

COMPARATIVE ANALYSIS OF ANTHOCYANIN COMPOSITION OF JUICES OBTAINED FROM SELECTED SPECIES OF BERRY FRUITS

Anna Stój, Agnieszka Malik, Zdzisław Targoński

Department of Food Technology and Storage, University of Agriculture, Lublin

Key words: anthocyanins, fingerprints, HPLC, berry fruits, juices

A qualitative and quantitative analysis of anthocyanins in juices of three varieties of strawberry (Senga, Ducat, Marmolada), raspberry (Beskid, Canby, Malling Seedling), black currant (Ben Lomond, Titania, Ojebyn) and red currant (Rondom, Jonker, Holenderska) picked in three following years: 1998, 1999 and 2000, was presented in this paper. An HPLC technique was applied using a Gilson chromatograph and a DAD detector. Prior to the chromatographic analysis, anthocyanins were purified on a mini-column Sep-Pak C₁₈ Waters.

It was indicated that within species the juices examined differed in the quantitative and qualitative composition of anthocyanins. Pelargonidin-3-glucoside and cyanidin-3-xylo-rutinoside were the main anthocyanins in strawberry and red currant juices, respectively, independently of variety. Those anthocyanins were not detected in raspberry and black currant juices, in which cyanidin-3-sophoroside as well as delphinidin-3-rutinoside and cyanidin-3-rutinoside were the main anthocyanins, respectively. Differences of anthocyanin composition of juices obtained from different berry fruits create the possibility of detecting the adulterations of expensive raspberry and black currant juices with cheap strawberry and red currant juices on the basis of anthocyanin analysis.

INTRODUCTION

Anthocyanins are a well-known group of flavonoids [Mazza & Miniati, 1993; Zajac & Wilska-Jeszka, 1991]. Anthocyanins obtained from various fruits have been separated using paper, thin-layer and high-performance liquid chromatography [Barrit & Torre, 1973; Bakker *et al.*, 1992; Boyles & Wrolstad, 1993; Landbo & Meyer, 2004; Mullen *et al.*, 2002; Tsao & Yang, 2003]. The HPLC technique is the most useful for determination of anthocyanins. Peak identification is the problem in the HPLC analysis of anthocyanins, since not all standards are commonly available. It refers particularly to polyglycosylated anthocyanins occurring, for example, in red currants [Goiffon *et al.*, 1991].

Particular juices differ in the quantity and type of anthocyanins. The diversity of anthocyanins is used in an analysis of adulteration in berry juices [Fügel *et al.*, 2004; Silva *et al.*, 2000]. The chromatographic profile of anthocyanins required after HPLC separation – fingerprint, might allow juice identification [Versari *et al.*, 1997]. Fingerprints of anthocyanins in berry juices mostly depend on the fruit variety juices were prepared from. In some sorts of juices, particularly blueberry and raspberry, different varieties had different chromatographic profiles of anthocyanins [Hofsommer, 1995].

Flavonoids are of particular importance as they have been found to possess antioxidant and free radical scavenging activity [Le Marchand, 2002; Mazza & Miniati, 1993; Tsao & Yang, 2003]. Native composition of juices is propitious to their healthy effect.

The quantitative and qualitative composition of anthocyanins in juices prepared from four species of berry fruits (strawberry, raspberry, black currant and red currant) growing in Poland was compared in this paper. The aim of the present paper was to identify the possibility of estimating the authenticity of juices on the basis of anthocyanins profile.

MATERIAL AND METHODS

Four berry species in three varieties each were collected in 1998, 1999 and 2000. Strawberries (*Fragaria ananassa*) of Senga, Ducat and Marmolada cv. originated from the plantation in Zemborzyce. Raspberries (*Rubus idaeus*) of Beskid, Canby and Malling Seedling cv. as well as black currants (*Ribes nigrum*) of Ben Lomond, Titania and Ojebyn cv. were from Experimental Farm in Felin. Red currants (*Ribes rubrum*) of Rondom and Holenderska cv. were collected in a garden in Klementowice and Jonker cv. – in Góra Puławska.

Berry fruits were stored for 6 months in a refrigerator at –28°C prior to analysis. Juices were made from 500 g of fruits defrosted at ambient temperature in a juice extractor Zelmmer 277.8 and then centrifuged in a centrifuge MPW 365 for 15 min at 4°C at 5135.97xg. Anthocyanins purification and HPLC separations were carried out according to the method described by Hong & Wrolstad [1990b] with modifications.

A mini-column Sep-Pak C₁₈ Waters was activated by means of washing it with 5 mL of methanol and then 5 mL of 0.01% HCl. Aliquots of 1 mL of juice were introduced into the mini-column. In order to remove saccharides and organ-

ic acids, the mini-column was washed with 2 mL of 0.01% HCl and anthocyanins were eluted with 2 mL of 0.01% HCl in methanol.

