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COLD STORAGE, FREEZING AND LYOPHILISATION AND ITS EFFECT ON TRANSFORMATIONS OF PHENOLIC COMPOUNDS IN LINGONBERRY (*VACCINIUM VITIS-IDAEA* L.)

***Beata Piłat*[1], *Ryszard Zadernowski*[2], *Sylwester Czaplicki*[1], *Maja Jeż*[3]**

[1] Chair of Food Plant Chemistry and Processing
University of Warmia and Mazury in Olsztyn, Poland
[2] Faculty of Agriculture and Economics
Higher School of Agribusiness in Łomża, Poland
[3] Institute of Animal Reproduction and Food Research
Polish Academy of Sciences in Olsztyn, Poland

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Abstract

The aim of the study was to determine the extent of changes in the content of bioactive substances in lingonberry fruit following cold storage, freezing and lyophilisation.

In the paper therapeutic properties of lingonberry fruits were presented, and all present in the fruits phenolic compounds were discussed, especially phenolic acids and anthocyanins. The effect of selected technological operations (freezing and lyophilisation)on the content of phenolic compounds in the fruit was described. The antioxidative activity of phenolic compounds present in fruits and juice was also analysed.

The results of the study indicate that lyophilisation had a negative impact on the level of all phenolic compounds in lingonberry fruits. During this operation the total content of phenolic compounds decreased for about 37%.At the same time phenolic acids concentration was decreased by 20%. The greatest change was observed in anthocyanins concentration, in lyophilised fruits anthocyanins concentration decreased by as much for about 97%. Such a significant degradation of polyphenolic compounds caused a substantial (36%) decrease in antioxidant activity.

Address: Beata Piłat, University of Warmia and Mazury in Olsztyn, pl. Cieszyński 1, 10-726 Olsztyn, Poland, phone: +48 (89) 523 37 70, e-mail: beata.pilat@uwm.edu.pl

PRZECHOWYWANIE CHŁODNICZE, ZAMRAŻANIE I LIOFILIZACJA ORAZ ICH WPŁYW NA PRZEMIANY ZWIĄZKÓW FENOLOWYCH W BORÓWCE BRUSZNICY (*VACCINIUM VITIS-IDAEA* L.)

***Beata Piłat*[1], *Ryszard Zadernowski*[2], *Sylwester Czaplicki*[1], *Maja Jeż*[3]**

[1] Katedra Przetwórstwa i Chemii Surowców Roślinnych
Uniwersytet Warmińsko-Mazurski w Olsztynie, Polska
[2] Wydział Rolniczo-Ekonomiczny, Wyższa Szkoła Agrobiznesu w Łomży, Polska
[3] Instytut Rozrodu Zwierząt i Badań Żywności
Polska Akademia Nauk w Olsztynie, Polska

Słowa kluczowe: borówka brusznica, związki fenolowe, kwasy fenolowe, antocyjany, niskie temperatury, aktywność antyoksydacyjna.

Abstrakt

Celem pracy było określenie wielkości zmian w zawartości substancji biologicznie aktywnych w owocach borówki brusznicy poddanych przechowywaniu chłodniczemu, zamrażaniu i liofilizacji.

W pracy przedstawiono właściwości terapeutyczne borówki brusznicy oraz omówiono występujące w niej grupy związków fenolowych, szczególnie kwasy fenolowe i antocyjany. Opisano wpływ wybranych operacji technologicznych (zamrażania i liofilizacji) na zawartość związków fenolowych w owocach. Analizowano również aktywność antyoksydacyjną związków fenolowych obecnych w soku z owoców.

Wyniki badań wskazują, że liofilizacja miała negatywny wpływ na poziom wszystkich związków fenolowych w owocach borówki brusznicy. Podczas tego procesu łączna zawartość związków fenolowych zmniejszyła się o ok. 37%. Jednocześnie zaobserwowano 20% ubytek kwasów fenolowych. Największą zmianę zaobserwowano podczas analizy zmian zawartości antocyjanów, w liofilizowanych owocach zmalała ona aż o ok. 97%. Tak znacząca degradacja związków polifenolowych spowodowała znaczny (ok. 36%) spadek aktywności antyoksydacyjnej.

