

PHENOLIC SUBSTANCES IN STRAWBERRIES

I.L. ZAMORSKA, Candidate of Sciences (Agr),

V.V. ZAMORSKYI, Doctor of Sciences (Agr)

The paper presents the results of quantitative and qualitative identification of the compounds of phenolic complex of strawberries.

Strawberry is one of the most valuable berry plants due to its fast ripening, high adaptive potential and very good flavor.

Strawberry berries are the source of phenolic substances, among them are: anthocyanins, flavonoids and phenolic acids. Qinglian Wang and others[1] state,

that general content of phenolic substances in the berries correlates well with their anti-oxidant ability ($R = 0,63$, $p < 0,01$), and high content of anthocyanins confirm high anti-oxidant activity of the berries [2]. Polyphenolic substances are known to have a protective role [3], they are protective mechanisms from oxidative stresses [4], and preventive ones against chronic and cardiovascular diseases. Besides, scientists assume that anti-oxidant potential has a considerable effect on the storage duration and berry quality [5], and proanthocyanidin content proves the capacity to be affected by grey mold [6]. Based on the data of various researchers, the total of phenolic substances in strawberry berries ranges from 159 to 289 mg/100g [7], 300 – 341mg equivalent of gallic acid (EGA)/ 100 g of raw mass [8], and even to 848,0 and 1210,8 $\mu\text{g}\cdot\text{g}^{-1}$ (EGA) [2].

Phenolic substances of strawberries are mainly represented by anthocyanins,

pelargonidin-3-glucoside predominating. Cyanidin-3glucoside and pelargonidin-3-rutinoside are present in small parts. Pelargonidin-3-arabinoside and cyanidin-3-rutinoside were found in some strawberry varieties [9]. The main pigment, typical for the varieties grown in Japan, is called pelargonidin-3 (6-malonilglucoside), it constitutes 5-30% of the total amount of anthocyanins [9, 10]. According to I.P. Lukina et al [11], 8-45 mg of anthocyanins per 100 g of berries are accumulated in the strawberries in terms of pelargonidin-3-glucoside.

The purpose of the work was to quantitatively and qualitatively identify compounds of phenolic complex of strawberries.

Research methodology. The work was done with the berries of varieties Ducat, Honey, Polka in the laboratory of the department of the technology of storage and processing of fruits and vegetables at Uman national university of horticulture and at the experimental center of foodstuff quality control at the National institute of grape and wine “Magarach”.

Quantitative analysis of individual phenolic compounds factions from the extract was made using the method of highly effective liquid chromatography on the chromatograph of Agilent Technologies Company (model 1100). To make the analysis, a chromatographic column (2.1 × 150 mm) filled with octadecylsilyl sorbent of granularity 3.5 mkm “ZORBAX” SB-C18, was used.

The following parameters of detecting were set: wave length 525 nm (for anthocyanins); wave length 313 nm (for phenolic acids and their derivatives); wave length 350 nm (for glycosides flavones); wave length 371 nm (for flavones). Parameters of specter recording – every peak 190-600 nm. Identification of phenolic compounds was done in accordance with the standard exposure time and spectral characteristics [12].

Results of the research. Total content of phenolic compounds in strawberry berries of the varieties studied was 33.2-56.3 mg/100 g (Table). Much higher content of phenolic compounds was found in Honey berries – 56.3 mg/100g, whereas the content in other varieties was lower – 26.5 and 41%, respectively.

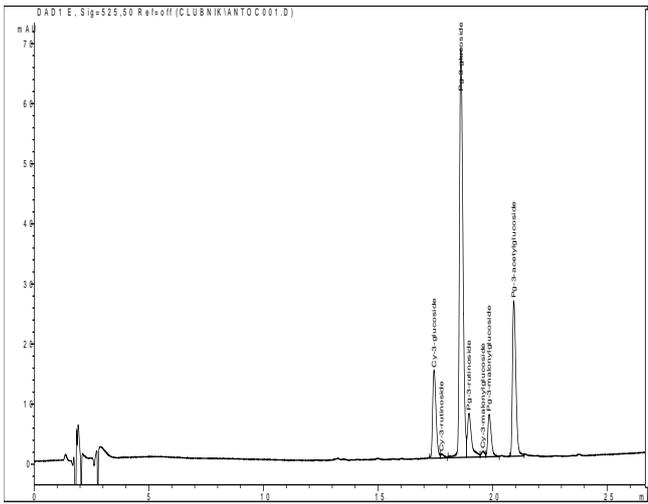
Phenolic compounds of strawberries (var. Ducat, Polka and Honey) are presented by anthocyanins and favonols, anthocyanins predominate among them: 58.1-81.0% of the total amount of phenolic compounds in berries; this is proved by the data/findings of many researchers [1, 9, 10].