An HPLC apparatus (Gilson) consisting of two pumps 306, dynamic mixer 811C, manometer 805 and detector UV-VIS DAD 170 was used for the separation of anthocyanins. The chromatograph was combined with the software for data acquisition UniPoint™ due to Interface 506C system. The separation was performed on a column Symmetry of 250 × 4.6 mm dimensions filled with C₁₈ Waters of 5 μm particle diameter. Two types of eluent were applied at gradient: A – 4.5% formic acid and B – 100% acetonitrile (Table 1). Other chromatographic parameters were as follows: dosing loop of Rheodyne 7725i injector – 20 μL, eluent flow rate – 1 mL/min, and detection wavelength – 520 nm.

TABLE 1. Gradient applied for separation of anthocyanins.

Time (min)	Eluent A (%)	Eluent B (%)
0	100	0
5	95	5
12	90	10
22	85	15
26	80	20
33	100	0

All samples were prepared and analysed in duplicate. Peak area on a chromatogram corresponds with 1 mL of juice taken for analysis.

Calibration curves were plotted for three standards: cyanidin-3-glucoside, cyanidin-3-rutinoside and pelargonidin-3-glucoside (Extrasynthese, France). A 2-mg portion of each standard was dissolved in 1 mL of 0.1% HCL in methanol and dilutions were prepared. Methanol solutions contained 2000, 1000, 500, 100 and 50 mg/L of particular standard.

Cyanidin-3-glucoside, cyanidin-3-rutinoside and pelargonidin-3-glucoside were identified in the juices examined on the basis of spectrum and retention time of available standards (Extrasynthese, France). The other anthocyanins were identified on the basis of spectrum, elution order and literature data [Bakker *et al.*, 1994; Goiffon *et al.*, 1991; Hong & Wrolstad, 1990 b; Versari *et al.*, 1997].

Determination results were analysed statistically using the Tuckey's test at a significance level of $\alpha=0.05$.

RESULTS AND DISCUSSION

The anthocyanins for which standards are not commonly available were identified on the basis of spectrum, elution order and literature data. According to the literature, the wavelength maxima (λ_{\max}) in the visible range are closely related to the hydroxylation pattern of the anthocyanin. Derivatives of pelargonidin ($\lambda_{\max}=502$ nm) can be distinguished from derivatives of cyanidin ($\lambda_{\max}=516$ –520 nm) and delphinidin ($\lambda_{\max}=525$ –528 nm) on the basis of their different visible spectra. The nature of sugar substitution has no relevant effect on the spectrum [Hong & Wrolstad, 1990b; Versari *et al.*, 1997]. The elution order of anthocyanins is

