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LC-MS/MS CHARACTERIZATION OF PHENOLIC COMPOUNDS IN THE QUINCE (*CYDONIA OBLONGA MILL.*) AND SWEET CHERRY (*PRUNUS AVIUM L.*) FRUIT JUICES

SUMMARY

Quince and sweet cherry are two common edible fruit-producing trees of temperate regions of Euroasia. The phenolic profiles of juices from quince and sweet cherry fruit extracted by the cold-pressing were analyzed by Ultra-High-Performance Liquid Chromatography (UHPLC). Chromatographical results identified 31 phenolic compounds while quantified thirteen for fruit juices. The quantitative data indicate that the predominant phenolic was 5-O-caffeoylquinic acid in quince (8.343 mg L-1) and cherry juice (6.407 mg L-1). Total Flavonoids (TF), Total Phenolic Content (TPC), and Total Antioxidant Capacity (TAC) were also investigated. In both fruit juices, the TF values varied between 0.30-0.97 g L-1 (Catechin Equivalent) and TPC between 0.36 to 0.94 g L-1 (Gallic Acid Equivalent). It is worth noting that the quince fruit juices possessed a higher TPC and TFC compared to sweet cherry fruit juices.

Keywords: quince, sweet cherry, fruit juices, phenolic compounds, antioxidant, cold-pressing

INTRODUCTION

Tree fruits present an essential source of nutrients such as carbohydrates, lipids, and non-nutrient phytochemicals like polyphenols, associated with health benefits (Wojdyło, Oszmianski, & Bielicki, 2013). Besides the water and the common primary metabolites such as carbohydrates as the main ingredients; fruits comprise a complex composition of several hundred substances,

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characterized by many secondary plant metabolites such as phenolic compounds, organic acids, amino acids, and minerals (Paredes-Lopez, Cervantes-Ceja, Vigna-Perez, & Hernandez-Perez, 2010). Recent evidence of an association between a healthy diet and fruit consumption by identifying edible fruits as an essential source of polyphenols (Manach, Scalbert, Morand, Remesy & Jimenez, 2004). Despite the common characteristics, specific fruits own their specific phytochemical composition pattern. A quantitative and qualitative correlation among the fruit phenolics with the tree variety, climate, and agriculture practices has already been proved. The presence of over 224 compounds is analyzed in orange juice, including flavones, carotenoids, flavanones, anthocyanins, and flavanols (McKay &Wilson, 2016). Fifty-six phenolic compounds are identified and quantified in strawberry fruits (Gasperotti, Masuero, Mattivi & Vrhovsek, 2015).

Quinces (*Cydonia oblonga* Mill.) belong to the *Rosaceae* family, specifically the *Maloideae* subfamily, and originate in Central Asia. Fruits are preferred for non-directly consumption because of hardness and astringency, but to prepare liqueur, jam, or marmalade (Wojdyło, Oszmianski, & Bielicki, 2013). The fruit is highly evaluated due to rich polyphenols content exerting antioxidant effects (Silva, Andrade, Ferreres, Domingues & Seabra, 2002; Fattouch *et al*. 2007), and anti-inflammatory activity in the human body (Szajdek & Borowska, 2008; Basu & Penugonda, 2009; McKay & Wilson, 2016). Sweet cherry (*Prunus avium* L.) and sour cherry (*Prunus cerasus* L.), belonging the *Rosaceae* family, are widely consumed. (Blando & Oomah, 2019). Their red color is associated with the presence of anthocyanin compounds (Sokół-Łętowska, Kucharska, Hodun & Gołba, 2020). Their consumption contributes to modulating blood glucose levels by lowering blood pressure, body protection from oxidative stress and anti-inflammatory activity ((Kelley, Aldkins, & Laugero, 2018; Blando & Oomah, 2019; Sokół-Łętowska, Kucharska, Hodun & Gołba, 2020).

