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ORIGINAL ARTICLE

Characterization and quantification of flavonoid glycosides in the *Prunus* genus by UPLC-DAD-QTOF/MS

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Apricot

Abstract Widely distributed in plants, flavonoids reduce the incidence of cancer and cardiovascular disease. In this study, flavonoid content and composition in members of the *Prunus* genus were evaluated using liquid chromatography with diode array and electrospray ionization mass spectrometric detection (UPLC-DAD-ESI/QTOF-MS). Flavonoids in plants of the *Prunus* genus include the basic structures of kaempferol, quercetin, and catechin, and exist as mono-, di-, or tri-glycoside compounds mono-acylated with acetic acid. A total of 23 individual flavonoids were isolated and confirmed, three of which appear to be newly identified compounds: quercetin 3-*O*-(2″-*O*-acetyl) neohesperidoside, quercetin 3-*O*-(4″-*O*-acetyl)rutinoside, and kaempferol 3-*O*-(4″-*O*-acetyl) rutinoside. Japanese apricot and Chinese plum contained the highest amounts of flavonoids in the *Prunus* genus. During the ripening stage of Japanese apricot, the total flavonol content was reduced, while the catechin content was increased.

1. Introduction

Flavonoids are widely distributed in plants and are an important part of the diet due to their health-promoting benefits, including reduced risk of cancer and cardiovascular disease (Price and Rhodes, 1997; Zhishen et al., 1999; Lin and Harnly, 2008). Flavonoids are a large group of phytochemicals that are derived from multiple branches of the shikimic acid pathways, one of the most-characterized secondary metabolic routes in plant systems (Khanam et al., 2012; Wang et al., 2012). All food plants contain significant levels of these com-

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pounds, which systematically identify glycosylated flavonoids (Price and Rhodes, 1997; Lin and Harnly, 2008).

The *Prunus* genus belongs to the Rosaceae family and consists of approximately 175 species distributed worldwide (Rashid et al., 2007), such as *P. armeniaca*, *P. mume*, *P. perisica*, *P. salicina*, *P. domestica*, *P. spinosa*, *P. tomentosa*, *P. cerasus*, etc. Recent reports confirm that these plants contain high levels of flavonoids. *P. armeniaca* contains quercetin 3-*O*-rutinoside (rutin), quercetin 3-*O*-glucoside (isoquercitrin), and kaempferol 3-*O*-rutinoside (nicotiflorin), with rutin present at the highest levels (Schmitzer et al., 2011; Sanz et al., 2010; Rashid et al., 2007). Isorhamnetin and quercetin derivatives were detected in the flowers of *P. mume*, and analysis of flavonoids in the fruits of *P. mume* using LC–MS identified glucoside, galactoside, and neohesperidoside (Nakamura et al., 2013; Yoshikawa et al., 2002; Yan, 2015). Flavonoids in *P. perisica* were studied in a variety of plant parts including the leaves, stem bark, and peels (Backheet et al., 2003; Tomas-Barberan et al., 2001). In the peels of *P. salicina* and *P. domestica*, the main flavonoids reported were quercetin 3-*O*-glucoside(isoquercitrin), quercetin 3-*O*-xyloside (reynoutrin), quercetin 3-*O*-rhamnoside (quercitrin), quercetin 3-*O*-galactoside (hyperoside), quercetin 3-*O*-rutinoside (rutin), quercetin 3-*O*-arabinoside (gvajaverin), and isorhamnetin 3-*O*-glucoside (Tomas-Barberan et al., 2001; Treutter et al., 2012). Further, kaempferol 3-*O*-arabinofuranoside (juglanin) and quercetin 3-*O*-arabinofuranoside (avicularin) were isolated from extracts of *P. spinosa* flowers (Olszewska and Wolbis, 2001). Analysis of flavonoids from *P. cerasus* identified kaempferol, quercetin, quercetin 3-*O*-glucoside, and isorhamnetin 3-*O*-rutinoside (Piccolella et al., 2008), and catechin-type flavonoids were found to be distributed in the peels of *P. domestica*, peels and pulps of *P. perica*, and fruits of *P. mume* and *P. cerasus* (Tomas-Barberan et al., 2001; Piccolella et al., 2008; Treutter et al., 2012). Anthocyanins were reported mainly in the peels of fruits, and cyanidin 3-*O*-glucoside (chrysanthemin) and cyanidin 3-*O*-rutinoside (keracyanin) are the predominant anthocyanins present in *P. armeniaca*, *P. domestica*, *P. salicina*, and *P. persica* (Tomas-Barberan et al., 2001; Bureau et al., 2009; Treutter et al., 2012). Comparative evaluation is important for evaluating flavonoid characteristics in the various plants of the *Prunus* genus.

In this paper, flavonoid glycosides were characterized and quantified in plants of the *Prunus* genus, including *P. armeniaca* (apricot), *P. mume* (Japanese apricot), *P. perisica* (peach), *P. salicina* (Chinese plum), *P. tomentosa*, and *P. cerasus* (cherry), using ultra performance liquid chromatography with diode array and quadrupole time-of-flight mass (UPLC-DAD/QTOF-MS).

Table 1 List of isolated flavonoids compounds and their mass spectrometric data in *Prunus* genus.

