and pomace (Table 1) were analyzed by one-way ANOVA. Comparison of means was done by using Fisher's Least Significant Difference (LSD) test to confirm the statistically significant differences between the years and between the fruits and pomace. To confirm the significant differences between the species, the average results were analyzed by two-way ANOVA. Different letters in the figures and table show statistically significant differences (*p< 0.05; **p< 0.01; ***p< 0.001).

Results

Total phenolic content

The TPC of aronia differed between experimental years, which had 1076 mg GAE 100 g⁻¹ in 2021 and 902 mg GAE 100 g⁻¹ in 2022 (Fig. 3), respectively. Similarly, the effect of the year was significant in the case of Japanese quince with contents of 773 and 478 mg GAE 100 g⁻¹ in 2021 and 2022, respectively. For grapes, the TPC was 407 mg GAE

100 g⁻¹ in 2021 and 373 mg GAE 100 g⁻¹ in 2022, and the difference between the two harvest years was significant. Comparing the averages of the two years revealed that aronia was the richest in TPC, while grapes had the lowest content.

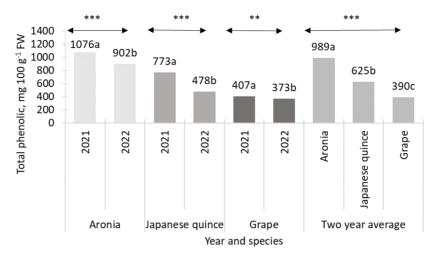


Fig. 3. Effect of harvest year and species on fruits' total phenolic content (mg GAE 100 g⁻¹). Different letters on the bars show statistically significant differences (**p< 0.01; ***p< 0.001).

The TPC in the aronia wine pomace was different between experimental years, which had 748 mg GAE 100 g⁻¹ in 2021 and 1297 mg GAE 100 g⁻¹ in 2022 (Fig. 4). Similarly, the effect of the year was significant in the case of Japanese quince, with contents of 898 and 547 mg GAE 100 g⁻¹ in 2021 and 2022, respectively. The TPC in the grape rosé wine pomace was in both years at 477 and 485 mg GAE 100 g⁻¹, with no significant effect of harvest year on TPC. The results of the analysis of wine raw materials showed that the highest TPC was determined in aronia wine pomace, followed by Japanese quince, and finally grape pomace.

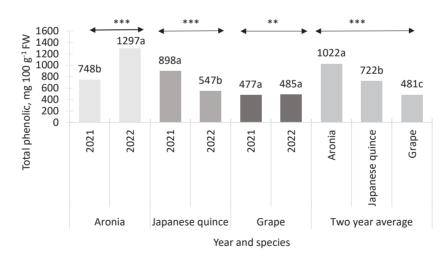


Fig. 4. Effect of harvest year and species on wine pomace's total phenolic content (mg GAE 100 g⁻¹). Different letters on the bars show statistically significant differences (**p< 0.01; ***p< 0.001).

Antioxidant activity

The AA varied across the experimental years, being 631 and 584 mg AAE 100 g⁻¹ for aronia fruits, 342 and 282 mg AAE 100 g⁻¹ for Japanese quince fruits, with significantly lower AA observed in 2022 (Fig. 5). In the case of grapes, the results also differed depending on the year (250 and 331 mg AAE 100 g⁻¹, respectively), but significantly higher values were obtained in 2022. When averaged over the experimental years, aronia had the highest AA, followed by Japanese quince and then grapes.

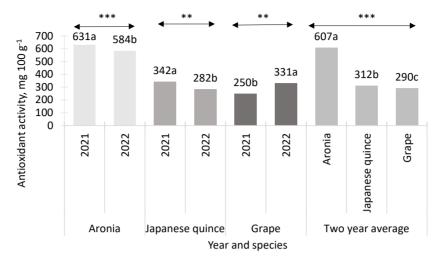


Fig. 5. Effect of harvest year and species on the fruit's antioxidant activity (mg AAE 100 g⁻¹). Different letters on the bars show statistically significant differences (**p< 0.01; ***p< 0.001).

The pomace AA varied significantly between experimental years (Fig. 6). Aronia and Japanese quince had higher AA in 2021. The pomace of the rosé wine had higher AA in 2022 (331 mg AAE 100g⁻¹) compared to 2021 (250 mg 100 g⁻¹). There were also significant differences in the average of years; pomace from aronia wine had the highest AA, followed by Japanese quince, while grapes had the lowest values.