Used for a long time as fresh and conserved specific fruits from local communities, nowadays together with juice fruits and other fruit confections such as jam, marmalades, jelly, juice, and cakes are widely infused to consumers diet globally. Fruit juice is a reliable source of bioactive compounds, such as phenolic compounds. Among them, cherry and quince juices are well-known as excellent sources. Studies on examining the polyphenol content in cherry juices have revealed a plethora of phenolic classes: anthocyanins, which include (-)-epicatechin (flavanol), neo-chlorogenic, chlorogenic, and 3-coumaroylquinic acid (hydroxycinnamic acids), as well as quercetin and kaempferol glycosides (flavonols) (Bonerz, Würth, Dietrich & Will, 2007).

Quince fruit has gained much attention because of its high antioxidant capacity resulting from phytochemicals, including phenolic compounds such as hydroxycinnamic acid and proanthocyanidins. The cold-pressing technique enables the transfer of most primary and secondary metabolites found in the original ripped and sound fruit, from the fruit to the juice through the fruit crush at room temperatures, at a low speed. The extraction process generates almost no

heat and preserves the juice's nutritional quality (Miguel, Dandlen, Antunes, Neves & Martins, 2004). Another critical factor associated with the juice nutritional value is the quality of storage conditions, mainly temperature and time (Gholamreza, Kitipong, Supaart, 2019).

Nowadays, studying of phenolic compounds both as bulk matrix as well as individually is of primary importance to researchers. Applying the liquid chromatography separation technique enables identifying and quantifying phenolic compounds. The major limitation is that the compound identification is achieved only by retention time and UV spectra. In recent years, to overcome this problem, applying liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS) has taken ground for the proper characterization of phenolic compounds in fruit juice.

In addition, noise reduction and sensitivity improvements are achieved by exploiting multiple reactions monitoring (MRM) scan mode (Hossain, Rai, Brunton, Martin-Diana & Barry-Ryan, 2010). This study aimed to evaluate the phenolic composition of cold-pressed fruit juices and provide relevant information on foods with high antioxidant content.

MATERIAL AND METHODS

Plant material and juice extraction

Quince (*Cydonia oblonga* Mill.) and sweet cherry (*Prunus aviums* L.) fruits were harvested at an optimum ripeness according to the season. Fruit coloring and peel were determining factors to the ripeness. The harvesting period was July 2018 and October 2018 for sour cherry and quince, respectively. The fruits were harvested at plantation orchards (40° 81′ N; 20° 74′ E), and (51° 99′ N; 20° 16′ E) from Korça region with plain elevation 850 m above sea level. Harvesting, transportation, preservation (in a controlled atmosphere and temperature 0-20 °C) to the laboratory were performed on the same day.

In this study, the cold-pressing method was employed to produce sweet cherry and quince juices. Overall, the cold extraction method was employed to 20 kg fruit of sweet cherry and quince, respectively. Juice extractions were processed in duplicate for both fruits. Finally, 1000 mL fruit juice was preserved in a dark bottle, 4^{o}C, until laboratory analysis. According to the 2001/112/EC Directive, the 'fruit juice' is obtained from the edible part of the ripped fruit through an extrusion and served or marketed as unfermented fresh or preserved, or fermentable liquid product (Directive 2012/12/EU, 2012).

Chemicals and reagents

Analyses were performed using analytical grade chemicals and reagents. Methanol Sodium carbonate, Sodium nitrite, Aluminum chloride, Gallic Acid, Folin-Ciocalteu reagent, and DPPH assay were obtained from Sigma Aldrich Chemical Co. (Steiheim, Germany). Deionized water from Milli-Q, (Merck-Millipore, Darmstadt, Germany) were used throughout the test analysis.

Quantification of Total Phenolic Content

The modified Folin-Ciocalteu procedure was applied to determine Total Phenolic Content (TPC) by Shimadzu UV-1280 UV-VIS spectrophotometry (Ljekočević *et al*. 2019). Overall, the juice sample was filtered by a 0.45 μm Captiva filter. A sample aliquot (0.25 mL), appropriately diluted, and Gallic acid standard solutions were mixed with 6 mL of deionized water. Further, Folin-Ciocalteu reagent (1.25 mL) was added and gently mixed. After 5 minutes, a volume of 1.0 mL of sodium carbonate (7.5%) was pipetted into the test tube and further vortex. Analyses were performed in triplicate, and absorbance was measured at 765 nm. The TPC was expressed as mg Gallic Acid Equivalent per liter (mg GAE L^{-1}).