Aglycones	Glycosides	Acylation*	Individual flavonoids	MW	Fragment ions (m/z)	UV spectrum pattern (λ_{max} → MeOH)
Kaempferol	Non		Kaempferol	286	287	
	Mono		Kaempferol 3-*O*-xyloside	418	441, 287	
			Kaempferol 3-*O*-rhamnoside (afzelin)	432	455, 433, 287	265,294sh,342
			Kaempferol 3-*O*-galactoside (trifolin)	448	471, 449, 287	266,301sh,346
			Kaempferol 3-*O*-glucoside (astragalin)	448	471, 287	266,298sh,346
	Di		Kaempferol 3-*O*-rutinoside (nicotiflorin)	594	617, 595, 449, 287	266,298sh,346
		Ac	Kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside (cerakorin)	636	659, 637, 287	265,294sh,320sh,343
Quercetin	Non		Quercetin	302	303	256,302sh,371
	Mono		Quercetin 3-*O*-xyloside (reynoutrin)	434	457, 435, 303	257,266sh,296sh,356
			Quercetin 3-*O*-arabinoside (gvajaverin)	434	457, 435, 303	257,265sh,300sh,354
			Quercetin 3-*O*-rhamnoside (quercitrin)	448	471, 449, 303	256,307sh,351
			Quercetin 3-*O*-galactoside (hyperoside)	464	487, 465, 303	257,265sh,298sh,355
			Quercetin 3-*O*-glucoside (isoquercitrin)	464	487, 465, 303	256,266sh,297sh,355
		Ac	Quercetin 3-*O*-(6″-*O*-acetyl)glucoside	506	529, 507, 303	256,267sh,298sh,356
		Ac	Quercetin 3-*O*-(2″-*O*-acetyl)glucoside	506	529, 507, 303	257,301sh,354
	Di		Quercetin 3-*O*-neohesperidoside	610	633, 611, 465, 449, 303	256,266sh,356
			Quercetin 3-*O*-rutinoside (rutin)	610	633, 611, 465, 449, 303	257,266sh,354
		Ac	Quercetin 3-*O*-(2″-*O*-acetyl)neohesperidoside (mumikotin B)	652	675, 653, 303	257,266sh,295sh,352
		Ac	Quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (mumikotin A)	652	675, 653, 303	257,266sh,293sh,354
		Ac	Quercetin 3-*O*-(4″-*O*-acetyl)rutinoside (cerakocetin)	652	675, 653, 303	257,301sh,354
	Tri		Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)galactoside	756	779, 757, 611, 465, 303	256,300sh,356
			Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl) glucoside	756	779, 757, 611, 465, 303	256,299sh,355
Catechin	Non		(−)-Epicatechin	290	291	234,280

* Ac, Acetic acid.

Table 2 LC–MS and NMR library of *Prunus* genus based on the literature sources.

No.	Compound names	MW	UV spectrum pattern (λ^{*}_{max})	States	Used parts	Plant resources	References
1	Kaempferol	286		NMR,MS	Flower[c], Fruits[f]	*spinosa*[c], *cerasus*[f]	Olszewska and Wolbis (2001) and Piccolella et al. (2008)
2	Quercetin	302		NMR,MS	Flower[c], Fruits[f]	*spinosa*[c], *cerasus*[f]	Olszewska and Wolbis (2001) and Piccolella et al. (2008)
3	Kaempferol 3-*O*-xyloside	418	[(4)]265,296sh,348	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2001)
4	Kaempferol 3-*O*-arabinofuranoside (juglanin)	418	[(4)]266,300sh,348	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2001)
5	Kaempferol 3-*O*-rhamnoside (afzelin)	432	[(4)]260,295sh,346	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2001)
6	Kaempferol 7-*O*-rhamnoside	432	[(4)]255sh,265,323,365	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2001)
7	quercetin 3-*O*-xyloside (reynoutrin)	434	[(11)]254,355	MS	Peels[d]	*salicina*[d]	Tomas-Barberan et al. (2001)
8	quercetin 3-*O*-arabinoside (gvajaverin)	434		MS	Peels[b]	*domestica*[b]	Treutter et al. (2012)
9	quercetin 3-*O*-arabinofuranoside (avicularin)	434	[(4)]256,269sh,300sh,358	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2001)
10	quercetin 3-*O*-rhamnoside (quercitrin)	448	[(11)]254,355	MS	Peels[d]	*salicina*[d]	Tomas-Barberan et al. (2001)
11	Kaempferol 3-*O*-glucoside (astragalin)	448	[(6)]265,300sh,351	NMR,MS	Leaves[e]	*persica*[e]	Backheet et al. (2003)
12	Kaempferol 3-*O*-galactoside (trifolin)	448	[(6)]265,289sh,351	NMR,MS	Leaves[e]	*persica*[e]	Backheet et al. (2003)
13	Isorhamnetin 3-*O*-rhamnoside	462		NMR,MS	Flowers[g]	*mume*[g]	Yoshikawa et al. (2002)
14	Quercetin 3-*O*-glucoside (isoquercitrin)	464	[(5)]258,354 [(6)]257,269sh,362 [(11)]254,355	NMR,MS	Peels[abde], Pulps[a] Fruits[bfg], Leaves[e]	*armeniaca*[a], *domestica*[b] *salicina*[d], *persica*[e] *cerasus*[f], *mume*[g]	Backheet et al. (2003), Piccolella et al. (2008), Schmitzer et al. (2011), Tomas-Barberan et al. (2001), Treutter et al. (2012) and Yan (2015)
15	Quercetin 3-*O*-galactoside (hyperoside)	464	[(11)]254,355	MS	Peels[bde] Pulps[e]	*domestica*[b] *salicina*[d], *persica*[e]	Tomas-Barberan et al. (2001) and Treutter et al. (2012)
16	Isorhamnetin 3-*O*-glucoside	478		MS	Peels[b], Flowers[g]	*domestica*[b], *mume*[g]	Nakamura et al. (2013) and Treutter et al. (2012)
17	Isorhamnetin 3-*O*-galactoside	478		NMR,MS	Flowers[g]	*mume*[g]	Nakamura et al. (2013)
18	Quercetin 3-*O*-(2″-*O*-acetyl)glucoside	506		NMR,MS	Flowers[g]	*mume*[g]	Nakamura et al. (2013)
19	Quercetin 3-*O*-(6″-*O*-acetyl)glucoside	506		MS (Presumed)	Peels[a], Flowers[g]	*armeniaca*[a], *mume*[g]	Nakamura et al. (2013), Sanz et al. (2010) and Schmitzer et al. (2011)
20	Isorhamnetin 3-*O*-(3″-*O*-acetyl)glucoside (mumeflavonoside A)	520		NMR,MS	Flowers[g]	*mume*[g]	Nakamura et al. (2013)
21	Kaempferol 3-*O*-(2″-O-*p*-coumaroyl) arabinofuranoside	564	[(4)]268,300sh,316,360	NMR,MS	Flower[c]	*spinosa*[c]	Olszewska and Wolbis (2007)
22	Quercetin 3-O-(6″-*O*-benzoyl)galactoside	568		NMR,MS	Flowers[g]	*mume*[g]	Nakamura et al. (2013)
23	Kaempferol 3-*O*-rutinoside (nicotiflorin)	594		NMR,MS	Peels[a]	*armeniaca*[a]	Sanz et al. (2010)
24	Kaempferol 3-*O*-glucosyl(1 → 4)galactoside	610	[(6)]267,289sh,350	NMR,MS	Leaves[e]	*persica*[e]	Backheet et al. (2003)
25	Quercetin 3-*O*-rutinoside (rutin)	610	[(5)]258,355 [(3)]254,355 [(11)]254,355	NMR,MS	Peels[abde], Pulps[a] Flowers[g], Fruits[bg]	*armeniaca*[a], *domestica*[b] *salicina*[d], *persica*[e] *mume*[g]	Sanz et al. (2010), Schmitzer et al. (2011), Slimestad et al. (2009), Tomas-Barberan et al. (2001), Treutter et al. (2012), Yan (2015) and Yoshikawa et al. (2002)