Introduction

Lingonberry *(Vaccinium vitis-idaea)* is a shrub which grows naturally in heathers and pine forests in Northern Europe, Asia and North America. Its fruit is picked and processed to obtain products with therapeutic properties. In recent years, the first cultivars have been grown in orchards in The Netherlands which are fit for cultivation as a commodity. Lingonberry fruit are picked in their natural habitat and, despite lively interest in the fruit from the food processing industry, no commodity plantations of the species exist in Poland. Lingonberry provides two kinds of raw materials: leaves and fruit, which are used in herbal medicine, pharmaceutical

and food industries. A number of studies have been carried out on phenolic compounds of lingonberry, especially phenolic acids, anthocyanins and flavonol glycosides. EK et al. (2006), HOKKANEN et al. (2009) found that leaves of lingonberry contain phenolic glycosides: arbutin, methylarbutin, pyranosides, flavonoids, mainly hyperoside), catechin tannins, minerals and organic acids. HOKKANEN et al. (2009) identified 51 different phenolic compounds in lingonberry, including: flavan-3-ols, proanthocyanidins, flavonols and their glycosides and conjugates of various phenolic acids. EK et. at. (2006) identified a total of 28 phenolic compounds, including flavonols, anthocyanidins, catechins and their glycosides, as well as acetylated radicals of caffeic acid and various caffeoyl and ferulic acid conjugates. The authors identified such conjugates as: coumaroyl-hexose-hydroxyphenol, caffeoyl-hexose-hydroxyphenol, coumaroyl-hexose-hydroxyphenol, quercetin-3-O-R arabinofuranoside, kaempferol-pentoside, and kaempferol-deoxyhexoside in the plant, and the flavonolacylglycosides quercetin-3-O-[4″-3-hydroxy-3-methylglutaroyl)]-R-rhamnose and kaempferol-3-O-[4″-3-hydroxy-3-methylglutaroyl)]-R-rhamnose.

IERI et al. (2013) reports that among the identified derivatives of cinnamic acid, chlorogenic acid was identified, which was the main phenolic acid present in fruit, whereas caffeoyl arbutin was the main compound in fruit and leaves of lingonberry. In terms of quantitative composition, hydroxycynnamic acids were the main components and they accounted for 52–84% of the total phenols.

Justification and aim of the study: in recent years, the possibility of using forest fruit in regional food products has been attracting increasing attention. Of the numerous technological options available, those which are the easiest to implement in small processing facilities are selected, such as cold storage, freezing or lyophilisation of fruit. The aim of the study was to determine the extent of changes in the content of bioactive substances in lingonberry fruit following cold storage, freezing and lyophilisation. Changes in the total content of phenolic compounds, anthocyanins and phenolic acids were analysed.

Material and Methods

Lingonberry fruit picked in forests in the north of Poland (near Łeba) were used as the study material. A five kilos batch of fruit was divided into three parts. One part was stored under refrigerated conditions at 6–8°C, one was frozen and stored at -18°C, and one was lyophilised. All the three fruit batches were vacuum-packed in plastic packaging. Lyophilised fruit

were stored at room temperature away from light. The samples were analysed after six months of storage. In all samples dry matter was measured gravimetrically.

Dry matter content. The fruits were determined: dry matter content by weight of *Przetwory owocowe…* PN-A-90 75101 03.

Total phenolic compounds content. Total content of phenolic compounds was determined colorimetrically with the use of Folin-Ciocalteu reagent according to the method described by AOAC, (1974) and SHAHIDI AND NACZK (1995). Phenolic compounds were extracted three times with 80% methanol. The collected supernatants were evaporated to dryness. The colour reaction of phenolic compounds was induced by Folin-Ciocalteu reagent solution (Sigma-Aldrich, St. Louis, MO, United States). Absorbance at a wavelength of 765 nm after 60 minutes was measured with the use a UNICAM UV/Vis UV2 spectrophotometer (ATI Unicam, Cambridge, UK). The content of phenolic compounds was expressed as gallic equivalent.

Anthocyanins content. Total anthocyanins in samples were analysed according to colorimetric method described by GIUSTI and WROLSTAD (2001), Quantitative analysis was weightd on external calibration curve prepared with the use of cyanidyn-3-glucoside.

Antioxidant activity. The DPPH Radical Scavenging Assay (DPPH test) was determined according to MOURE et al. (2001). The DPPH radical scavenging activity was calculated and the antioxidant capacity of samples was expressed as μmol Trolox equivalent per 1 mg of sample.