Quantification of Total Flavonoids Content

The total flavonoids were analyzed according to the colorimetric assay proposed by Kim *et al*. (2003). A volume of 1.2 ml deionized water was pipetted to the test tube with 0.3 ml of the fruit juice sample. Consecutively, were pipetted a volume of 0.09 ml of 5% sodium nitrite, followed by 0.09 ml of $AlCl_3$ solution (10%). The test tube was incubated at a temperature of 25°C, for 6 minutes. A volume of 1 ml of sodium hydroxide (1 M) was added to the mixture. Immediately, the reaction mixture volume was made to 2.4 ml with deionized water. The mixture was thoroughly vortexed, and absorbance was measured at 510 nm. The calibration curve was produced by using aqueous solutions of known concentrations varied 0.05; 0.1; 0.2; 0.3, and 0.4 mg/cm^3. The results were expressed as g Catching equivalents (CEQ)/ L of juice sample.

Radical Scavenging Activity Determination

The scavenging activity assay method was compiled by Silva *et al*. (2004). A sample volume of 0.2 ml (0.100; 0.050; 0.020; 0.005 and 0.001 mg mL^{-1}) mixed with DPPH solution (1.8 mL) (0.04 mg L^{-1} in ethanol) incubated for 30 minutes in the darkroom. The absorbance measurements were performed at 517 nm. The calibration curve was prepared using Trolox (0.01, 0.025, 0.05, 0.075 and 0.1 mg mL^{-1}). Measurements were performed in triplicates. The scavenging activity was calculated through the following equation:

$$\text{DDPH scavenging activity (\%)} = 100 \times (A_c - A_s)/A_c$$

where: A_c-the control absorbance, and A_s -sample absorbance. IC50 calculated values denote the sample concentration required to decrease the absorbance at 517 nm by 50%). Presentation of the DPPH values was expressed as mg Trolox L^{-1}.

Solid-phase extraction

Vacuum device SPE Vacuum Manifold Baker SPE-12G using Oasis HLB bcc/200 μm cartridges were employed for extraction. 5 mL of MeOH followed by 5 mL of deionized water was applied for the cartridge conditioning.

A fruit juice sample (5 mL) passed through the cartridge, washed with 2 mL of water, and eluted with 2 mL of MeOH. Samples were collected and consecutively analyzed by LC-MS/MS.

LC-MS/MS characterization of phenolic compounds

LC-MS/MS analysis was performed using the Accela 600 UHPLC system connected to an LTQ OrbiTrap XL mass spectrometer (Thermo Fisher Scientific, Bremen, Germany) in negative ionization mode (heated electrospray ionization–HESI). The analytical column used for separation was Syncronis C18 (50 × 2.1 mm, 1.7 μm particle size). The exact UHPLC conditions and MS parameters have been reported (Vasić *et al*., 2019). Xcalibur software (version 2.1, Thermo Fisher Scientific, Waltham, MA, USA) was used for instrument control and data analysis. The molecule editor program, ChemDraw (version 12.0, Cambridge Soft, Cambridge, MA, USA), was used to draw the structures and calculate the exact masses of compounds of interest. Tentative identification of some compounds with no available standards was confirmed using previously reported MS fragmentation data (Stojković *et al*. 2020).

Phenolic compounds were identified by direct comparison with commercial standards. The total amounts of each compound were evaluated by calculation of the peak areas and are expressed as mg/kg. The limits of detection (LOD) and quantification (LOQ) were calculated using standard deviations of the responses (SD) and the slopes of the calibration curves (S) according to the formulas: LOD = 3(SD/S) and LOQ = 10 (SD/S) (Kostić *et al*. 2019).