Content of phenolic compounds in strawberry berries, mg/100g

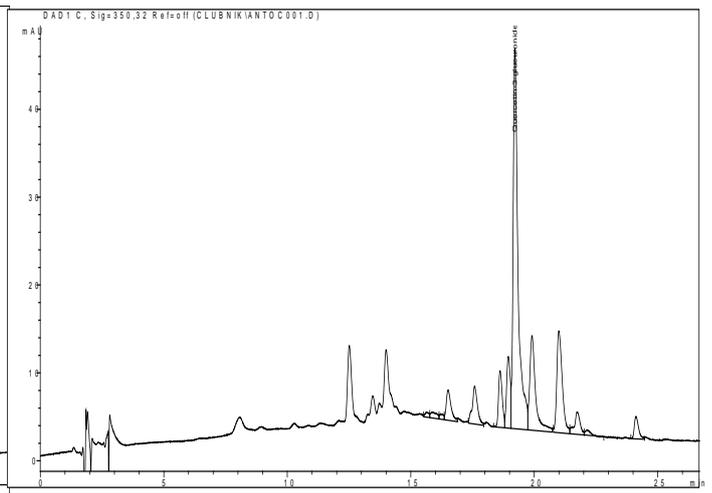
Expos. time, min	Name of a compound	Variety		
		Ducat	Polka	Honey
<i>Anthocyanins (in terms of cyanidin-3-O-glucoside)</i>				
17.44	Cyanidin-3-O-glucoside	2,2	2,6	2,3
17.77	Cyanidin-3-O-rutinoside	0,1	0,2	0
18.61	Pelargonidin-3-O-glucoside	10,5	21,8	32,9
18.97	Pelargonidin-3-O- rutinoside	1,4	2,5	2,0
19.58	Cyanidin-3-O-(6"-malonil) glucoside	0,1	0,2	0,4
19.85	Pelargonidin-3-O-(6"-malonil) glucoside	1,1	1,0	1,1
20.92	Pelargonidin-3-O-(6'-acetyl) glucoside	3,9	6,5	6,9
<i>Total anthocyanins</i>		19,3	34,8	45,6
<i>HIP₀₅</i>		0,6		
<i>Flavonols (in terms of quercetin)</i>				
19.22	Quercetin-3-O-glucoronide	13,9	6,6	10,7
<i>Total phenolic compounds</i>		33,2	41,4	56,3
<i>HIP₀₅</i>		1,1		

Anthocyanin complex of the berries is mainly presented by pelargonidin-3-O-glucoside, pelargonidin-3-O-(6'-acetyl) glucoside and cyanidin-3-O-glucoside (Fig.)

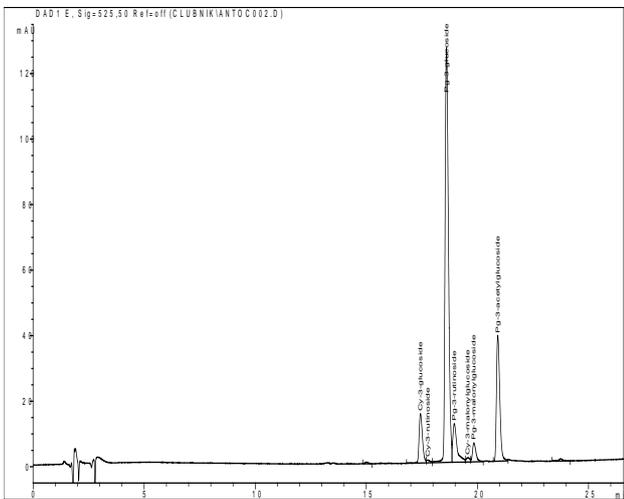
Pelargonidin-3-O-glucoside is the main anthocyanin of the berries, which corresponds to the data published [9, 10, 13]. Its amount in the berries ranges from 10.5 to 32.9 mg/100 g, which is 54.4 -72.1% of the total amount of anthocyanins. The percentage is much higher in variety Honey – 32,9 mg/100 g, this explains its intensive coloring.