Phenolic acids content. The phenolic acid assay was conducted by the method described by ZADERNOWSKI (1987).The qualitative and quantitative composition of phenolic acids in individual fractions was analysed by high-performance liquid chromatography (HPLC). The compounds under analysis were separated on a Synergi-Fusion column (150 mm x 2 mm; 4 μm) (Phenomenex) with an HPLC 1200 unit manufactured by Agilent Technologies. The chromatogram was developed in a gradient flow of the mobile phase, which consisted of acetonitrile with 0.15% formic acid and water, also acidified with 0.15% formic acid. The mobile phase flow rate was 0.2 cm^3 min^{-1}. The detection was effected with a photodiode detector (PDA Agilent Technologies) for the wavelength of 260 and 320 nm. Individual compounds were identified by comparing the retention time and an UV-Vis spectrum with the reference standards of the compounds. The quantitative analysis was carried out with the calibration curves for external reference standards of the phenolic acids under analysis.

Statistical analysis. The results of all analysis performed in triplicate experiments were statistically analysed using Statistica 12.0 PL software

(StatSoft Inc., Kraków, Poland). In order to indicate the significance of differences between samples, unvaried analysis of variance (ANOVA) with a Duncan test at $p \leq 0.05$ significance level was used.

Results and Discussion

After the lingonberry fruit was dried at the temperature of 110°C it was shown that water and components of the fruit volatile in steam, i.e. volatile organic acids and flavour compounds accounted for 96% of the fruit weight. Dehydrated components of the pulp, fruit skin and seeds (small pits), defined as dried matter, accounted for the remaining part, i.e. 4%.

Table 1

The dry matter and the extract content in fruit lingonberry

Fruits	Dry weight [%]	Extract content [%]
Stored inrefrigeration	13.96 ± 0.11	12.55± 0.13
Frozen	14.32 ± 0.19	13.00± 0.10
Lyophilized	81.08 ± 1.09	–

Lyophilising drying resulted in 5.7-fold concentration of components of the dry matter. Lyophilisation of lingonberry fruit yielded the product containing 81.08% of dry matter (Table 1). ZADERNOWSKI and OSZMIAŃSKI (1994) report that carbohydrates at 5–12% account for the major part of lingonberry fruit dry matter. An extract which determines the percentage of water-soluble components, other than volatile in steam, is another important determinant which characterises the technological value of fruit. The extract value is determined mainly by sugars soluble in cell juice. The extract accounted for 12.55 % of the cold-stored fruit weight, and for 13.00% of the frozen fruit. The slight increase in the percentage of extract in frozen fruit may be caused by inversion of sugars during storage in a freezer.

ZADERNOWSKI and OSZMIAŃSKI (1994), CIOŁKOWSKA-PALUCH (2000), HO et al. (2001), PLISZKA (2003) report that dry matter also contains, apart from carbohydrates, pectins, organic acids (mainly benzoic acid), ascorbic acid, carotenoids and polyphenols: flavans, procyanidines, cinnamic acid, trans-resveratrol and *p*-coumaric acid. Lingonberry fruit contains 11 to 20 mg of vitamin C in 100 g of dry matter. Carotenoids are present mainly as: lutein at 0.36 mg·100 g^{-1} of dry matter, and ß-carotene at 0.2 mg·100 g^{-1} of dry matter. These components are the main source of the therapeutic properties of lingonberry fruit.

There are the two main groups of phenolic compounds: flavonoids (which include anthocyanins) and non-flavonoid compounds, whose main groups include phenolic acids, derivatives of cinnamic and benzoic acids.

The term "total phenolic compounds", which is used in the literature, refers to polyphenolic species isolated from plant material by extraction with methanol or acetone. Most of these compounds react with the Folin--Ciocalteau reagent and they are determined colorimetrically.

The results of the study are given on a dry and fresh weight basis. This makes it easier to interpret the results of this experiment and other results. It was found that the content of phenolic compounds and their antioxidant activity were different and depended on whether the lingonberry fruit was stored under refrigerated conditions, frozen or lyophilised. The total phenolic compounds expressed as gallic acid on a dry basis was 3844.77 mg·100 g^{-1} and 536.73 mg·100 g^{-1} on a fresh weight basis in refrigerated fruit, whereas it was slightly higher in frozen 5283,10 mg·100 g^{-1} on the basis of dry matter weight of frozen fruit and 756.54 mg·100 g^{-1} on fresh matter basis. These findings are consistent with the content of phenolic compounds in fresh fruit, published by KÄHKÖNEN et al. (2001), and SZAJDEK and BOROWSKA (2008). The process of sublimation resulted in a decrease in the total phenolic compounds in lyophilised lingonberry by approx. 37% compared to the cold-stored and 54% to the frozen fruit. The total phenolic compounds content in lyophilised fruit was 2428.81 mg·100 g^{-1} on a dry weight basis (Table 2). This resulted from the fact that lyophilisation degrades phenolic compounds to colourless species, which do not give coloured products in reactions with the Folin-Ciocalteau reagent.