RESULTS AND DISCUSSION

Total phenolics and flavonoids estimation

Edible fruits have historically held a place in the consumer's diet. Sweet cherries composition in phenolic compounds is distinguished among other fruits. Their presence is essential and directly influences the fruit juice quality by contributing into organoleptic characteristics, affecting the color, astringency, and aroma. They are essential in preventing chronic diseases like cancer and cardiovascular and neurodegenerative diseases. All these effects are attributed to the antioxidant properties of these molecules. This study has quantified the phenolic compound by the total phenolic content (TPC), total flavonoids content (TFC), together with DPPH radical scavenging activity of fruit juices from sweet cherry and quince fruits grown in Eastern region of Korca, Albania. The results are shown in Table 1.

Total phenolic content measured by Folin-Ciocalteu method, gives an estimate of different phenolic compounds including phenolic acids, flavonols and others. The TPC values were compared with data from literature, (Prvulovic *et al*., 2012; Tianyi *et al*., 2021). The TPC value from sweet cherry grown in Serbia show similarity 76 ± 4.85 mg GAE/100g (Prvulovic *et al*., 2012), and Australian grown sweet cherry 0.87 ± 0.09 mg GAE/g (Tianyi *et al*., 2021). Sweet cherry comprises another important source of flavonoids.

Table 1. Total phenolic, anthocyanin content and DPPH radical scavenging activity of fruit juices.

Fruit juice	Total phenolic content[a](mg GAE g^{-1})	Total flavonoids content[a] (g CEQ g^{-1})	DPPH radical scavenging activity[a] ($IC_{50\%}$)
Sweet cherry	0.60 ± 0.04^{b}	0.58 ± 0.04^{c}	10.92 ± 0.24^{d}
Quince	0.94 ± 0.02^{b}	0.97 ± 0.05^{c}	5.78 ± 0.13^{d}

[a]The results are displayed as mean ± standard deviation (n=3); [b-d]shows that means in a row are different at significant level ($p<0.05$) using One-way analysis of variance (ANOVA) and Tukey's test[c] DPPH (IC50%) mg Trolox L^{-1}, GAE-Gallic acid equivalent, CEQ-Catechin Equivalent.

De Sourza (2014) presented the TFC in sweet cherry grown in Brasil (59.92 ± 3.76 mg QE/100g. Tianyi *et al* (2021) presented data on TFC 0.31 ± 0.05 mg QE/g and 0.47± 0.01 mg QE/g. Variations in reported data are influenced by a number of agro-climatic factors, such as cultivar, land latitude of the orchards. Accordingly, the TPC and TFC of quince juice were about 1.5-fold, higher compared with sweet cherry juice. In a study, Fattouch *et al*. (2007) concluded that TPC range from 37 - 47 mg/g in quince pulp. Another study showed TPC content 6.3, 2.5, and 0.4g/kg for quince peel, pulp, and seeds, respectively (Magalhaes *et al*., 2009). In another study the TPC in Japanese quince fruit ranged from 3906 to 4550 mgGAE/100 g (Urbanaviciute *et al*., 2020).

Evaluation of anti-DPPH radical activity

The results of the anti-DPPH radical assay confirmed that the fruit juices had significant antioxidant capacities. The results supported a correlation between anti-DPPH radical activity and total phenolic content. As shown in Tab. 1, the antioxidant properties of quince juice were $IC_{50\%}$ 5.78, while the cherry juice showed antioxidant capacity $IC_{50\%}$ 10.92. Individual antioxidants do not exert separately but in concert with other antioxidants (Strazzulo *et al*., 2007). Such interactions can affect total antioxidant capacity, producing synergistic or antagonistic effects (Niki & Noguchi, 2000). A study of quince fruit methanolic extracts (pulp, peel, and seed) showed that peel extract presented the highest antioxidant capacity. The $IC_{50\%}$ values of quince pulp, peel, and jam extracts were correlated with the caffeoylquinic acid's total content (Silva *et al*. 2004). More recently, phytochemicals exerting anti-oxidative properties have taken the focus.