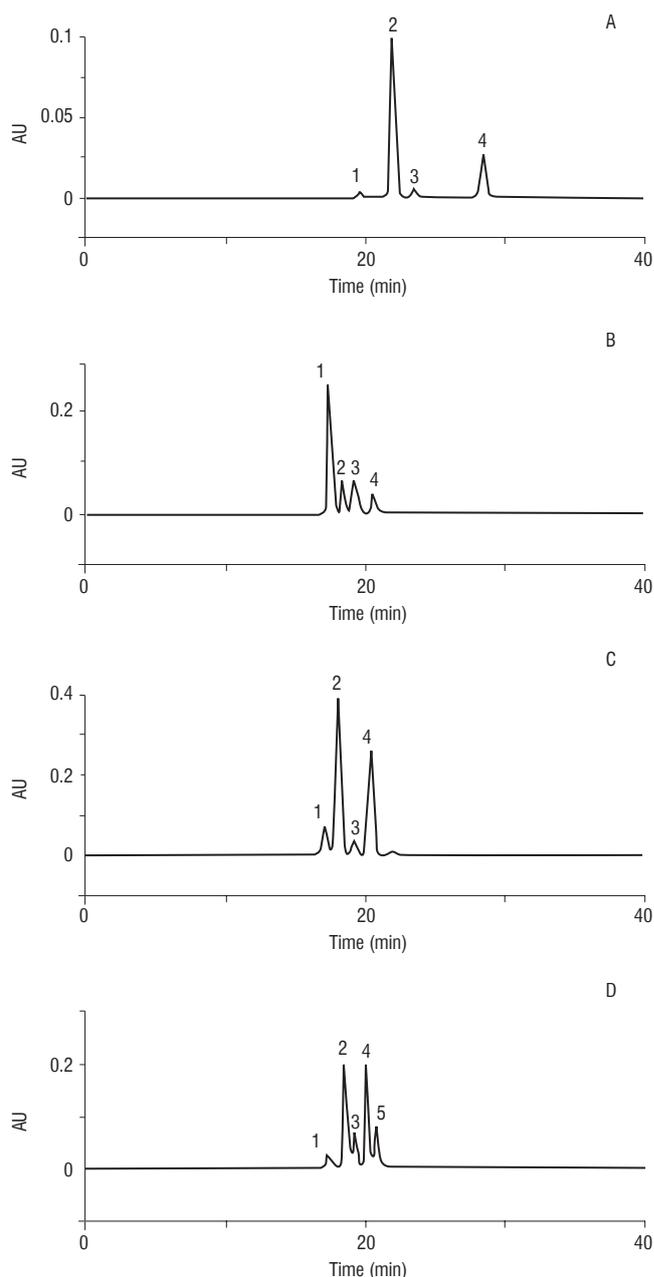


FIGURE 1. HPLC chromatograms of anthocyanins occurring in juices: A-strawberry of Senga cv., B-raspberry of Beskid cv., C-black currant of Ben Lomond cv., D- red currant of Random cv. harvested in 1998. Peak identification in Table 2, 3, 4, 5, respectively.

correlated with their hydrophobicity. The most hydrophilic anthocyanins are eluted at first. Following anthocyanins are less hydrophilic and more hydrophobic. According to the literature [Bakker *et al.*, 1994; Goiffon *et al.*, 1991], elution order of aglycones is: delphinidin < cyanidin < pelargonidin. With and identical aglycone, the addition of a second carbohydrate increases its polarity, thus generally resulting in a decrease in retention time. However, the presence of a hydrophobic methyl group in the rhamnose molecule leads to cyanidin-3-rutinoside elution after cyanidin-3-glucoside [Bakker *et al.*, 1994; Goiffon *et al.*, 1991].

An HPLC chromatogram and UV-VIS spectra of anthocyanins in strawberry juice of Senga cv. were shown in Figure 1A and Figure 2A, respectively, and contents of anthocyanins

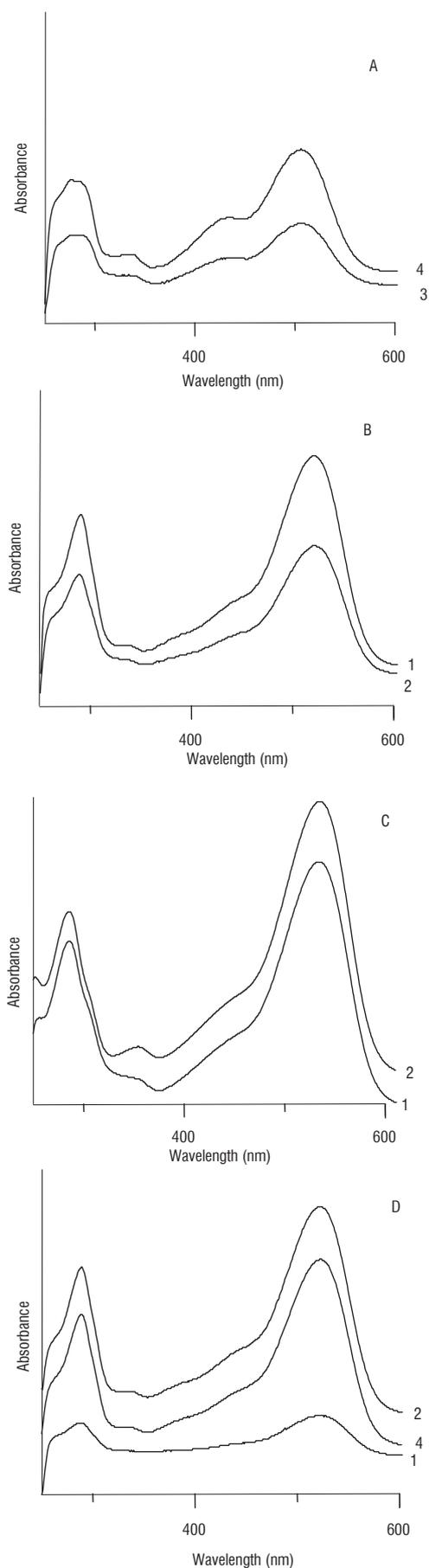


FIGURE 2. UV-VIS spectra of anthocyanins occurring in juices: A – strawberry of Senga cv., B – raspberry of Beskid cv., C – black currant of Ben Lomond cv., D – red currant of Rondon cv. harvested in 1998. Peak identification in Table 2, 3, 4, 5, respectively.