Table 2 (*continued*)

No.	Compound names	MW	UV spectrum pattern (λ^{*}_{max})	States	Used parts	Plant resources	References
26	Quercetin 3-*O*-neohesperidoside	610		NMR,MS	Flowers[g], Fruits[g]	*mume*[g]	Yan (2015) and Yoshikawa et al. (2002)
27	Isorhamnetin 3-*O*-rutinoside (narcissin)	624		NMR,MS	Fruits[f]	*cerasus*[f]	Piccolella et al. (2008)
28	Kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside (cerakorin)	636		MS (Presumed)	Fruits[f]	*cerasus*[f]	
29	Quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (2″-*O*-acetylrutin) (mumikotin A)	652	[(10)]258,270sh,354	NMR,MS	Flowers[g]	*mume*[g]	Yoshikawa et al. (2002)
30	Quercetin 3-*O*-(2″-*O*-acetyl)neohesperodoside (mumikotin B)	652		MS (Presumed)	Fruits[g]	*mume*[g]	
31	Quercetin 3-*O*-(4″-*O*-acetyl)rutinoside (cerakocetin)	652		MS (Presumed)	Fruits[f]	*cerasus*[f]	
32	3,5,7,4'-tetrahydroxy-3',5'-dimethoxy flavone3-*O*-robinobioside	654	[(1)]252,357	NMR,MS	Fruits[a]	*armeniaca*[a]	Rashid et al., 2007
33	Isorhamnetin 3-*O*-(2″-*O*-acetyl)rutinoside (2″-*O*-acetylnarcissin)	666	[(10)]254,269sh,354	NMR,MS	Flowers[g]	*mume*[g]	Yoshikawa et al., 2002
34	quercetin 3-*O*-(2″,6″-di-*O*-Rhamnosyl) glucoside	756		MS (Presumed)	Fruits[g]	*mume*[g]	
35	Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl) galactoside	756		NMR,MS	Flowers[g]	*mume*[g]	Yoshikawa et al. (2002)
36	Apigenin 5-*O*-glucoside	432	[(8)]258,329	MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
37	Luteolin 5-*O*-glucoside	448		MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
38	Apigenin 7-*O*-mannosyl (1 → 2)alloside	594	[(1)]272,333	NMR,MS	Fruits[a]	*armeniaca*[a]	Rashid et al. (2007)
39	Tectochrysin 5-*O*-glucoside	430	[(9)]243sh,258,304	NMR,MS	Bark[f]	*cerasus*[f]	Geibel et al. (1990, 1991)
40	Genkwanin 5-*O*-glucoside	446	[(8)]257,326	MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
41	Naringenin	272	[(6)]291,328sh	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
42	Eriodictyol	288	[(6)]289,324sh	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
43	Dihydrokaempferol (aromadendrin)	288	[(6)]290,327sh	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
44	Hesperitin 5-*O*-glucoside	464	[(6)]281,325	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
45	5,3'-dihydroxy-7,4′-dimethoxy flavanone (persicogenin)	316	[(6)]285,332	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
46	Pinostrobin 5-*O*-glucoside	432	[(8)]279,305sh	MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
47	Sakuranin	448		MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
48	Persicogenin 3'-*O*-glucoside	478	[(6)]286,332	NMR,MS	Stem bark[e]	*persica*[e]	Backheet et al. (2003)
49	Neosakuranin	448	[(8)]254sh,310sh,364	MS	Bark[f]	*cerasus*[f]	Geibel et al. (1991)
50	(+)-catechin	290	[(11)]280	MS	Peels[be], Pulps[e]	*domestica*[b], *persica*[e]	Tomas-Barberan et al. (2001) and Treutter et al. (2012)
51	(−)-Epicatechin	290	[(11)]280	NMR,MS	Peels[be], Pulps[e] Fruits[g]	*domestica*[b], *persica*[e] *mume*[g]	Tomas-Barberan et al. (2001), Treutter et al. (2012) and Yan (2015)
52	(−)-Epicatechin 3-*O*-malate	406	[(7)]217	NMR,MS	Fruits[f]	*cerasus*[f]	Piccolella et al. (2008)
53	(−)-Epicatechin 3-*O*-(1″-*O*-methyl)malate	420	[(7)]216	NMR,MS	Fruits[f]	*cerasus*[f]	Piccolella et al. (2008)

(*continued on next page*)

Table 2 (*continued*)