LC-MS/MS phenolic compound identification and quantification

Thirty-one phenolic compounds were identified in both fruit juices through UHPLC analysis including *hydroxybenzoic acids* (6): Dihydroxybenzoic

acid hexoside, Protocatechuic acid, Dihydroxybenzoic acid hexosyl-pentoside, p-Hydroxybenzoic acid, Ellagic acid, Vanillic acid; *hydroxycinnamic acids* (14): Caffeoylquinic acid hexoside, 3-O-Caffeoylquinic acid, Caffeic acid hexoside, 3-O-p-Coumaroylquinic acid, 4-O-Caffeoylquinic acid, 3-O-Feruoylquinic acid, Caffeic acid, Coumaric acid hexoside, 5-O-Caffeoyl-quinic acid, 5-O-p-Coumaroylquinic acid, Caffeoylshikimic acid, 4-O-Feruoylquinic acid, 4-O-p-Coumaroylquinic acid, p-Coumaric acid; *flavan-3-ols* (2): Catechin and Epicatechin; *procyanidins* (2): Procyanidin dimer B type isomer 1, and Procyanidin dimer B type isomer 2; *flavonols* (6): Quercetin 3-O-(6"-rhamnosyl) glucoside, Quercetin 3-O-glucoside, Kaempferol 3-O-(6"-rhamnosyl) glucoside, Quercetin 3-O-pentoside, Quercetin 3-O-rhamnoside, and Quercetin; and *dihydrochalcone* (1): Phloretin 2'-O-glucoside, with specific retention times (Table 2). Each phenolic compound was identified based on the exact mass and respective MS2, MS3 and MS4 fragments m/z. These findings were consulted with Phenolic compounds Mass spectra databank.

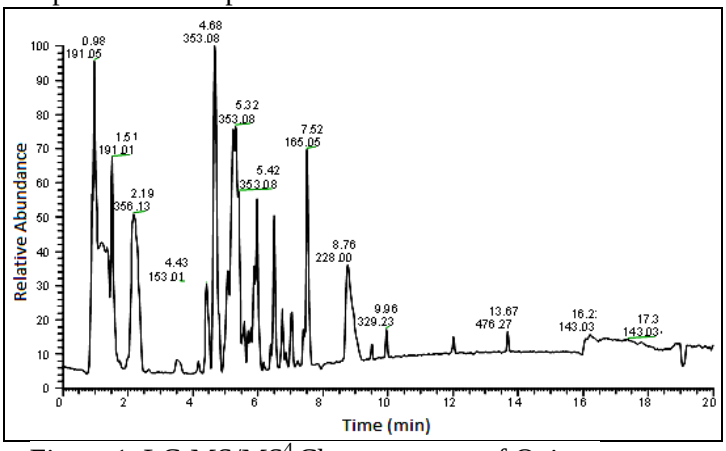

Figure 1. LC-MS/MS^4 Chromatogram of Quince

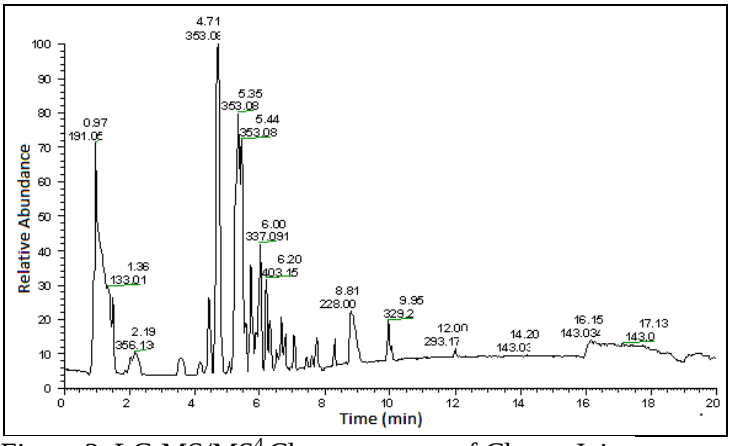

Figure 2. LC-MS/MS^4 Chromatogram of Cherry Juice

Table 2. Phenolic compounds detected and quantified in cherry and quince juices by LC–MS/MS^4 in negative ionization mode.