in juices of the three strawberry varieties picked in three years were presented in Table 2. Chromatograms of anthocyanins in strawberry juices of Senga, Ducat and Marmolada cv. differed from one another. Four anthocyanins were found in juice of Senga cv., and three in each juice of Ducat and Marmolada cv. Cyanidin-3-glucoside (peak 1) and pelargonidin-3-glucoside (peak 2) were identified in all strawberry juices by comparison of spectra and retention times. Pelargonidin-3-glucoside was the main anthocyanin. The content of pelargonidin-3-glucoside in strawberry juice of Marmolada cv. was statistically lower – 1198 mg/L (81.3% of total anthocyanin peak area) than that in juice of Senga cv. – 1681 mg/L (76.9%) and in juice of Ducat cv. – 1684 mg/L (86.6%). In addition Bakker *et al.* [1992, 1994], Goiffon *et al.* [1991], Hong & Wrolstad [1990b], Skrede *et al.* [1992] and Versari *et al.* [1997], applying the HPLC technique, found that strawberry juices contained the highest levels of pelargonidin-3-glucoside. According to Bakker *et al.* [1992], pelargonidin-3-glucoside constituted 80% of the total anthocyanin peak area, and according to Bakker *et al.* [1994] – from 82% in juice of Pantagruella cv. and up to 100% in juice of Cambridge Favourite cv. Cyanidin-3-glucoside occurred in small amounts. The content of cyanidin-3-glucoside was significantly lower in juice of Marmolada cv. – 32 mg/L (4.5%) than in juices of Senga and Ducat cv. – 68 mg/L (4.2%) and 83 mg/L (7.8%), respectively. In studies performed by Bakker *et al.* [1992], the peak area for cyanidin-3-glucoside constituted 3.3% of anthocyanin peak area and in experiments by Bakker *et al.* [1994] – from 0.6% in Domanil cv. juice to 12.3% in Cambridge Vigour cv. juice. On the basis of spectra, it was found that other anthocyanins in strawberry juices – peaks 3 and 4 – were pelargonidin derivatives. These peaks had maximum absorption at a wavelength of *ca.* 503 nm and extension of absorption in the range of 400–600 nm, which is characteristic for pelargonidin derivatives. Peak 3 eluted immediately after pelargonidin-3-glucoside, thus carbohydrate was more hydrophobic than glucose. Long time of peak 4 suggested acylation by acetic acid. Literature data enable suggesting that peaks 3 and 4 were probably pelargonidin-3-rutinoside and pelargonidin-3-glucoside acylated with acetic acid [Hong & Wrolstad, 1990b]. Peaks 3 and 4 in juice of Senga cv. were 5.9% and 11.3% of total anthocyanin peak area, respectively, peak 3 in juice of Ducat cv. – 5.6% and peak 4 in juice of Marmolada cv. – 14.2%. Three or four anthocyanins were found in these strawberry juices depending on strawberry variety. Bakker *et al.* [1994] achieved up to 13 chromatographic peaks characteristic for anthocyanins in Totem cv. strawberry juice, including 8 ones being pelargonidin derivatives, 2 – cyanidin derivatives, and 3 anthocyanins were not identified. Furthermore, juices made of 14 strawberry varieties contained 10 or more anthocyanins. Such a high number of anthocyanin peaks achieved by Bakker *et al.* [1994] could have been due to genetic modifications of strawberry varieties the juices were prepared from.

HPLC chromatogram and UV-VIS spectra of anthocyanins in raspberry juice of Beskid cv. were shown in Figure 1B and Figure 2B, respectively, and the contents of anthocyanins in juices of three raspberry varieties picked in three years were presented in Table 3. Chromatographic profiles for raspberry juices from Beskid and Canby cv. were similar referring to retention times for four anthocyanins present

TABLE 2. Contents of anthocyanins in juices of three strawberry varieties picked in three years.

Strawberry variety	Year of strawberry harvest	Anthocyanins			
		Peak 1 cy-3-glu (mg/L)	Peak 2 pg-3-glu (mg/L)	Peak 3* area $\times 10^4$	Peak 4** area $\times 10^4$
Senga	1998	31	1436	99	480
	1999	67	1678	233	261
	2000	105	1929	271	357
	$\bar{x} \pm SD$	68 ^B ±37	1681 ^B ±247	201 ^B ±90	366 ^B ±110
Ducat	1998	19	532	34	0
	1999	121	2512	287	0
	2000	110	2009	234	0
	$\bar{x} \pm SD$	83 ^B ±56	1684 ^B ±1029	185 ^A ±133	0
Marmolada	1998	60	2206	0	529
	1999	30	1201	0	276
	2000	6	186	0	62
	$\bar{x} \pm SD$	32 ^A ±27	1198 ^A ±1010	0	289 ^A ±234

A, B – values in the columns with different letters are significantly different at $\alpha=0.05$; * – pelargonidin-3-rutinoside (probably); ** – pelargonidin-3-glucoside acylated with acetic acid (probably); cy-3-glu – cyanidin-3-glucoside; pg-3-glu – pelargonidin-3-glucoside

TABLE 3. Contents of anthocyanins in juices of three raspberry varieties picked in three years.