No.	Compound names	MW	UV spectrum pattern (λ^*_{max})	States	Used parts	Plant resources	References
54	Genistein 5-*O*-glucoside	432	(9)252	NMR,MS	Bark[f]	*cerasus*[f]	
55	Prunetin 5-*O*-glucoside (prunetinoside)	446	(9)253	NMR,MS	Bark[f]	*cerasus*[f]	
56	Cyanidin 3-*O*-glucoside (chrysanthemin)	449	(2)280,517 (5)280,517 (3)280,520 (11)280,520	MS	Peels[abde], Pulps[de] Fruits[b]	*armeniaca*[a], *domestica*[b] *salicina*[d], *persica*[e]	Bureau et al. (2009), Sanz et al. (2010), Slimestad et al. (2009), Tomas-Barberan et al. (2001) and Treutter et al. (2012)
57	Cyanidin 3-*O*-galactoside (idaein)	449	(11)280,520	MS	Peels[d]	*salicina*[d]	Tomas-Barberan et al. (2001) and Treutter et al. (2012)
58	Peonidin 3-*O*-glucoside	463	(5)519	MS	Peels[b], Fruits[b]	*domestica*[b]	Slimestad et al. (2009)
59	Cyanidin 3-*O*-(6″-*O*-acetyl)glucoside	491	(11)280,520	MS	Peels[d]	*salicina*[d]	Tomas-Barberan et al. (2001)
60	Cyanidin 3-*O*-rutinoside (keracyanin)	595	(2)280,519 (5)281,518 (3)280,520 (11)280,520	MS	Peels[abd], Pulps[de] Fruits[bf]	*armeniaca*[a], *domestica*[b] *salicina*[d], *persica*[e] *cerasus*[f]	Bureau et al. (2009), Sanz et al. (2010), Simunic et al. (2005), Slimestad et al. (2009), Tomas-Barberan et al. (2001) and Treutter et al. (2012)
61	Peonidin 3-*O*-rutinoside	609	(2)280,519 (5)274,520	MS	Peels[ab], Fruits[b]	*armeniaca*[a], *domestica*[b]	Bureau et al. (2009), Slimestad et al. (2009) and Treutter et al. (2012)
62	Cyanidin 3-*O*-(2″-*O*-glucosyl)rutinoside	757		MS	Fruits[f]	*cerasus*[f]	Simunic et al. (2005)

*Glu: glucoside(glucose), Gal: galactoside(galactose), Rham: rhamnoside(rhamnose), Ara: arabinoside(arabinose), Araf: arabionofuranoside (arabinofuranose), Rut: rutinoside(rutinose), Neo: neohesperidoside(neohesperidose), Ben: benzoic acid, Ac: acetic acid, Coum: *p*-coumaric acid, Rob: robinobioside(robinobiose), Man: mannoside(mannose), All: alloside(allose).
*(1)Rashid et al., 2007 (2)Bureau et al., 2009 (3)Ruiz et al., 2005 (4)Olszewska and Wolbis, 2007 (5)Slimestad et al., 2009 (6)Backheet et al., 2003 (7)Piccolella et al., 2008 (8)Pflanzenbau et al., 1991 (9)Pflanzenbau et al., 1990 (10)Yoshikawa et al., 2002 (11)Tomas-Barberan et al., 2001.
*UV spectrum pattern, (1)(2)(4)(5)(6)(7)(8)(9)(10)MeOH, (3)(11)80%MeOH.

2. Materials and methods

2.1. Materials

For this study, *P. armeniaca* (apricot), *P. persica* (peach) (white, heavenly, and yellow), *P. salicina* (Chinese plum), and *P. tomentosa* (Korean cherry, sweet cherry, and cherry) were purchased in 2015 from the market. The "Imju", "Namgo", and "Suyangmae" varieties of *P. mume* (Japanese apricot), distributed in 2015 from Research Center, was in accordance with three different harvest times. These samples were freeze dried and finely ground with a sample mill for use as analytical samples.

2.2. Instrumentation and reagents

The instruments used during the pretreatment process included a refrigerated multi-purpose centrifuge (Hanil Science Industrial Co. Ltd., Korea) and a digital precise shaking bath (Daihan Scientific Co. Ltd., Korea). Acetonitrile, methanol, and water were obtained from Fisher Scientific (Fair Lawn, NJ, USA). Formic acid was provided by Junsei Chemical Co., Ltd., Japan. Galangin (Sigma, St. Louis, MO, USA) was used as the internal standard solution.

2.3. Extraction

Ground samples (1 g) in conical tubes (50 mL) were centrifuged (3000 rpm, 10 min, 4 °C) following extraction with 10 mL of methanol:water:formic acid (50:45:5, v/v/v) containing internal standard (galangin)in a shaking bath at room temperature for 5 min. The supernatant was immediately filtered with a syringe filter (PVDF, 0.2 μm, 25 mm; Whatman), and 1 mL of supernatant was concentrated with N_2 gas. The extract was dissolved with 0.5 mL of methanol:water:formic acid (50:45:5, v/v/v) and diluted with 4.5 mL of water. A Sep-Pak C_{18} cartridge (Waters Co., Milford, MA, USA) was flushed with methanol and water for activation, and 1 mL of the diluted supernatant was loaded onto the cartridge. The cartridge was then washed with water and eluted with 1 mL of methanol. The extract was concentrated using N_2 gas, and then re-dissolved in 0.5 mL of methanol:water:formic acid (50:45:5, v/v/v) prior to analysis by UPLC-DAD-ESI/QTOF-MS.

2.4. Quantitative and qualitative analysis of flavonoids by UPLC-DAD-ESI/QTOF-MS

Flavonoids in *Prunus* genus samples were identified and quantified using an UPLC-DAD-ESI/QTOF-MS system (Waters

Table 3 Comparison of flavonoids composition and contents from extracts of the fruits in *Prunus* genus.[a]