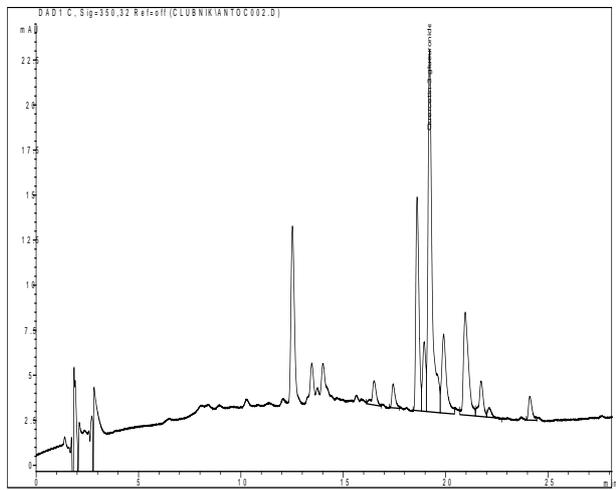
A) Ducat



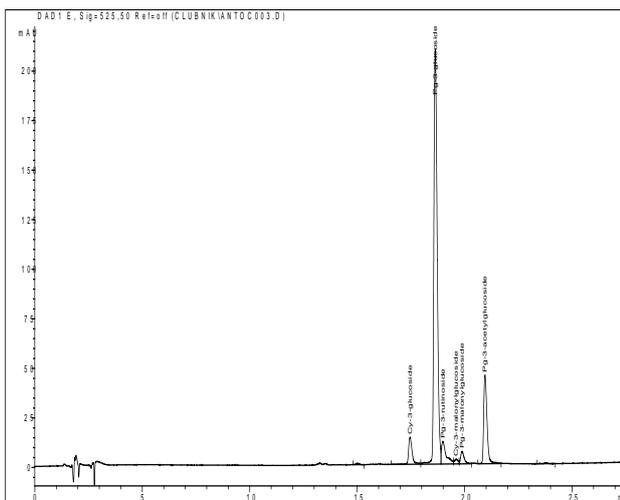
B) Ducat



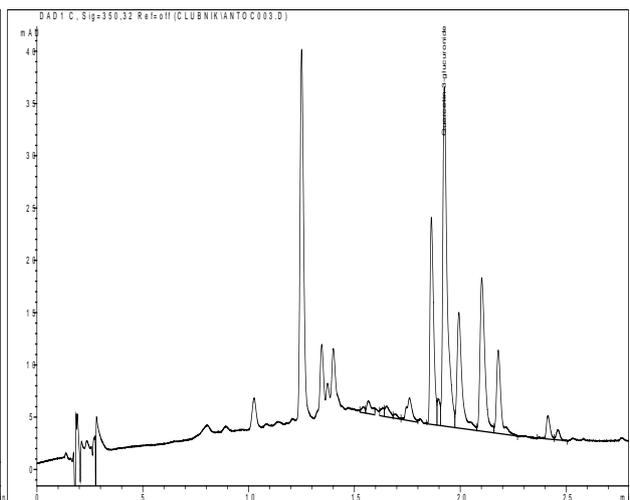
A) Polka



B) Polka



A) Honey



B) Honey

Chromatography of phenolic complex of the strawberries:
A – anthocyanins; B – flavonols.

The second large in number anthocyanin was pelargonidin-3-O-(6'-acetyl) glucoside, its mass ranged from 3.9 to 6.9 mg/100g, and it was 15.1-20.2% of the total amount of anthocyanins in the berries. The berries of variety Honey were characterized by larger amount – 6.9 mg/100 g, however, its share in the total anthocyanins was 3.6% lower than that of variety Polka.

Cyanidin-3-O-glucoside was found in the amount of 2.2-2.6 mg/100g, which was 5-11.4% of the total amount of anthocyanins. The berries of variety Polka showed much higher indicators – 2.6 mg/100 g, its share in the total amount was 7.5%, whereas the berries of variety Ducat had 11.4% and variety Honey – 5.0%.