Raspberry variety	Year of raspberry harvest	Anthocyanins			
		Peak 3 cy-3-glu (mg/L)	Peak 4 cy-3-rut (mg/L)	Peak 1* area $\times 10^4$	Peak 2** area $\times 10^4$
Beskid	1998	428	756	5515	1042
	1999	218	769	1745	1112
	2000	641	520	5505	819
	$\bar{x} \pm SD$	429 ^B ±212	682 ^B ±140	4255 ^B ±2174	991 ^B ±153
Canby	1998	119	119	912	169
	1999	560	407	3954	519
	2000	492	626	2597	496
	$\bar{x} \pm SD$	390 ^A ±237	384 ^A ±254	2488 ^A ±1524	395 ^A ±196
Malling Seedling	1998	453	0	4459	0
	1999	366	0	4851	0
	2000	465	0	5141	0
	$\bar{x} \pm SD$	428 ^B ±54	0	4817 ^B ±342	0

A, B – values in the columns with different letters are significantly different at $\alpha=0.05$; * – cyanidin-3-sophoroside (probably); ** – cyanidin-3-glucorutinoside (probably); cy-3-glu – cyanidin-3-glucoside; cy-3-rut – cyanidin-3-rutinoside

in juices, but they differed with area of particular anthocyanins. Spectra comparison of anthocyanins present in raspberry juices indicated that all anthocyanins were cyanidin derivatives. The anthocyanins had maximum absorption at about 518 nm. Peaks 3 and 4 were identified as cyanidin-3-glucoside and cyanidin-3-rutinoside on the basis of available standards. Peaks 1 and 2 contained more hydrophilic sugars than glucose and rutinose caused elution before cyanidin-3-glucoside and cyanidin-3-rutinoside. Peaks 1 and 2 were probably cyanidin-3-sophoroside and cyanidin-3-glucorutinoside [Boyles & Wrolstad, 1993]. Raspberry juice made of Malling Seedling cv. contained only 2 anthocyanins: cyanidin-3-sophoroside and cyanidin-3-glucoside. Cyanidin-3-sophoroside was the main anthocyanin in raspberry juices. The area of cyanidin-3-sophoroside in juice of Canby cv. was significant-

ly lower – 2488×10^4 (56.6% of total anthocyanin peak area) than in juices of Beskid and Malling Seedling cv. – 4255×10^4 (56.2%) and 4817×10^4 (78.9%). A number of authors have also found that cyanidin-3-sophoroside was the main anthocyanin in raspberry juices. Cyanidin-3-sophoroside constituted from 42.0% of the total anthocyanin peak area on chromatogram achieved after the HPLC separation of anthocyanins in juice of Marcy cv. up to 85.3% in juice of Willamette cv. [Spanos & Wrolstad, 1987], from 58.8% in juice of Chilcotin cv. to 80.7% in juice of Willamette cv., except juices of Norna and Vetten cv. [Boyles & Wrolstad, 1993], 71% in juice of Meeker cv. [Rommel *et al.*, 1990], from 74.2% up to 78.8% in juice of Willamette cv. and from 62.3% to 77.0% in raspberry juices commercially available, except juice denoted with letter H [Wrolstad *et al.*, 1993]. Cyanidin-3-glucoside

TABLE 4. Contents of anthocyanins in juices of three black currant varieties picked in three years.

Black currant variety	Year of black currant harvest	Anthocyanins			
		Peak 3 cy-3-glu (mg/L)	Peak 4 cy-3-rut (mg/L)	Peak 1* area $\times 10^4$	Peak 2** area $\times 10^4$
Ben Lomond	1998	208	6550	1492	9048
	1999	113	3771	881	4879
	2000	170	6579	1353	8736
	$\bar{x} \pm SD$	164 ^A ± 48	5633 ^B ± 1613	1242 ^A ± 320	7554 ^B ± 2322
Titania	1998	297	6588	2940	10354
	1999	150	3525	1588	5165
	2000	262	6809	2669	8812
	$\bar{x} \pm SD$	236 ^B ± 77	5641 ^B ± 1836	2399 ^B ± 715	8110 ^B ± 2665
Ojebyn	1998	273	6148	1638	6793
	1999	94	2114	633	2250
	2000	268	6927	1555	6170
	$\bar{x} \pm SD$	212 ^B ± 102	5063 ^A ± 2583	1275 ^A ± 558	5071 ^A ± 2463

A, B – values in the columns with different letters are significantly different at $\alpha=0.05$; * – delphinidin-3-glucoside (probably); ** – delphinidin-3-rutinoside (probably); cy-3-glu – cyanidin-3-glucoside; cy-3-rut – cyanidin-3-rutinoside

had the largest peak area on chromatogram after the separation of anthocyanins in raspberry juice from Vetten cv. – 34.5% [Boyles & Wrolstad, 1993] and commercially available juice denoted with letter H – 49.7% [Wrolstad *et al.*, 1993], cyanidin-3-rutinoside in juices from Norna cv. – 32.1% and 31.5% [Boyles & Wrolstad, 1993] as well as cyanidin-3-glucorutinoside in juice from Marcy cv. – 44.9% [Withy *et al.*, 1993].