Peak No.	Compound	Apricot	Japanese apricot (suyangmae)	White peach	Heavenly peach	Yellow peach	Chinese plum	Korean cherry	Sweet cherry	Cherry
1	(−)-Epicatechin	32.5 ± 0.4^{d}	50.9 ± 1.0^{k}	ND	ND	ND	77.3 ± 13.0^{d}	ND	ND	ND
2	Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)galactoside	ND	18.1 ± 0.1^{g}	ND	ND	ND	ND	ND	ND	ND
3	Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)glucoside	ND	18.8 ± 0.1^{h}	ND	ND	ND	ND	ND	ND	ND
4	Quercetin 3-*O*-neohesperidoside	ND	6.9 ± 0.0^{f}	ND	ND	ND	ND	ND	ND	ND
5	Quercetin 3-*O*-rutinoside (rutin)	31.0 ± 0.6^{c}	22.4 ± 0.0^{i}	0.3 ± 0.0^{b}	1.1 ± 0.1^{c}	0.8 ± 0.0^{c}	17.1 ± 0.3^{b}	1.7 ± 0.1^{d}	6.3 ± 0.1^{c}	8.2 ± 1.4^{c}
6	Quercetin 3-*O*-galactoside (hyperoside)	ND	3.5 ± 0.3^{b}	1.4 ± 1.7^{b}	4.0 ± 0.1^{e}	0.5 ± 0.0^{ab}	0.5 ± 0.0^{a}	ND	ND	ND
7	Quercetin 3-*O*-glucoside (isoquercitrin)	1.7 ± 0.0^{b}	4.9 ± 0.0^{d}	0.5 ± 0.0^{c}	4.6 ± 0.2^{f}	0.5 ± 0.0^{b}	32.7 ± 0.5^{c}	0.4 ± 0.0^{ab}	0.3 ± 0.0^{a}	0.3 ± 0.0^{a}
8	Quercetin 3-*O*-xyloside (reynoutrin)	ND	ND	ND	ND	ND	2.4 ± 0.1^{a}	0.6 ± 0.1^{b}	ND	ND
9	Kaempferol 3-*O*-galactoside (trifolin)	ND	ND	0.1 ± 0.0^{a}	0.9 ± 0.1^{b}	0.4 ± 0.0^{a}	ND	ND	ND	ND
10	Kaempferol 3-*O*-rutinoside (nicotiflorin)	0.6 ± 0.0^{a}	ND	1.2 ± 0.1^{d}	0.4 ± 0.1^{a}	0.8 ± 0.2^{c}	ND	2.6 ± 0.1^{e}	3.0 ± 0.1^{b}	2.1 ± 0.4^{b}
11	Quercetin 3-*O*-arabinoside (gvajaverin)	ND	ND	ND	ND	ND	13.0 ± 0.3^{b}	ND	ND	ND
12	Kaempferol 3-*O*-glucoside (astragalin)	0.4 ± 0.0^{a}	ND	2.1 ± 0.2^{e}	2.5 ± 0.4^{d}	2.5 ± 0.1^{d}	ND	1.1 ± 0.0^{c}	ND	0.2 ± 0.1^{a}
13	Quercetin 3-*O*-rhamnoside (quercitrin)	ND	ND	ND	ND	ND	4.5 ± 0.1^{a}	31.2 ± 0.8^{h}	ND	ND
14	Quercetin 3-*O*-(6″-*O*-acetyl)glucoside	1.8 ± 0.1^{b}	4.4 ± 0.1^{c}	ND	ND	ND	1.4 ± 0.3^{a}	ND	ND	ND
15	Kaempferol 3-*O*-xyloside	ND	ND	ND	ND	ND	ND	0.4 ± 0.0^{ab}	ND	ND
16	Quercetin 3-*O*-(2″-*O*-acetyl)neohesperidoside (mumikotin B)	ND	5.7 ± 0.1^{e}	ND	ND	ND	ND	ND	ND	ND
17	Quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (mumikotin A)	ND	22.8 ± 0.1^{j}	ND	ND	ND	ND	ND	ND	ND
18	Kaempferol 3-*O*-rhamnoside (afzelin)	ND	ND	ND	ND	ND	ND	23.6 ± 0.6^{g}	ND	ND
19	Quercetin 3-*O*-(2″-*O*-acetyl)glucoside	ND	1.3 ± 0.0^{a}	ND	ND	ND	ND	ND	ND	ND
20	Quercetin 3-*O*-(4″-*O*-acetyl)rutinoside (cerakocetin)	ND	ND	ND	ND	ND	ND	6.0 ± 0.1^{f}	ND	ND
21	Kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside (cerakorin)	ND	ND	ND	ND	ND	ND	42.0 ± 0.9^{i}	ND	ND
22	Quercetin	ND	ND	ND	ND	ND	0.2 ± 0.0^{a}	ND	ND	0.1 ± 0.0^{a}
23	Kaempferol	ND	ND	ND	ND	ND	ND	0.6 ± 0.1^{b}	ND	0.1 ± 0.0^{a}
Total flavonoids contents		68.0 ± 1.0	159.8 ± 0.9	4.6 ± 0.3	16.5 ± 0.6	5.5 ± 0.2	149.1 ± 13.4	110.1 ± 2.3	9.5 ± 0.1	10.9 ± 1.8

ND, not detected.

[a] mg per 100 g dry weight (DW); each value calculated as means ± SD of three replicates using internal standard (galangin).

Co., Milford, MA, USA) equipped with a Kinetex 1.7 μ XB C_{18} 100A column (150 × 2.1 mm i.d., Phenomenex, Torrance, CA, USA). The analysis was conducted at a flow rate of 0.3 mL/min and detection wavelengths of 280 (for catechins) and 350 nm (for flavonols). The column oven was kept at 30 °C. The mobile phases used were 0.5% formic acid in water (phase A) and 0.5% formic acid in acetonitrile (phase B). The pretreated sample was analyzed using the following protocol: 0 min (B) 5%, constantly increasing to (B) 90% over 30 min, constant (B) 90% until 32 min, further (B) 5% 35 min, and then constant (B) 5% until 40 min. QTOF-MS analysis was run in positive ionization mode using an electrospray ionization (ESI) source. The MS parameters were set to a cone voltage of 30 V, source temperature of 120 °C, desolvation temperature of 500 °C, and desolvation N_2 gas flow of 1020 L/h. The range of molecular weights was *m*/*z* at 200–1200 in full scan mode.

2.5. LC–MS library for qualitative analysis of flavonoids

Based on a variety of literature sources, a LC–MS library of 35 flavonols, five flavones, eight flavanones, one chalcone, four flavanols, two isoflavones, and seven anthocyanins was created and used for the identification of individual flavonoid components.