No	t_R, min	Compound name	Molecular formula $[M-H]^-$	Calculated mass $[M-H]^-$, *m/z*	Exact mass $[M-H]^-$, *m/z*	Δ ppm	MS^2 Fragments, *m/z* (% Base Peak)	MS^3 Fragments, *m/z* (% Base Peak)	MS^4 Fragments, *m/z* (% Base Peak)	Cherry	Quince
Hydroxybenzoic acids											
1.	3.92	Dihydroxybenzoic acid hexoside	$C_{13}H_{15}O_9^-$	315.07216	315.07207	0.29	153(100) 152(50) 109(15) 108(10)	109(100)	123(25) 109(10) 85(10) 81(100)	+	+
2.	4.44	Protocatechuic acid*	$C_7H_5O_4^-$	153.01933	153.01932	0.07	109(100) 95(75) 79(20) 59(10)	81(100) 68(25) 65(15)	–	1.145	1.265
3.	4.58	Dihydroxybenzoic acid hexosyl-pentoside	$C_{18}H_{23}O_{13}^-$	447.11441	447.11434	0.16	315(100) 285(10) 153(10)	153(100) 123(10)	123(100)	+	+
4.	5.37	*p*-Hydroxybenzoic acid*	$C_7H_5O_3^-$	137.02442	137.02423	1.39	109(10) 93(100)	93(10)	–	0.827	0.716
5.	6.79	Ellagic acid	$C_{14}H_5O_8^-$	300.99899	300.99890	0.30	284(40) 271(60) 257(100) 229(85) 185(40)	229(100) 213(20) 185(85)	201(100) 185(95) 157(30) 145(20) 129(10)	–	+
6.	6.93	Vanillic acid*	$C_8H_7O_4^-$	167.03498	167.03484	0.84	153(10) 152(80) 124(10) 123(100) 108(20)	108(100)	79(100)	2.945	6.478
Hydroxycinnamic acids											
7.	4.53	Caffeoylquinic acid hexoside	$C_{22}H_{27}O_{14}^-$	515.14008	515.13977	0.60	353(40) 341(100) 335(30) 323(10) 191(15) 179(45)	179(100) 135(10)	135(100)	+	+
8.	4.72	3-*O*-Caffeoylquinic acid	$C_{16}H_{17}O_9^-$	353.08781	353.08656	3.54	191(100) 179(30) 135(10)	173(75) 127(100) 111(40) 93(60) 85(90)	109(30) 99(40) 85(100)	+	–
9.	5.24	Caffeic acid hexoside	$C_{15}H_{17}O_9^-$	341.08781	341.08658	3.61	179(100) 135(10)	135(100)	107(100) 79(20)	+	+
10.	5.27	3-*O*-*p*-Coumaroylquinic acid	$C_{16}H_{17}O_8^-$	337.09289	337.09201	2.61	191(10) 173(10) 163(100) 119(10)	119(100)	119(100)	+	+
11.	5.33	4-*O*-Caffeoylquinic acid	$C_{16}H_{17}O_9^-$	353.08781	353.08624	4.45	191(60) 179(75) 173(100) 135(15)	115(20) 111(50) 93(100) 71(20)	–	+	+
12.	5.55	3-*O*-Feruoylquinic acid	$C_{17}H_{19}O_9^-$	367.10346	367.10220	3.43	193(100) 134(10)	149(25). 134(100)	106(100)	+	
13.	5.97	Caffeic acid*	$C_9H_7O_4^-$	179.03498	179.03464	1.90	135(100)	135(60). 117(15) 107(100) 91(55). 79(15)	–	0.672	0.553
14.	5.45	Coumaric acid hexoside	$C_{15}H_{17}O_8^-$	325.09289	325.09277	0.37	289(20) 265(20) 187(40) 163(80) 145(100) 119(10)	117(100)	–	+	–
15.	5.80	5-*O*-Caffeoyl-quinic acid*	$C_{16}H_{17}O_9^-$	353.08781	353.08627	4.36	191(100) 179(5)	173(75) 127(100) 111(40) 93(60) 85(90)	109(40) 99(50). 85(100)	8.343	6.407
16.	6.00	5-*O*-*p*-Coumaroylquinic acid	$C_{16}H_{17}O_8^-$	337.09289	337.09128	4.78	191(100) 179(5) 163(10)	173(75) 127(100) 111(40) 93(60) 85(90)	109(30) 99(40). 85(100)	+	+
17.	6.06	Caffeoylshikimic acid	$C_{16}H_{13}O_8^-$	335.07724	335.07608	3.46	179(100) 135(25)	135(100)	107(100)	+	+
18.	6.24	4-*O*-Feruoylquinic acid	$C_{17}H_{19}O_9^-$	367.10346	367.10330	0.44	193(10) 191(5) 173(100)	155(20) 111(20) 93(100) 71(20)	–	+	–
19.	6.38	4-*O*-*p*-Coumaroylquinic acid	$C_{16}H_{17}O_8^-$	337.09289	337.09238	1.51	191(5) 173(100) 163(10)	115(20). 111(50). 93(100). 71(20)	–	+	+