HPLC chromatogram and UV-VIS spectra of anthocyanins in black currant juice of Ben Lomond cv. were shown in Figure 1C and Figure 2C, respectively, and the contents of anthocyanins in juices of three black currant varieties picked in three years were presented in Table 4. Fingerprints of anthocyanins in juices from three black currant varieties were similar referring to anthocyanin retention times and differed with anthocyanin peak area. Four anthocyanins were detected in juices made of Ben Lomond, Titania and Ojebyn cv. each. Peaks 3 and 4 were identified as cyanidin-3-glucoside and cyanidin-3-rutinoside. It was found that peaks 1 and 2 were delphinidin derivatives on the basis of λ_{max} – ca. 528 nm and elution before cyanidin derivatives. Peaks 1 and 2 were probably delphinidin-3-glucoside and delphinidin-3-rutinoside [Skrede *et al.*, 1992]. It should be underlined that similar proportions of anthocyanins were found in all juices from black currant. Delphinidin-3-rutinoside and cyanidin-3-rutinoside were the main anthocyanins in black currant juices. Peak area for delphinidin-3-rutinoside in juice of Ojebyn cv. was significantly lower – 5071×10^4 (43.4% of total anthocyanin peak area) than in juice of Ben Lomond cv. – 7554×10^4 (51.8%) and in juice of Titania cv. – 8110×10^4 (49.1%). Also the content of cyanidin-3-rutinoside in juice of Ojebyn cv. was significantly lower – 5063 mg/L (39.9%) than in juices of Ben Lomond and Titania cv. – 5633 mg/L (36.2%) and 5641 mg/L (31.9%) respectively. Similarly, according to Hong & Wrolstad [1990a] and Iversen [1999], delphinidin-3-rutinoside was 44% and 53.2%, respectively, and cyanidin-3-rutinoside – 42% and 34%, respectively. Analyses performed by Skrede [1987] revealed that black currant juices, except juice from Sunderbyn cv., contained the highest level of del-

phinidin-3-rutinoside – from 36.9% in juice of Leepan Musta cv. up to 52.7% in juice of Ben Lomond cv., as well as cyanidin-3-rutinoside – from 32.2% in juice of Ben Nevis cv. up to 46.5% in juice of Leepan Musta cv. The main anthocyanins in juice from Sunderbyn cv. were: cyanidin-3-rutinoside – 64.6% and cyanidin-3-glucoside – 19.9%.

HPLC chromatogram and UV-VIS spectra of anthocyanins in red currant juice of Rondon cv. were shown in Figure 1D and Figure 2D, respectively, and the contents of anthocyanins in juices of three red currant varieties picked in three years were presented in Table 5. Chromatographic profiles of juices made of Rondon and Holenderska cv. were similar referring to retention times for five anthocyanins present in juices, but they differed with particular anthocyanin peak area. An analysis of anthocyanin spectra indicated that all anthocyanins were cyanidin derivatives. Peaks 3 and 5 were identified as cyanidin-3-glucoside and cyanidin-3-rutinoside. According to the literature, in red currant juices polyglycosylated anthocyanins eluted among monoglycosylated anthocyanins. Peaks 1, 2 and 4 were probably cyanidin-3-sophoroside, cyanidin-3-glucorutinoside and cyanidin-3-xylorutinoside, respectively [Goiffon *et al.*, 1991]. Cyanidin-3-glucorutinoside and cyanidin-3-xylorutinoside were the main anthocyanins in juices from Rondon and Holenderska cv. Peak area for cyanidin-3-glucorutinoside in juice of Holenderska cv. was significantly lower – 858×10^4 (24.4% of total anthocyanin peak area) than in juice of Rondon cv. – 1073×10^4 (38.4%). Differences referring to peak areas for cyanidin-3-xylorutinoside in juices from Rondon and Holenderska cv. were not statistically significant – 1045×10^4 (37.0%) and 1437×10^4 (40.7%). The above anthocyanins occurred in the largest amounts in juice made of red currants studied by Goiffon *et al.* [1991]. Juice of Jonker cv. contained three anthocyanins: cyanidin-3-glucoside, cyanidin-3-xylorutinoside and cyanidin-3-rutinoside. The largest peak area in this juice was reported for cyanidin-3-xylorutinoside – 2596×10^4 (73.1% of the total anthocyanin peak area). It was significantly higher than for juices of Rondon and Holenderska cv.

TABLE 5. Contents of anthocyanins in juices of three red currant varieties picked in three years.