3. Results and discussion

A library containing 62 compounds identified in previous studies was used for identification of flavonoids (Table 1). A total of 23 different compounds, including four unknown compounds, were isolated and identified by UPLC-DAD-QTOF/MS with reference to the LC–MS library of *Prunus* genus flavonoids (Table 2). These detected compounds included seven kaempferol derivatives, 15 quercetin derivatives, and (−)-epicathechin (Table 3). The chemical structures of the individual flavonoids were determined by analysis of fragment patterns, in which acylated phenolic acids such as acetic acid (*m*/*z* 42) were cut out from their structures with glucose, galactose (*m*/*z* 162), rhamnoside (*m*/*z* 146), arabonoside, arabinofuranoside, xyloside (*m*/*z* 132), rutinoside, and neohesperidoside (*m*/*z* 308) found to appear independently was cut off from whole structure step by step (Backheet et al., 2003; Piccolella et al., 2008; Olszewska and Wolbis, 2001; Slimestad et al., 2009; Nakamura et al., 2013).

Previous studies reported the isolation of (−)-epicatechin from peach, plum, and Japanese apricot (Tomas-Barberan et al., 2001; Treutter et al., 2012; Yan, 2015). Tomas-Barberan et al., 2001,isolated (−)-epicatechin from the peels and pulps of peach, but this study was not isolated (−)-epicatechin, only showed apricot, Japanese apricot, and Chinese plum. Japanese apricot and Chinese plum contained flavonol glycosides as well as catechin-type flavonoids, and these samples contained the highest amounts of flavonoids in the *Prunus* genus (Table 4).

We did not detect any kaempferol-type flavonoids in Japanese apricot, but kaempferol 3-*O*-rutinoside (nicotiflorin) and kaempferol 3-*O*-glucoside (astragalin) were detected in apricot. Although astragalin was detected previously in leaves of peach (Backheet et al., 2003), this study was the first to detect astragalin in apricot (0.4 mg/100 g DW). The compound fragment

Table 4 Comparison of flavonoids composition and contents in Japanese apricot (*Prunus mume*) by variety and during ripening.

No.	Compound	Imju			Namgo			Suyangmae		
		June 3	June 15	June 22	June 3	June 15	June 22	June 3	June 15	June 22
1	(−)-Epicatechin	35.8 ± 2.5^{g}	45.8 ± 5.9^{g}	77.9 ± 2.1^{g}	20.3 ± 1.8^{g}	17.6 ± 0.2^{i}	30.1 ± 0.7^{h}	50.9 ± 1.0^{i}	84.6 ± 3.5^{g}	99.8 ± 1.9^{d}
2	Quercetin 3-*O*-(2″,6′-di-*O*-rhamnosyl)galactoside	25.9 ± 1.1^{f}	21.9 ± 0.9^{f}	11.3 ± 0.2^{f}	19.7 ± 0.7^{f}	14.4 ± 0.4^{g}	11.3 ± 0.2^{g}	18.1 ± 0.1^{f}	13.7 ± 0.2^{d}	8.0 ± 0.2^{b}
3	Quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)glucoside	7.7 ± 0.4^{e}	6.9 ± 0.4^{e}	3.7 ± 0.1^{d}	9.1 ± 0.3^{e}	6.8 ± 0.4^{e}	5.4 ± 0.2^{e}	18.8 ± 0.1^{g}	15.0 ± 0.4^{de}	8.4 ± 0.2^{b}
4	Quercetin 3-*O*-neohesperidoside	7.5 ± 0.3^{e}	7.8 ± 0.5^{e}	4.1 ± 0.0^{d}	4.3 ± 0.4^{c}	3.6 ± 0.2^{c}	3.0 ± 0.0^{c}	4.8 ± 3.6^{e}	6.4 ± 0.1^{c}	2.9 ± 0.0^{a}
5	Quercetin 3-*O*-rutinoside (rutin)	10.9 ± 0.6^{d}	11.8 ± 0.5^{de}	7.3 ± 0.2^{e}	8.1 ± 0.5^{de}	7.4 ± 0.3^{f}	6.1 ± 0.0^{f}	22.4 ± 0.0^{h}	22.0 ± 0.5^{f}	6.3 ± 4.7^{b}
6	Quercetin 3-*O*-galactoside (hyperoside)	7.1 ± 0.3^{e}	8.2 ± 0.2^{cd}	3.8 ± 0.1^{d}	2.2 ± 0.2^{b}	ND	ND	3.5 ± 0.3^{b}	3.4 ± 0.2^{b}	1.3 ± 0.3^{a}
7	Quercetin 3-*O*-glucoside (isoquercitrin)	3.9 ± 0.2^{b}	4.9 ± 0.3^{bc}	2.3 ± 0.0^{bc}	1.8 ± 0.1^{b}	1.8 ± 0.3^{b}	1.5 ± 0.2^{b}	4.9 ± 0.0^{c}	5.2 ± 0.1^{bc}	1.8 ± 0.0^{a}
8	Quercetin 3-*O*-(6″-*O*-acetyl)glucoside	3.3 ± 0.2^{b}	3.6 ± 0.1^{ab}	1.3 ± 0.0^{ab}	7.0 ± 0.2^{d}	5.7 ± 0.6^{d}	4.2 ± 0.4^{d}	4.4 ± 0.1^{c}	3.9 ± 0.1^{b}	1.4 ± 0.0^{a}
9	Quercetin 3-*O*-(2″-*O*-acetyl)neohesperidoside (mumikotin B)	7.6 ± 0.4^{e}	5.7 ± 0.2^{bc}	3.2 ± 0.2^{cd}	10.4 ± 0.4^{f}	7.9 ± 0.2^{f}	5.7 ± 0.1^{e}	5.7 ± 0.1^{d}	4.1 ± 0.1^{b}	3.2 ± 0.2^{a}
10	Quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (mumikotin A)	18.0 ± 0.8^{e}	11.3 ± 0.5^{de}	6.8 ± 0.2^{e}	23.4 ± 0.9^{b}	15.9 ± 0.5^{h}	11.1 ± 0.1^{g}	22.8 ± 0.1^{h}	16.0 ± 0.3^{e}	12.1 ± 0.2^{c}
11	Quercetin 3-*O*-(2″-*O*-acetyl)glucoside	1.2 ± 0.1^{a}	1.4 ± 0.2^{a}	1.0 ± 0.1^{a}	0.4 ± 0.0^{a}	0.3 ± 0.0^{a}	0.2 ± 0.0^{a}	1.3 ± 0.0^{a}	0.9 ± 0.1^{a}	0.6 ± 0.0^{a}
Total flavonoids contents		128.9 ± 6.6	129.4 ± 7.3	122.8 ± 2.7	106.8 ± 4.7	81.2 ± 1.8	78.8 ± 0.7	157.7 ± 2.9	175.2 ± 5.4	145.9 ± 2.9

ND, not detected.
[a] mg per 100 g dry weight (DW); each value calculated as means ± SD of three replicates using internal standard (galangin).