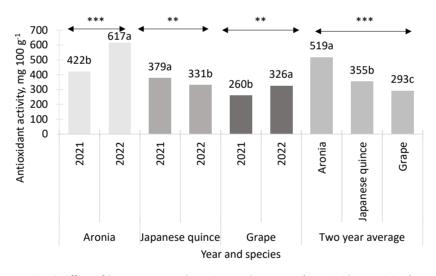


Fig. 6. Effect of harvest year and species on the pomace's antioxidant activity (mg AAE 100 g⁻¹). Different letters on the bars show statistically significant differences (**p< 0.01; ***p< 0.001).

Profile of polyphenols

The content of individual polyphenolic compounds differed in fruit compared to pomace (Table 1). Aronia wine pomace had a lower content of phenolic acids compared to the fruit, with chlorogenic acid being 51% and neochlorogenic acid 46% lower. The most abundant anthocyanidin determined in aronia fruit and wine pomace was cyanidin-3-galactoside, which was less in the pomace. However, the content of flavanols and flavonols in the pomace was higher, with only the content of rutin being lower. In the case of Japanese quince, the main polyphenols were flavanols, and the content of most of them was lower in the pomace, with only the content of catechin being higher. The content of anthocyanins and flavonols was higher in the rosé wine pomace compared to the grapes. However, the content of flavanols in the pomace was significantly lower.

Polyphenols mg 100g ⁻¹ FW	Aronia		Japanese quince		Grape	
	Fruit	Pomace	Fruit	Pomace	Fruit	Pomace
Phenolic acids						
Chlorogenic acid	281.42a	145.33b	18.83b	26.01a	nd	nd
Neochlorogenic acid	85.71a	40.09b	nd	0.12	nd	nd
Anthocyanins						
Cyanidin-3-galactoside	287.32a	267.50b	nd	0.15	nd	nd
Cyanidin-3-glucoside	nd	nd	nd	nd	1.84b	4.71a
Delphinidin-3-galactoside	13.36b	17.26a	0.22b	0.38a	0.43b	1.28a
Delphinidin-3-glucoside	9.77b	11.14a	0.21b	0.95a	4.67b	14.66a
Malvidin	0.18a	0.10b	nd	nd	0.42b	0.99a
Malvidin-3-glucoside	nd	0.12	nd	nd	22.10b	49.00a
Peonidin-3-glucoside	0.02b	0.13a	nd	nd	9.74b	23.64a
Flavanols						
Catechin	0.19a	0.20a	1.82b	2.15a	5.24a	1.84b
Epicatechin	1.00a	0.98a	85.64a	78.85b	2.30a	0.47b
Procyanidin B2	2.66a	2.35a	137.22a	122.22b	2.72a	0.48b
Procyanidin C1	31.14a	27.42a	1119.70a	1019.40b	20.46	nd
Flavonols						
Kaempferol-3-glucoside	0.13a	0.17a	0.03b	0.08a	0.26b	1.01a
Quercetin	0.90b	5.22a	nd	0.38	nd	0.19
Quercetin-3-galactoside	2.98b	3.85a	0.05b	0.10a	0.11b	0.31a
Quercetin-3-glucoside	3.30a	3.62a	0.11b	0.33a	1.76b	5.26a
Rutin	7.33a	6.75b	0.29a	0.25a	0.03b	0.06a

Table 1. The most abundant polyphenols (mg $100g^{-1}$ FW) in the fruits, and wine pomace of aronia, Japanese quince, and grape. Different letters in the same row between fruit and pomace represent statistically significant differences at $p \le 0.05$.

nd = not detected

Discussion

The TPC and AA of aronia, Japanese quince, and grape as wine raw materials were significantly different. These differences may be explained by the different structures and morphological parameters (for example, fruit size, shape, the proportion of skin and pulp, skin thickness, etc.) of the fruits, as well as the localization of chemical compounds in different parts of the fruit. Additionally, variations were observed between harvest years. In 2021, the warmest months were June and July, coinciding with the beginning of fruit development, when the temperatures were 20 and 22 °C, respectively. Additionally, relatively low precipitation levels (45 mm and 15 mm, respectively) during those two months may have caused additional stress to the plants. In contrast, in 2022, the warmest month was August, corresponding to the time of fruit expansion and ripening, with a monthly average temperature of 20 °C. The amount of precipitation varied significantly throughout the period from May to September in both experimental years. The difference between the test fruits could also be related to unequal light conditions in the canopy. The leaves had been removed around the grape clusters at the beginning of berry veraison; therefore, the warmer and drier weather conditions in August and September may have had a greater effect. Similarly, we have previously described a strong positive correlation between the content of polyphenols and radiation flux in August during grape veraison in one of our previous studies (Maante-Kuljus et al. 2020). For Japanese quince and aronia, the fruits are located in partial shade caused by the leaves, leading to different effects of weather conditions on their development.