20.	6.78	*p*-Coumaric acid*	$C_9H_7O_3^-$	163.04007	163.03984	1.41	119(100)	119(60) 101(20) 93(25) 91(100) 72(10)	–	0.636	0.191
		Flavan-3-ols									
21.	5.39	Catechin*	$C_{15}H_{13}O_6^-$	289.07176	289.07126	1.73	271(5) 245(100) 205(40) 179(15) 125(5)	227(30) 205(100) 187(25) 175(10) 161(20)	188(70) 185(20) 175(100) 161(40) 157(10)	0.413	0.725
22.	5.92	Epicatechin*	$C_{15}H_{13}O_6^-$	289.07176	289.07095	2.80	271(5) 245(100) 205(40) 179(15) 125(5)	227(35) 205(100) 187(30) 175(15) 161(25)	188(60) 185(20) 175(100) 161(35) 157(15)	0.918	1.911
Procyanidins											
23.	4.97	Procyanidin dimer B type isomer 1	$C_{30}H_{25}O_{12}^-$	577.13515	577.13440	1.30	559(15) 451(25) 425(100) 407(50) 289(30) 287(10)	407(100) 381(5) 287(5) 273(10)	389(30) 297(30) 285(100) 281(90)	+	+
24.	5.60	Procyanidin dimer B type isomer 2	$C_{30}H_{25}O_{12}^-$	577.13515	577.13330	3.21	559(5) 451(20) 425(100) 407(50) 289(20) 287(10)	407(100) 381(10) 273(10)	389(40) 297(40) 285(100) 243(75)	+	+
Flavonols											
25.	6.50	Quercetin 3-*O*-(6"-rhamnosyl) glucoside*	$C_{27}H_{29}O_{16}^-$	609.14611	609.14447	2.69	343(5) 301(100) 300(30) 271(10) 255(5)	273(25) 257(20) 179(100) 151(75)	151(100)	0.450	2.104
26.	6.73	Quercetin 3-*O*-glucoside*	$C_{21}H_{19}O_{12}^-$	463.08820	463.08710	2.38	301(100) 300(30)	273(25) 257(20) 179(100) 151(75)	151(100)	0.527	0.960
27.	6.85	Kaempferol 3-*O*-(6"-rhamnosyl) glucoside	$C_{27}H_{29}O_{15}^-$	593.15119	593.15112	0.12	285(100) 284(10)	257(100) 241(30) 229(40) 213(30) 151(5)	255(10) 239(30) 229(100) 163(40)	–	+
28.	6.97	Quercetin 3-*O*-pentoside	$C_{20}H_{17}O_{11}^-$	433.07763	433.07724	0.90	343(5) 301(80) 300(100)	271(100) 255(60) 179(10) 151(10)	243(100) 227(80) 215(20) 199(20)	–	+
29.	7.25	Quercetin 3-*O*-rhamnoside*	$C_{21}H_{19}O_{11}^-$	447.09329	447.09222	2.39	301(100) 300(35) 284(20)	273(25) 257(20) 179(100) 151(75)	151(100)	0.034	0.077
30.	8.83	Quercetin*	$C_{15}H_9O_7^-$	301.03538	301.03534	0.13	271(50) 255(20) 179(100) 151(80) 107(5)	151(100)	107(100) 83(10)	1.612	1.861
Dihydrochalcon											
31.	7.60	Phloretin 2'-*O*-glucoside*	$C_{21}H_{23}O_{10}^-$	435.12967	435.12784	4.21	274(5) 273(100)	167(100) 125(5) 123(5)	125(10) 123(100)	0.325	0.596
*Identification with standard. Other compounds were tentatively identified by MS fragmentation; Δ ppm – mean mass accuracy; + stands for detected and – stands for not detected compound. t_R - retention time.									Σ	18.846	23.844