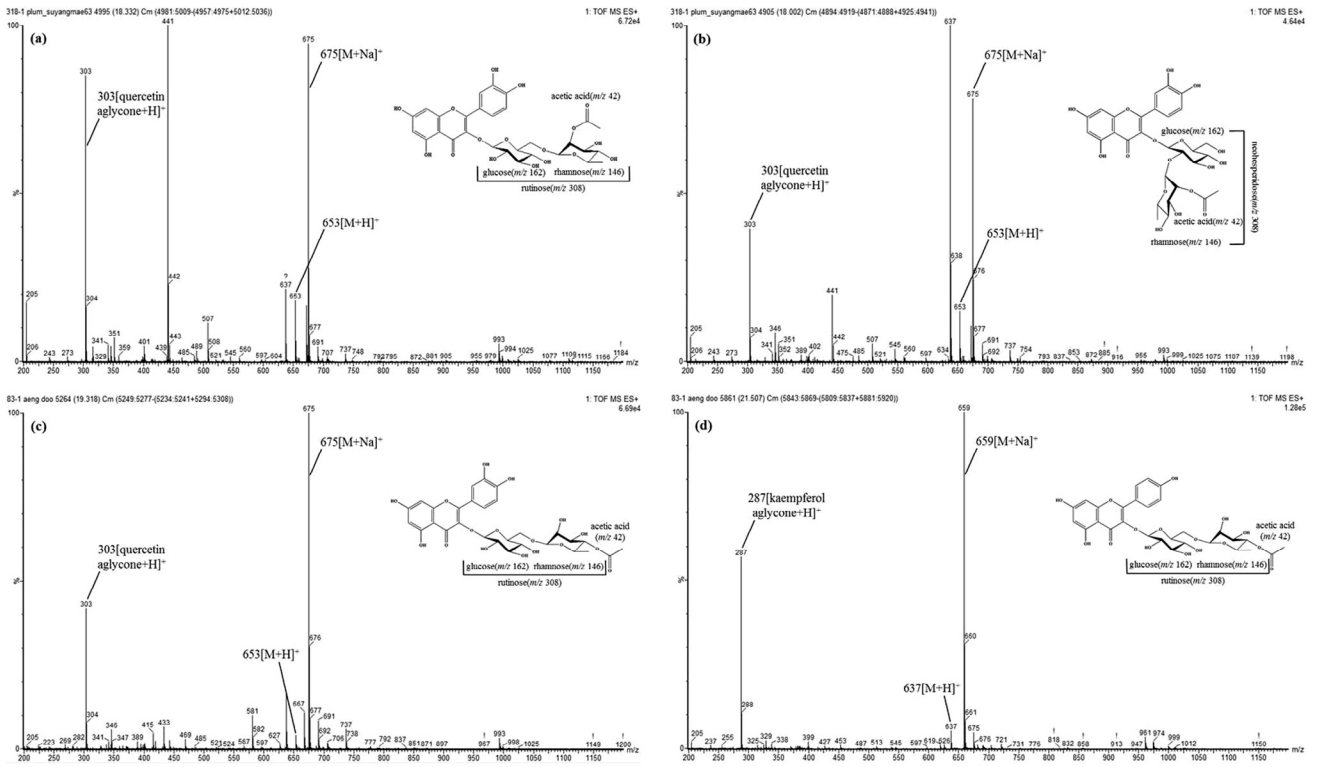

Figure 1 Chemical structures and the full scan product ion mass spectra (positive mode) of new named compound (a: quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (mumikotin A), b: quercetin 3-*O*-(2″-*O*-acetyl)neohesperidoside (mumikotin B), c: quercetin 3-*O*-(4″-*O*-acetyl) rutinoside (cerakocetin) and d: kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside (cerakorin)).

ion pattern was $[M+Na]^+$ at *m/z* 471, $[M+H]^+$ at *m/z* 449, and $[M+H\text{-Glu}]^+$ at *m/z* 287 (Table 2). In addition, nicotiflorin was isolated from peels of apricot in a previous report (Sanz et al., 2010).

The flavonol glycoside contents of the different peach varieties are shown in Table 3. The flavonol contents in the heavenly peach were generally three times higher than in white and yellow peaches, and the amounts of quercetin 3-*O*-galactoside (hyperoside) and quercetin 3-*O*-glucoside (isoquercitrin) were greater than those of other compounds in the heavenly peach. In previous studies, flavonols were found mainly in the peels of peaches (Tomas-Barberan et al., 2001) and the leaves and stem bark when analyzed by NMR (Backheet et al., 2003). Accordingly, the composition and content of flavonol glycosides will need studying depending on the cultivars and parts of the plant in the peach. Analysis of Chinese plum revealed (−)-epicatechin and quercetin derivatives, with (−)-epicatechin (77.3 mg/100 g DW) and quercetin 3-*O*-glucoside (isoquercitrin) (32.7 mg/100 g DW) present in the highest amounts.