The polyphenolic composition of pomace significantly depends on the characteristics of the raw material species, the year of harvest, and the extraction process during the winemaking process. While it is widely known that only the skins of grape berries contain significant amounts of polyphenols, aronia, and Japanese quince also have a significant quantity of polyphenols in the pulp. Therefore, it could be assumed that the previous processing of the raw material before fermentation had an effect. Grapes are typically crushed with a destemmer, but there

are different options for preparing the raw material of Japanese quince and aronia. Both a destemmer and a crusher can be used for aronia, but fruits of Japanese quince require crushing before fermentation. The intensity of crushing and the particle size of the skins and fruit flesh are important factors in terms of extraction efficiency. Similarly, Ćujić et al. (2016) demonstrated the improvement of polyphenol extraction from dried aronia fruits as the particle size decreased.

Winemaking technologies have a significant effect on the wine and pomace polyphenol content, as reported by Ghanem et al. (2019) and Zhao et al. (2024). Different methods are used to make wine from grapes. For instance, in the case of making rosé wine, fermentation occurs using only pure juice, with no fermentation with the skins. However, in the case of red wines, fermentation takes place with the skins, resulting in more polyphenols being released into the wine. As a result, the skins from fermented red wine grape pomace lose a significant quantity of phenolic compounds during the maceration process. Thus, it can be concluded that pomace from wine production has a very different polyphenolic composition.

Polyphenols, as significant antioxidants, exert an influence on AA (Gündeşli et al. 2019, Wojtunik-Kulesza et al. 2020). In addition to the TPC, the AA is also influenced by the profile of polyphenols (Lingua et al. 2016). Therefore, fruits with the highest content of polyphenols may not always have the highest AA. Furthermore, there are other antioxidants present in fruits and berries, such as vitamin C, that also affect the AA. In the case of Japanese quince fruits, the high acidity and antioxidant capacity were influenced by the high content of vitamin C and phenolic compounds (Ros et al. 2004). Some studies suggest that anthocyanins exhibit higher AA than vitamins C or E, with a linear relationship reported between AA and anthocyanin content in some fruits (Castañeda-Ovando et al. 2009).

The composition profiles of polyphenols were qualitatively and quantitatively different between the fruits of aronia, Japanese guince, grape, and their pomaces. Most research on aronia and Japanese guince has focused on pomace from juicing. Studies have shown that pomace from aronia juice production has a higher content of phenolics than the juice and fruits alone (Oszmianski and Wojdylo 2005), and similar results have been obtained with Japanese quince (Urbanavičiūtė et al. 2020). Juicing is a rapid process that releases only a fraction of the biologically active compounds from the fruit, leaving most of them still in the pomace, especially in the case of dense fruit skin and flesh. Therefore, fermentation with crushed fruits may cause a reduction of polyphenols in the pomace. The release of polyphenols from fruits is also influenced by the alcohol produced during fermentation. Experimental results have shown that this tendency depends on the culture and different polyphenols. For example, in aronia pomace, the contents of phenolic acids and the main anthocyanin, cyanidin-3-galactoside, were lower. Similarly, the content of epicatechin, procyanidin B2, and procyanidin C1 in Japanese quince pomace was significantly reduced compared to the fruit. However, the content of total anthocyanins and various anthocyanidins was significantly higher in grape pomace, where there was no fermentation on the skins. In addition to the above, the release of polyphenols could be affected by their different locations depending on the fruit's structure, as polyphenols exist inside the cells. The morphology and composition of skin cell walls differ from pulp cell walls. For example, Japanese quince has dense and hard pulp, while aronia has softer fruits, leading to differences in the release of polyphenols. Aronia fruit polyphenols are distributed in different parts of the fruit (Mayer-Miebach et al. 2012), whereas, in grapes, the skins contain the highest levels of polyphenols, primarily anthocyanins (Peixoto et al. 2018). While the experiment focused on one cultivar for each fruit, it is important to consider the influence of the cultivar on biochemical characteristics. For instance, the experimental hybrid grape cultivar 'Hasansky Sladky' has a significantly lower content of polyphenols and anthocyanins than the cultivar 'Rondo' (Maante-Kuljus et al. 2020). The experimental results were obtained with the Japanese quince cultivar 'Rasa', in which the total content of proanthocyanidins differed significantly from cultivars 'Rondo' and 'Darius' (Urbanavičiūtė et al. 2020). The content of polyphenols in aronia cultivars has shown less variability, with cultivars like 'Nero', 'Valkira', and 'Chernookaya' having the same content of total polyphenols and anthocyanins (Arus and Rätsep 2022). Therefore, future studies should investigate the variability of press residues among different hybrid grape cultivars and Japanese quince.