A number of these phenolics are found in olive oil and red wines (Topi, Guclu, Kelebek & Selli, 2020). Among them, thirteen phenolic compounds were quantified. Despite their species variation, apple juices comprise an essential source of phenolic compounds (Soler, Soriano & Mañes, 2009). Grapefruit also contains many phytochemicals, including twenty carotenoids, particularly beta-carotene and lycopene, as well as 13 polyphenols, mostly naringin and narirutin (McKay & Wilson, 2016). Besides vitamin C, citrus fruits are rich in flavanones and carotenoids (Baghurst, 2003; Manners, 2007; Topi, 2020). Even their fermented products, such as wines, are rich in phenolic compounds (Topi, Kelebek, Guclu, & Selli, 2021).

5-*O*-caffeoylquinic acid was the main phenolic compound identified in sweet cherry juice. Meanwhile important levels of protocatechuic and vanillic acid from hydroxybenzoic acids group; and quercetin from flavonol group were quantified. Sokół-Łetovska *et al*. (2020) examined the fruit chemical composition of 21 sour cherry cultivars in Poland and found neochlorogenic, chlorogenic, and *p*-coumaric acids dominant in cherry fruit. Other publication identifies quercetin, kaempferol, isorhamnetin rutinosides, and glucosides as dominant constituents in sweet cherry cultivars (Levaj, Dragović-Uzelac, Ganić, Banović & Kovačević, 2010; Cao, Jiang, Lin, Li & Sun, 2015). According to the literature, sour cherry fruits contain glucose, fructose, sucrose, organic acids, and malic acid. Among phenolic compounds, the main group is phenolic acids, with 5-caffeoylquinic, *p*-coumaric, and 3-caffeoylquinic most relevant. Flavanols and flavonols are also important phenolic groups present in cherry fruit (Sut, Dall'Acqua, Poloniato, Maggi, & Malagoli, 2019).

5-*O*-caffeoylquinic acid and vanillic acid were the main phenolic compounds quantified in quince juice. In addition, significant amount of quercetin and its glucosides (table 2) were present. In a study, Magalhaes and colleagues (2009) evaluated the phenolic compounds' profile of the quince fruit (peel, pulp, and seeds) and showed that 5-O-caffeoylquinic acids were major phenolic while seeds were rich in 6,8-di-*C*-glucosyl chrysoeriol. Similarly, chlorogenic acid (5-*O*-caffeoylquinic acid, 37%) and rutin (36%) were primary phenolics (Fattouch *et al*., 2007).

CONCLUSIONS

Phenolic compounds in quince and sweet cherry cold-pressed juice were successfully estimated by liquid chromatography tandem mass spectrometry, as well as spectrophotometry. Quince juice had the highest TPC and TFC values compared to sweet cherry juice. Regarding to antioxidant scavenging activity was fond that inverse value, with sweet cherry possessing higher anti-DPPH radical activity comparing with quince juice. Phenolic acids were the main phenolic class in both investigated fruit juices—with a significant correlation with total phenolic content. According to LC-MS/MS4 analysis, a total of 31 phenolic compounds

were identified including 6 hydroxybenzoic acids, 14 hydroxycinnamic acids, two flavan-3-ols, six flavonols, and one dihydrochalcone.

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