UPLC analysis of extracts obtained from Korean cherry, sweet cherry, and cherry revealed various flavonol glycosides. Analysis of the flavonoids showed a similar profile for sweet cherry and cherry; however, significant differences were detected in Korean cherry. The flavonoid contents of Korean cherry were 110.1 mg/100 g DW (Table 3), roughly ten times greater than the flavonoid contents of sweet cherry and cherry. Quercetin 3-*O*-rutinoside (rutin) and kaempferol 3-*O*-rutinoside (nicotiflorin) were detected for the first time in Korean cherry, sweet cherry, and cherry, although in small amounts. Although catechin-type flavonoids were reported in cherry in a previous study (Piccolella et al., 2008), the present study did not detect catechin-type flavonoids. Finally, quercetin 3-*O*-xyloside (reynoutrin), quercetin 3-*O*-rhamnoside (quercitrin), kaempferol 3-*O*-xyloside, and kaempferol 3-*O*-rhamnoside (afzelin) were shown as new flavonoids (Shrivastava, 1982; Yoshioka et al., 1990; Matsuda et al., 2002; Jeong et al., 2006; Sultana and Anwar, 2008; Slinestad et al., 2009).

Based on the fact that quercetin ($[M+H]^+$ at *m/z* 303) and kaempferol ($[M+H]^+$ at *m/z* 287) were the 3,5,7,3′,4′-pentahydroxyflavone and 3,5,7,4′-tetrahydroxyflavone, respectively (Olszewska and Wolbis, 2001; Piccolella et al., 2008). In Fig. 1, the UV data (λ_{max} 257,266sh,293sh,354 nm) and MS data ($[M+Na]^+$ at *m/z* 675, $[M+H]^+$ at *m/z* 653, $[M+H\text{-Ac-rut}]^+$ at *m/z* 303) from analysis of peak 17 suggested this was quercetin 3-*O*-(2″-*O*-acetyl)rutinoside. Peak 16 (t_R = 18.10 min, λ_{max} 257,266sh,295sh,352 nm, $[M+Na]^+$ at *m/z* 675, $[M+H]^+$ at *m/z* 653, $[M+H\text{-Ac-Neo}]^+$ at *m/z* 303) was identified as a quercetin 3-*O*-(2″-*O*-acetyl) neohesperidoside. These compounds are novel flavonoids, identified for the first time in Japanese apricot. Quercetin 3-*O*-(2″-*O*-acetyl)rutinoside and quercetin 3-*O*-(2″-*O*-acetyl) neohesperidoside were named mumikotin A and B, respectively, by combining the scientific name of '*Prunus* ***mume***', '**Ko**rea', and '**rutin**oside'. Peak 20 (t_R = 19.42 min, λ_{max} 257,301sh,354 nm, $[M+Na]^+$ at *m/z* 675, $[M+H]^+$ at *m/z* 653, $[M+H\text{-Ac-Rut}]^+$ at *m/z* 303) was identified as a quercetin 3-*O*-(4″-*O*-acetyl)rutinoside. Furthermore, UV data (λ_{max} 265,294sh,320sh,343 nm) and MS data ($[M+Na]^+$ at *m/z*

659, $[M+H]^+$ at *m*/*z* 637, $[M+H\text{-Ac-Rut}]^+$ at *m*/*z* 287) from analysis of peak 21 suggested this was a kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside (Fig. 1). These compounds are also novel compounds isolated for the first time, and the kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside was the major flavonol in Korean cherry (42.0 mg/100 g DW). These compounds were named by combining 'cera' from the scientific name *Prunus* ***cera****sus*, 'ko' of **Ko**rea, and 'cetin' of quer**cetin**; hence, carakocetin (quercetin 3-*O*-(4″-*O*-acetyl)rutinoside) and cerakorin (kaempferol 3-*O*-(4″-*O*-acetyl)rutinoside) (Geibel and Feucht, 1990, 1991; Babaei et al., 2008; Fischer et al., 2007; Jaiswal et al., 2013).

Among the *Prunus* genus, the Japanese apricot contained the greatest amount of flavonoids (Table 2). The flavonoids detected in Japanese apricot were (−)-epicatechin and quercetin derivatives, and the most predominant flavonoids were (−)-epicatechin, quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)galactoside, quercetin 3-*O*-rutinoside (rutin), and quercetin 3-*O*-(2″-*O*-acetyl)rutinoside (mumikotin A) (Table 4). Importantly, the composition and amounts of flavonols in Japanese apricot varied in accordance with the variety and stage of ripening (Table 4). When comparing varieties, the suyangmae variety showed the highest flavonoid contents. When analyzed based on ripening stage, although overall flavonol contents decreased upon ripening, levels of (−)-epicatechin increased. Thus, it appears that catechins are synthesized from flavonols during maturation. In a previous study, quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)galactoside was identified in flowers of the Japanese apricot by NMR (Yoshikawa et al., 2002). In the present study, peak 3 was confirmed to be the same compound based on MS fragment data (λ_{max} 256,300sh,356 nm, $[M+Na]^+$ at *m*/*z* 779, $[M+H]^+$ at *m*/*z* 757, $[M+H\text{-Rham}]^+$ at *m*/*z* 611, $[M+H\text{-2Rham}]^+$ at *m*/*z* 465, $[M+H\text{-Gal-2Rham}]^+$ at *m*/*z* 303). Furthermore, peak 2 produced the same MS fragment profile as peak 3, and this was estimated to galactose (*m*/*z* 162) instead of glucose (*m*/*z* 162). If so, this compound would be identified as quercetin 3-*O*-(2″,6″-di-*O*-rhamnosyl)glucoside and will have been first discovered in the fruit of the Japanese apricot.

4. Conclusions

A total of 23 different compounds were isolated from members of the *Prunus* genus and identified by UPLC-DAD-QTOF/MS. Galangin was used as an internal standard solution for flavonoid quantification. The *Prunus* genus flavonoids include the basic structures of kaempferol, quercetin, and catechin, and exist as mono-, di-, or tri-glycoside compounds mono-acylated with acetic acid. In this study, four flavonoid species were detected for the first time in the Japanese apricot and Korean cherry. The Japanese apricot and Chinese plum contained flavonol glycosides as well as catechin-type flavonoids, and these two plants contained the highest amounts of flavonols in the *Prunus* genus. During ripening of the Japanese apricot, although the overall flavonol contents decreased, the amount of catechin-type flavonoids increased. Thus, it appears that catechins are synthesized from flavonols during maturation. Future studies are needed to determine the bioactive properties of each flavonoid compound and promote the use of extracts derived from members of the *Prunus* genus.

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