Conclusions

The hypothesis of the experiment was confirmed. The content of polyphenols and antioxidant activity of the wine raw materials and pomace of Japanese quince, aronia, and grape were significantly different and varied between harvest years. As a two-year average, aronia had the highest total polyphenol content in fruits and pomace, followed by Japanese quince and then grapes. Aronia fruits and wine pomace also had higher antioxidant activity compared to Japanese quince and grapes. The content of individual polyphenolic compounds differed between fruits and pomace. Compared to the fruits, aronia pomace had less chlorogenic acid and neochlorogenic acid.

The content of anthocyanins increased; only the content of cyanidin-3-galactoside decreased. Flavanols were the main polyphenols in the Japanese quince, and the content of most of them was lower in the pomace, with only catechin content being higher. The content of anthocyanins and flavonols was found to be higher in the rosé wine pomace compared to the fruits of grapes. However, the content of flavanols in the pomace was significantly lower. This study revealed that winemaking residues from aronia, Japanese quince, and grape wine production are good sources of polyphenolic compounds with high antioxidant activity that could be used further for the food, cosmetics, or pharmaceutical industries.

Acknowledgments

This research was funded by the European Union's Horizon 2020 research and innovation program project VALORTECH under grant agreement No. 810630, and supported by the European Regional Development Fund's project "PlantValor — full-scale product development service in synergy with the traditional activities of Polli Horticultural Research Centre" 2020–2023.

References

Abouelenein, D., Mustafa, A.M., Caprioli, G., Ricciutelli, M., Sagratini, G. & Vittori, S. 2023. Phenolic and nutritional profiles, and antioxidant activity of grape pomaces and seeds from Lacrima di Morro d'Alba and Verdicchio varieties. Food Bioscience 53: 102808. https://doi.org/10.1016/j.fbio.2023.102808

Arus, L. & Rätsep, R. 2022. Sordi mõju aroonia (Aronia sp.) viljade kvaliteedile. Agronoomia 2022: 206–213 (in Estonian).

Ben-Othman, S., Bleive, U., Kaldmäe, H., Aluvee, A., Rätsep, R., Karp, K., Maciel, L.S., Herodes, K. & Rinken, T. 2023. Phytochemical characterization of oil and protein fractions isolated from Japanese quince (*Chaenomeles japonica*) wine by-product. LWT - Food Science and Technology 178: 114632. https://doi.org/10.1016/j.lwt.2023.114632

Ben-Othman, S., Kaldmäe, H., Rätsep, R., Bleive, U., Aluvee, A. & Rinken, T. 2021. Optimization of ultrasound-assisted extraction of phloretin and other phenolic compounds from apple tree leaves (*Malus domestica* Borkh.) and comparison of different cultivars from Estonia. Antioxidants 10: 189. https://doi.org/10.3390/antiox10020189

Brand-Williams, W., Cuvelier, M.E. & Berset, C. 1995. Use of a free radical method to evaluate antioxidant activity. LWT -Food Science and Technology 28: 25–30. https://doi.org/10.1016/S0023-6438(95)80008-5

Castañeda-Ovando, A., Pacheco-Hernandez, M.L., Paez-Hernandez, M.E., Rodriguez, J.A. & Galan-Vidal C.A. 2009. Chemical studies of anthocyanins: A review. Food Chemistry 113: 859–871. https://doi.org/10.1016/j.foodchem.2008.09.001

Ćujić, N., Šavikin, K., Janković, T., Pljevljakušić, D., Zdunić, G. & Ibrić, S. 2016. Optimization of polyphenols extraction from dried chokeberry using maceration as traditional technique. Food Chemistry 194: 135–142. https://doi.org/10.1016/j.foodchem.2015.08.008

Denev, P., Kratchanova, M., Petrova, I., Klisurova, D., Georgiev, Y., Ongyanov, M. & Yanakieva, I. 2018. Black chokeberry (*Aronia melanocarpa* (Michx.) Elliot) Fruits and Functional Drinks Differ Significantly in their Chemical Composition and Antioxidant Activity. Journal of Chemistry: 9574587. https://doi.org/10.1155/2018/9574587