The content of anthocyanins in cold-stored fruit was 489.61 mg·100 g^{-1} on a dry weight basis and it was slightly higher in frozen fruit – 549.37 mg·100 g^{-1} on a dry weight basis. Converted to the fresh weight basis, the content of anthocyanins was: 68.35 mg·100 g^{-1} in cold-stored fruit and 78.67 mg·100 g^{-1}. (Tab. 2.). LEE and FINN (2012), VOLLMANNOVA et al. (2009), KÄHKÖNEN et al. (2001) report that the content of anthocyanins in lingonberry fruit ranges from 17 to 50 mg·100 g^{-1} on afresh weight basis. The slightly higher content of phenolic compounds and anthocyanins in the frozen fruit was caused by a higher content of dry matter. Anthocyanins accounted 12,73% of the total phenolic compounds in the cold-stored fruit, for 10.40% in the frozen fruit and for only 0.62% in the lyophilised fruit.

The process of sublimation was found to have a destructive effect on the total phenolic compounds, especially on anthocyanins. The anthocyanin contents in lyophilised fruit was 10.37 mg·100 g^{-1} on a dry weight basis (Table 2). Compared to the anthocyanin content in the cold-stored

fruit, the process of sublimation reduced the anthocyanin content in the lyophilised fruit by up to 97%. A visual observation showed that the red colour of the lyophilised lingonberry fruit was much brighter than cold-stored and frozen fruit.

Table 2

The total amount of phenolic compounds, anthocyanins and phenolic acids in fruit lingonberry stored inrefrigeration, frozen and lyophilized

Fruits	Total phenolic compounds		Anthocyanins		Phenolic acids	
	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g^{-1} fresh weight	mg·100 g $^{-1}$ dry weight
Stored inrefrigerator	536.73 ±32.20	3844.77^{a} ±32.13	68.35 ±8.35	489.61^{a} ±28.12	108.35 ±8.12	756.68^{a} ±20.00
Frozen	756.54 ±52.60	5283.10^{b} ±88.00	78.67 ±9.60	549.37^{a} ±37.02	109.22 ±6.19	760.00^{a} ±18.45
Lyophilized	1969.33 ±121.43	2428.81^{c} ±149.76	10.37 ±1.94	15.12^{b} ±2.15	492.62 ±10.13	607.54^{b} ±25.00

a, *b*, *c* – mean values indicated by the same letter do not differ significantly ($p \leq 0.05$)

The destructive effect of lyophilisation on phenolic compounds, especially on anthocyanins, was confirmed by MAZUR and BOROWSKA (2007), who examined the effect of sublimation drying on transformations of phenolic compounds in cranberry.

The lyophilisation process resulted in a 50% reduction in the polyphenol content and a 7-fold reduction in the anthocyanins content compared to fresh cranberry fruit. MAZUR and BOROWSKA (2007) claim that adverse transformations of anthocyanins during the process of berry fruit processing are affected by oxidation and formation of brown-red polymerised compounds.

Phenolic acids and their derivatives were another group of phenolic compounds in lingonberry fruit. Free phenolic acids are present in small amounts in plants and their presence usually results from the fact that they have not been transformed into bound forms during physiological processes which take place during fruit ripening. Phenolic acids were usually found to occur mainly in a bound form as components of low- or high--molecular weight polyphenolic compounds. For example, free phenolic acids and various forms of depsides are low-molecular polyphenols. High--molecular polyphenols include lignins, procyanidins, hydrolysing tannins, with which phenolic acids form conjugates bound by ester or glycosidic bonds (SHAHIDI and NACZK 1995).

GAWLIK-DZIKI (2004) reports that some derivatives of cinnamic acid are commonly present as free forms or as depsides, and they also form esters with carboxylic acids or glucose, while derivatives of benzoic acid usually occur as glycosides. Most depsides occur in bound forms, for example, they are parts of hydrolysing tannins and they form complexes with proteins and polysaccharides. Apart from the structures described above, phenolic acids bind with lipids, sterols, polysaccharides, peptides.