Red currant variety	Year of red currant harvest	Anthocyanins				
		Peak 3 cy-3-glu (mg/L)	Peak 5 cy-3-rut (mg/L)	Peak 1* area × 10 ⁴	Peak 2** area × 10 ⁴	Peak 4*** area × 10 ⁴
Rondom	1998	35	175	52	472	462
	1999	26	517	68	1167	1013
	2000	138	629	315	1580	1659
	$\bar{x} \pm SD$	66 ^A ± 62	440 ^A ± 237	145 ^A ± 147	1073 ^B ± 560	1045 ^A ± 599
Jonker	1998	51	615	0	0	2481
	1999	76	647	0	0	2061
	2000	120	1047	0	0	3246
	$\bar{x} \pm SD$	82 ^A ± 35	770 ^B ± 241	0	0	2596 ^B ± 601
Holenderska	1998	289	340	256	1035	1528
	1999	205	196	190	544	876
	2000	209	286	206	995	1908
	$\bar{x} \pm SD$	234 ^B ± 47	274 ^A ± 73	217 ^B ± 34	858 ^A ± 273	1437 ^A ± 522

A, B – values in the columns with different letters are significantly different at $\alpha=0.05$; * – cyanidin-3-sophoroside (probably); ** – cyanidin-3-glucuronoside (probably); *** – cyanidin-3-xylo-rutinoside (probably); cy-3-glu – cyanidin-3-glucoside; cy-3-rut – cyanidin-3-rutinoside

Results of chromatographic separations of anthocyanins indicated that strawberry, raspberry, black currant and red currant juices differed in the composition of anthocyanins. Differences of anthocyanin composition of juices obtained from different berry fruits create the possibility of detecting adulterations of expensive raspberry and black currant juices with cheap strawberry and red currant juices on the basis of anthocyanins analysis. It was found that pelargonidin-3-glucoside was characteristic anthocyanin in strawberry juices, absent in authentic raspberry and black currant juices. Pelargonidin-3-glucoside could indicate the addition of strawberry to raspberry and black currant juices. Instead cyanidin-3-xylo-rutinoside could indicate the adulterations of raspberry and black currant juices with red currant juices.

CONCLUSIONS

1. It was indicated that within species the juices examined differed in the quantitative and qualitative composition of anthocyanins.

2. Pelargonidin-3-glucoside and cyanidin-3-xylo-rutinoside were the main anthocyanins in strawberry and red currant juices, respectively, independently of variety. Those anthocyanins were not identified in raspberry and black currant juices, in which cyanidin-3-sophoroside as well as delphinidin-3-rutinoside and cyanidin-3-rutinoside were the main anthocyanins, respectively.

3. The examinations suggest that it is possible to detect adulterations of expensive berry juices with cheap juices on the basis of anthocyanins analysis. The presence of pelargonidin-3-glucoside from strawberry juice could indicate the adulteration of raspberry and black currant juices with strawberry juice, whereas the presence of cyanidin-3-xylo-rutinoside – adulteration with red currant juice. Further examinations in adulterated juices are necessary.

REFERENCES

- Bakker J., Bridle P., Bellworthy S.J., Strawberry juice colour: a study of the quantitative and qualitative pigment composition of juices from 39 genotypes. *J. Sci. Food Agric.*, 1994, 64, 31–37.
- Bakker J., Bridle P., Koopman A., Strawberry juice colour: the effect of some processing variables on the stability of anthocyanins. *J. Sci. Food Agric.*, 1992, 60, 471–476.
- Barritt B.H., Torre L.C., Cellulose thin-layer chromatographic separation of Rubus fruit anthocyanins. *J. Chromatogr.*, 1973, 75, 151–155.
- Boyles M.J., Wrolstad R.E., Anthocyanin composition of red raspberry juice: influences of cultivar, processing and environmental factors. *J. Food Sci.*, 1993, 58, 1135–1141.
- Fügel R., Carle R., Schieber A., A novel approach to quality and authenticity control of fruit products using fractionation and characterization of cell wall polysaccharides. *Food Chem.*, 2004, 87, 141–150.
- Goiffon J.P., Brun M., Bourrier M.J., High-performance liquid chromatography of red fruit anthocyanins. *J. Chromatogr.*, 1991, 537, 101–121.
- Hofsommer H.J., Determination of anthocyanins and carotenoids in fruit juices. *Fruit Processing*, 1995, 4, 90–93.
- Hong V., Wrolstad R.E., Characterization of anthocyanin – containing colorants and fruit juices by HPLC/photodiode array detection. *J. Agric. Food Chem.*, 1990a, 38, 698–708.
- Hong V., Wrolstad R.E., Use of HPLC separation/photodiode array detection for characterization of anthocyanins. *J. Agric. Food Chem.*, 1990b, 38, 708–715.
- Iversen C.K., Black currant nectar: effect of processing and storage on anthocyanin and ascorbic acid content. *J. Food Sci.*, 1999, 64, 37–41.
- Landbo A.K., Meyer A.S., Effects of different enzymatic maceration treatments on enhancement of anthocyanins and other phenolics in black currant juice. *Innov. Food Sci. Emerg. Technol.*, 2004, 5, 503–513.
- Le Marchand L., Cancer preventive effects of flavonoids – a review. *Biomed Pharmacother*, 2002, 56, 296–301.
- Mazza G., Miniati E., Introduction. 1993, *in: Anthocyanins in Fruits, Vegetables and Grains*. Boca Raton: CRC Press Inc., Florida, pp. 1–28.