Fraige, K., Pereira-Filho, E.R. & Carrilho, E. 2014. Fingerprinting of anthocyanins from grapes produced in Brazil using HPLC-DAD-MS and exploratory analysis by principal component analysis. Food Chemistry 145: 395–403. https://doi.org/10.1016/j.foodchem.2013.08.066

Ghanem, C., Taillandier, P., Rizk, Z., Nehme, N., Souchard, J. P. & El Rayess, Y. 2019. Evolution of polyphenols during syrah grapes maceration: time versus temperature effect. Molecules 24: 2845. https://doi.org/10.3390/molecules24152845

Guaita, M., Motta, S., Messina, S., Casini, F. & Bosso, A. 2023. Polyphenolic Profile and Antioxidant Activity of Green Extracts from Grape Pomace Skins and Seeds of Italian Cultivars. Foods 12: 3880. https://doi.org/10.3390/foods12203880

Gündeşli, M.A., Korkmaz, N. & Okatan, V. 2019. Polyphenol content and antioxidant capacity of berries: A review. International Journal of Agriculture Forestry and Life SciencesInt 3: 350–361. https://dergipark.org.tr/en/download/article-file/874337

Jakobek, L., Šeruga, M., Medvidović-Kosanović, M. & Novak, I. 2007. Antioxidant Activity and Polyphenols of Aronia in Comparison to Other Berry Species. Agriculturae Conspectus Scientificus 72: 301–306. https://hrcak.srce.hr/19396

Jeppsson, N. & Johansson, R. 2000. Changes in fruit quality in black chokeberry (*Aronia melanocarpa*) during maturation, The Journal of Horticultural Science and Biotechnology 75: 340–345. https://doi.org/10.1080/14620316.2000.11511247

Kaloudi, T., Tsimogiannis, D. & Oreopoulou, V. 2022. Aronia Melanocarpa: Identification and Exploitation of Its Phenolic Components. Molecules 27: 4375. https://doi.org/10.3390/molecules27144375

Kaufmane, E. & Ruisa, S. 2020. Breeding of new cultivars of the fruit crop Japanese quince (*Chaenomeles japonica*) in Latvia. Acta Horticulturae 1281: 51–58. https://doi.org/10.17660/ActaHortic.2020.1281.9

Kaufmane, E., Seglina, D. & Górnaś, P. 2021. Japanese quince: from field via lab to table: the role of "green technologies". Latvian Academy of Sciences Yearbook 2021: 121–123.

Lingua, M.S., Fabani, M.P., Wunderlin, D.A. & Baroni, M.V. 2016. From grape to wine: Changes in phenolic composition and its influence on antioxidant activity. Food Chemistry 208: 228–238.https://doi.org/10.1016/j.foodchem.2016.04.009

Maaeluministeerium 2022. https://maablogi.ee/2022/02/11/eesti-arvati-pohjapoolseimasse-viinamarjakasvatusvoodisse/?fbclid=IwAR1jrerjJPzm58ayeCycwTnfK_T2ZdkIoIZdN1oGP5JTHcWemPFo9AV6FCI. Accessed 29 February 2024 (in Estonian). Maante-Kuljus, M., Rätsep, R., Mainla, L., Moor, U., Starast, M., Põldma, P. & Karp, K. 2019. Technological maturity of hybrid vine (Vitis) fruits under Estonian climate conditions. Acta Agriculturae Scandinavica Section B - Soil & Plant Science 69: 706–714. https://doi.org/10.1080/09064710.2019.1641547

Maante-Kuljus, M., Rätsep, R., Moor, U., Mainla, L., Põldma, P., Koort, A. & Karp, K. 2020. Effect of vintage and viticultural practices on the phenolic content of hybrid winegrapes in very cool climate. Agriculture 10: 169. https://doi.org/10.3390/agriculture10050169

Mayer-Miebach, E., Adamiuk, M. & Behsnilian, D. 2012. Stability of chokeberry bioactive polyphenols during juice processing and stabilization of a polyphenol-rich material from the by-product. Agriculture 2: 244–258. https://doi.org/10.3390/agriculture2030244

Mišina, I., Sipeniece, E., Rudzińska, M., Grygier, A., Radzimirska-Graczyk, M., Kaufmane, E., Seglina, D., Lacis, G. & Górnaś, P. 2020. Associations Between Oil Yield and Profile of Fatty Acids, Sterols, Squalene, Carotenoids and Tocopherols in Seed Oil of Selected Japanese Quince Genotypes During Fruit Development. European Journal of Lipid Science and Technology 122: 1900386. https://doi.org/10.1002/ejlt.201900386