Pigments pelargonidin-3-O-rutinoside (from 1.4 to 2.5 mg/100g), pelargonidin-3-O-(6"-malonil) (1.0-1.1 mg/100g) were indentified in small amounts in the strawberries. Cyanidin-3-O-(6"-malonil) glucoside in the strawberries amounted to 0.1-0.4 mg/100g, its higher amount – 0.4 – being registered in variety Honey.

Cyanidin-3-O-rutinoside was found only in the berries of Ducat variety – 0.1 mg/100 g and in Polka variety – 0.2 mg/100g, its traces were not identified in pigment complex of the berries of Honey variety.

Flavonols in the berries were presented by quercetin-3-O-glucoronide, its amount being 6.6-13.9 mg/100 g in terms of quercetin, which was equal to 19-41.9% of the total content of phenolic compounds in the berries.

Reference date [2] proves the availability of hydroxicoric, benzoic and ellagic acids in phenolic complex of the strawberries – 9.57% and 4.83 and 2.09% – of the total amount of phenolic compounds correspondingly. Also, derivatives of campferol [7] were singled out in the total amount of flavonols. However, these compounds were not identified in the berry samples studied.

Conclusions. The berries of the varieties studied were the source of phenolic substances, their total amount being 33.2-56.3 mg/100 g. Phenolic compounds were presented by anthocyanins and flavonols with the predominance of the former: 58.1-81.0% of the total content of phenolic compounds. Anthocyanin complex of the berries consists mainly of pelargonidin-3-O-glucoside (54.4 -72.1% of the total anthocyanin amount), pelargonidin-3-O-(6'-acetyl) glucoside and cyanidin-3-O-glucoside. Considerably higher content of phenolic compounds was found in the berries of Honey variety, namely, 56.3 mg/100 g.

REFERENCE

1. Wang, Q., Rekika, D., Charles, M. T., Wang, X., Tsao, R., Yang, R.,... & Khanizadeh, S. Phenolic Compositions and Antioxidant Activities of Newly Developed Day-neutral Strawberry Lines. Agriculture and Agri-Food Canada.
2. Rekika, D., Khanizadeh, S., Deschênes, M., Lévasseur, A., Charles, M. T., Tsao, R., & Yang, R. (2005). Antioxidant capacity and phenolic content of selected strawberry genotypes. Hortscience, 40(6), 1777-1781.
3. LATTANZIO, Vincenzo; LATTANZIO, Veronica MT; CARDINALI, Angela. Role of phenolics in the resistance mechanisms of plants against fungal pathogens and insects. Phytochemistry: Advances in research, 2006, 661: 23-67.

4. URQUIAGA, INES; LEIGHTON, FEDERICO. Plant polyphenol antioxidants and oxidative stress. *Biological Research*, 2000, 33.2: 55-64.
5. Hébert, C. and Willemot, C. 1997. Antioxidant Potential and Strawberry Preservation. *Hortscience*. 32(3):434.
6. Hébert, C., Charles, M.T., Gauthier, L., Willemot, C., Khanizadeh, S. and Cousineau, J. 2002. Strawberry proanthocyanidins: biochemical markers for *Botrytis cinerea* resistance and shelf-life predictability. *Acta Hortic*. 567: 659-662.
7. Cordenunsi, B. R., Oliveira do Nascimento, J. R., Genovese, M. I., & Lajolo, F. M. (2002). Influence of cultivar on quality parameters and chemical composition of strawberry fruits grown in Brazil. *Journal of Agricultural and Food Chemistry*, 50(9), 2581-2586.
8. BURSAC KOVAČEVIĆ, Danijela; LEVAJ, Branka; DAGOVIĆ-UZELAC, Verica. Free radical scavenging activity and phenolic content in strawberry fruit and jam. *Agriculturae Conspectus Scientificus (ACS)*, 2009, 74.3: 155-159.
9. DA SILVA, Fatima Lopes, et al. Anthocyanin pigments in strawberry. *LWT-Food Science and Technology*, 2007, 40.2: 374-382.
10. Tamura, H., Takada, M., & Yoshida, Y. (1995). Pelargonidin 3-O-(6-Omalonyl-b-D-glucopyranoside) in *Fragaria x ananassa* Duch cv Nyoho. *Bioscience, Biotechnology and Biochemistry*, 59, 1157–1158.
11. Лукина И. П. Антоцианы малины и земляники: накопление в плодах и сохранение в продуктах переработки [Текст] [Электронный ресурс] / И. П. Лукина, В.И. Дейнека, Л.А. Дейнека, [и др.] // *Хранение и переработка сельхозсырья*. – 2009. – №3. – С.19-22.
12. Justesen V. Quantitative analysis of flavonoids. Flavonones in fruits, vegetables and beverages by HPLC with photo-diode array and mass spectrometry detection / V. Justesen, P. Knuthsen, F. Lefh // *J. Chromatogr.* — 1998. — Vol. 799. — P. 101—110.
13. LOPES-DA-SILVA, Fátima, et al. Identification of anthocyanin pigments in strawberry (cv Camarosa) by LC using DAD and ESI-MS detection. *European Food Research and Technology*, 2002, 214.3: 248-253.