14. Mullen W., Lean M.E.J., Crozier A., Rapid characterization of anthocyanins in red raspberry fruit by high-performance liquid chromatography coupled to single quadrupole mass spectrometry. *J. Chromatogr. A*, 2002, 966, 63–70.
15. Rommel A., Heatherbell D.A., Wrolstad R.E., Red raspberry juice and wine: effect of processing and storage on anthocyanin pigment composition, color and appearance. *J. Food Sci.*, 1990, 55, 1011–1017.
16. Silva B.M., Andrade P.B., Valentao P., Mendes G.C., Seabra R.M., Ferreira M.A., Phenolic profile in the evaluation of commercial quince jellies authenticity. *Food Chem.*, 2000, 71, 281–285.
17. Skrede G., Evaluation of colour quality in blackcurrant fruit grown for industrial juice and syrup production. *Norw. J. Agric. Sci.*, 1987, 1, 67–74.
18. Skrede G., Wrolstad R.E., Lea P., Enersen G., Color stability of strawberry and blackcurrant syrups. *J. Food Sci.*, 1992, 57, 172–177.
19. Spanos G.A., Wrolstad R.E., Anthocyanin pigment, non-volatile acid and sugar composition of red raspberry juice. *J. Assoc. Off. Anal. Chem.*, 1987, 70, 1036–1046.
20. Tsao R., Yang R., Optimization of a new mobile phase to know the complex and real polyphenolic composition: towards a total phenolic index using high-performance liquid chromatography. *J. Chromatogr. A*, 2003, 1018, 29–40.
21. Versari A., Barbanti D., Biesenbruch S., Farnell P.J., Analysis of anthocyanins in red fruits by use of HPLC/spectral array detection. *Ital. J. Food Sci.*, 1997, 9, 141–147.
22. Withy L.M., Nguyen T.T., Wrolstad R.E., Heatherbell D.A., Storage changes in anthocyanin content of red raspberry juice concentrate. *J. Food Sci.*, 1993, 58, 190–192.
23. Wrolstad R.E., McDaniel M.R., Durst R.W., Micheals N., Lampi K.A., Beaundry E.G., Composition and sensory characterization of red raspberry juice concentrated by direct – osmosis or evaporation. *J. Food Sci.*, 1993, 58, 633–637.
24. Zając K.B., Wilska-Jeszka J., Anthocyanins – natural pigments for food industry. Structure, properties and obtainment methods of anthocyanin pigments – a review. *Przem. Ferment. Owoc. Warz.*, 1991, 12, 21–24 (in Polish).

Received July 2004. Revisions received February, May and October 2005 and accepted June 2006.

PORÓWNANIE SKŁADU ANTOCYJANÓW SOKÓW UZYSKANYCH Z WYBRANYCH GATUNKÓW OWOCÓW JAGODOWYCH

Anna Stój, Agnieszka Malik, Zdzisław Targoński

Katedra Technologii Żywności i Przechowalnictwa, Akademia Rolnicza, Lublin

W pracy oznaczono skład ilościowy i jakościowy antocyjanów w sokach otrzymanych z trzech odmian truskawek (Senga, Ducat, Marmolada), malin (Beskid, Canby, Malling Seedling), czarnych porzeczek (Ben Lomond, Titania, Ojebyn) i czerwonych porzeczek (Rondom, Jonker, Holenderska) zebranych w trzech kolejnych latach: 1998, 1999 i 2000. Wykorzystano technikę HPLC używając chromatografu Gilson i detektora DAD. Przed analizą antocyjany oczyszczano na minikolumnie Sep – Pak C₁₈ Waters.

Wykazano, że badane soki w obrębie gatunków różniły się składem ilościowym i jakościowym antocyjanów. Niezależnie od odmiany, dominującymi antocyjanami w sokach truskawkowych i z czerwonych porzeczek były odpowiednio pelargonidyno-3-głukozyd i cyjanidyno-3-ksylorutynozyd. Obecności tych antocyjanów nie stwierdzono w sokach malinowych i z czarnych porzeczek, w których głównymi antocyjanami były odpowiednio cyjanidyno-3-soforozyd oraz delfinidyno-3-rutynozyd i cyjanidyno-3-rutynozyd. Przypuszcza się, że na podstawie analizy antocyjanów można wykryć zafałszowania drogich soków malinowych i z czarnych porzeczek tanimi sokami truskawkowymi i z czerwonych porzeczek.