Negro, C., Aprile, A., Luvisi, A., De Bellis, L. & Miceli, A. 2021. Antioxidant Activity and Polyphenols Characterization of Four Monovarietal Grape Pomaces from Salento (Apulia, Italy). Antioxidants 10: 1406. https://doi.org/10.3390/antiox10091406

Oszmiański, J. & Lachowicz, S. 2016. Effect of the production of dried fruits and juice from chokeberry (Aronia melanocarpa L.) on the content and antioxidative activity of bioactive compounds. Molecules 21: 1098. https://doi: 10.3390/molecules21081098

Oszmiański, J. & Wojdylo, A. 2005. Aronia melanocarpa phenolics and their antioxidant activity. European Food Research and Technology 221: 809–813. https://doi.org/10.1007/s00217-005-0002-5

Peixoto, C.M., Dias, M.I., Alves, M.J., Calhelha, R.C., Barros, L., Pinho, S.P. & Ferreira, I.C.F.R. 2018. Grape pomace as a source of phenolic compounds and diverse bioactive properties. Food Chemistry 253: 132–138. https://doi.org/10.1016/j.foodchem.2018.01.163

Roda-Serrat, M.C., Parjikolaei, B.R, Mohammadifakhr, M., Martin, J., Norddahl, B. & Errico, M. 2022. A Case Study for the Extraction, Purification, and Co-Pigmentation of Anthocyanins from *Aronia melanocarpa* Juice Pomace. Foods 11: 3875. https://doi.org/10.3390/foods11233875

Ros-García, J., Laencina Sánchez, J., Hellín, P., Jordán, M., Vila, R. & Rumpunen, K. 2004. Characterization of juice in fruits of different Chaenomeles species. LWT - Food Science and Technology 37: 301–307. https://doi.org/10.1016/j.lwt.2003.09.005

Rumpunen, K. 2002. Chaenomeles. Potential new crop for northern Europe. In: Janick, J. & Whipkey, A. (eds). Trends in New Crops and New Uses. ASHA Press. p. 385–392.

Song, F.L., Gan, R.Y., Zhang, Y., Xiao, Q., Kuang, L. & Li, H. 2010. Bin Total phenolic contents and antioxidant capacities of selected Chinese medicinal plants. International Journal of Molecular Sciences 11: 2362–2372. https://doi.org/10.3390/ijms11062362

Urbanavičiūtė, I., Liaudanskas, M., Bobinas, Č., Šarkinas, A., Rezgienė, A. & Viskelis, P. 2020. Japanese Quince (*Chaenomeles japonica*) as a Potential Source of Phenols: Optimization of the Extraction Parameters and Assessment of Antiradical and Antimicrobial Activities. Foods 9: 1132. https://doi.org/10.3390/foods9081132

Urbanavičiūtė, I. & Viškelis, P. 2022. Biochemical composition of Japanese quince (*Chaenomeles japonica*) and its promising value for food, cosmetic, and pharmaceutical industries. In: Kahramangolu A.P.I. & Wan, C. (eds.). Fruit industry. InTechOpen. https://doi.org/10.5772/intechopen.102361

Vagiri, M. & Jensen, M. 2017. Influence of juice processing factors on quality of black chokeberry pomace as a future resource for color extraction. Food Chemistry 217: 409–417. https://doi:10.1016/j.foodchem.2016.08.121

Wojtunik-Kulesza, K., Oniszczuk, A., Oniszczuk, T., Combrzyński, M., Nowakowska, D. & Matwijczuk, A. 2020. Influence of In Vitro Digestion on Composition, Bioaccessibility and Antioxidant Activity of Food Polyphenols-A Non-Systematic Review. Nutrients 12: 1401. https://doi.org/10.3390/nu12051401

Yang, J., Martinson, T. & Liu, R. 2009. Phytochemical profiles and antioxidant activities of wine grapes. Food Chemistry 116: 332–339. https://doi.org/10.1016/j.foodchem.2009.02.021

Zhao, J., Guo, M., Martins, P., Ramos, J., Li, L. & Sun, B. 2024. Effect of fermentation technologies on the structural composition of polymeric polyphenols in aged red wines. Journal of Food Composition and Analysis 125: 105782. https://doi.org/10.1016/j.jfca.2023.105782