Одержано 12.03.13

I.L. Zamorska, V.V. Zamorskyi. Phenolic substances in strawberries

The compounds of strawberry phenolic complex were studied using the method of highly effective liquid chromatography. The total content of phenolic compounds in the berries of such varieties as Ducat, Polka and Honey was 33.2-56.3 mg/100 g. Considerably higher content of phenolic compounds was found in the berries of Honey variety, namely, 56.3 mg/100 g.

Phenolic compounds were presented by anthocyanins and flavonols with the predominance of the former: 58.1-81.0% of the total content of phenolic compounds. Anthocyanin complex of the berries consists mainly of pelargonidin-3-O-glucoside, pelargonidin-3-O-(6'-acetyl) glucoside and cyanidin-3-O-glucoside. The main anthocyanin of the strawberries is pelargonidin-3-O-glucoside. Its share is 54.4 -

72.1% of the total anthocyanin amount.

Pigments pelargonidin-3-O-rutinoside (1.4-2.5 mg/100g), pelargonidin-3-O-(6''-malonil) glucoside (1.0-1.1 mg/100 g) were identified in small amounts in the strawberries. The amount of cyanidin-3-O-(6''-malonil) glucoside found in the strawberries was 0.1-0.4 mg/100 g. The share of flavonols in the berries studied was identified in the amount of 6.6-13.9 mg/100 g in terms of quercetin, which was equal to 19-41.9% of the total content of phenolic compounds in the berries.

Keywords: strawberry, phenolics, anthocyanins, flavonols.

Заморская И.Л., Заморский В.В. Фенольные вещества в ягодах земляники

Исследованы соединения фенольного комплекса ягод земляники с помощью метода высокоэффективной жидкостной хроматографии. Общее содержание фенольных соединений в ягодах земляники сортов Дукат, Полка и Хоней составляло 33,2 – 56,3 мг/100 г. Существенно большее содержание фенольных соединений обнаружено в ягодах сорта Хоней — 56,3 мг/100 г.

Фенольные соединения ягод представлены антоцианами и флавонолами, среди которых преобладают антоцианы: 58,1 – 81,0% от общего содержания фенольных соединений. Антоциановый комплекс ягод, в основном, представлен пеларгонидин-3-О-глюкозидом, пеларгонидин-3-О-(6'-ацетил) глюкозидом и цианидин-3-О-глюкозидом. Основной антоциан ягод земляники пеларгонидин-3-глюкозид. Его доля составила 54,4 -72,1% от общего количества антоцианов.

В незначительном количестве в ягодах земляники идентифицированы пигменты пеларгонидин-3-О-рутинозид (от 1,4 до 2,5 мг/100 г), пеларгонидин 3-О-(6''-малонил) глюкозид (1,0 – 1, 1 мг/100 г). Цианидин 3-О-(6''-малонил) глюкозид в ягодах земляники обнаружен на уровне 0,1 – 0,4 мг/100 г. Доля флавонолов в исследуемых образцах ягод установлена на уровне 6,6 – 13,9 мг/100 г в пересчете на кверцетин, что составило

19 – 41,9% от общего содержания фенольных соединений в ягодах.

Ключевые слова: земляника, фенольные вещества, антоцианы, флавонолы