The total content of phenolic acids in cold-stored and frozen lingonberry fruit was, respectively: 756.68 ± 20 mg·100 g^{-1} on the d.m. (108.35 ± 8.12 mg·100 g^{-1} on the fresh weight) and 760.00 ± 18.45 mg·100 g^{-1} on the d.m.(109.22 ± 6.19 mg·100 g^{-1} on the fresh weight) and the mean content was 758.34mg·100 g^{-1} on the dry weight (108.35mg·100 g^{-1} on the fresh weight (Table 2). This comprised free phenolic acids (15%) and phenolic acids bound by glycosidic bonds with other components (67%) and phenolic acids bound by ester bonds (18%). Total phenolic acids accounted for about 20% of the total phenolic compounds (Figure 1). The process of sublimation reduced the content of phenolic acids in the lyophilised fruit to 607.54 ± 25 mg·100 g^{-1} on the dry weight or 492.62 ± 10.13 mg·100 g^{-1} on the fresh weight. The total phenolic acids accounted for approx. 25% of total phenolic compounds present in lyophilised fruit (Table 2, Figure 1.). Lyophilisation caused destruction of ester and glycosidic bonds and, as a result, the percentage of free phenolic acids increased to 34% while the content of phenolic acids bound by ester bonds decreased to 52% and those bound by glycosidic bonds – to 14% (Figure 1).

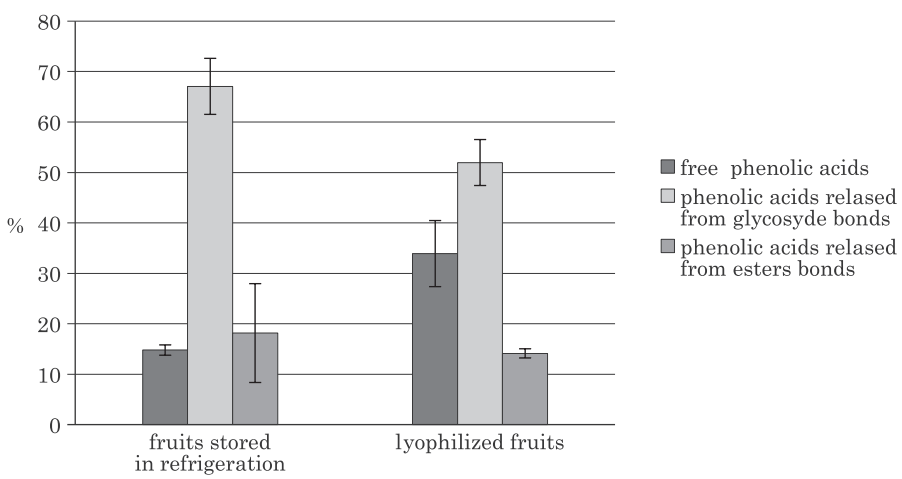

Fig. 1 The percentage of free phenolic acids and released from the ester and glycosidec bonds

Table 3

The amount of free phenolic acids and released from the ester and glycosidic bounds, founded in fruits

Phenolic acids	Free phenolic acids		Phenolic acids released from the bounds				Total phenolic acids	
			esters		glicosides			
	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g^{-1} fresh weight	mg·100 g $^{-1}$ dry weight	mg·100 g^{-1} fresh weight	mg·100 g^{-1} dry weight
Protocatechuic	1.08 ± 0.23	7.57 ± 1.59	30.75 ± 5.12	214.71 ± 35.75	12.01 ± 4.84	83.85 ± 33.82	43.84	306.13
p-OH-Benzoic	1.69 ± 0.01	11.79 ± 0.10	3.89 ± 0.07	27.18 ± 0.48	3.69 ± 0.19	25.80 ± 1.31	9.27	64.77
Vanillic	3.33 ± 0.12	23.23 ± 0.83	1.08 ± 0.00	7.52 ± 0.01	2.54 ± 0.09	17.73 ± 0.65	6.95	48.48
Caffeic	0.00 ± 0.00	0.00 ± 0.00	1.47 ± 0.52	10.25 ± 4.61	0.54 ± 0.27	3.80 ± 1.38	2.01	14.05
p-Coumaric	4.56 ± 0.08	31.86 ± 0.58	19.98 ± 0.91	139.50 ± 6.37	0.57 ± 0.09	4.01 ± 0.66	25.11	175.37
Ferulic	5.35 ± 0.54	37.39 ± 3.74	15.51 ± 0.13	108.34 ± 0.89	0.31 ± 0.05	2.15 ± 0.37	21.17	147.88
Total	16.01	111.84	72.68	507.50	19.66	137.34	108.35 ± 8.12	756.68 ± 20.00

Table 4

The amount of free phenolic acids and released from the ester and glycosidic bounds, contained in the lyophilized fruits

Phenolic acids	Free phenolic acids		Phenolic acids released from the bounds				Total phenolic acids	
			esters		glicosides			
	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g $^{-1}$ fresh weight	mg·100 g^{-1} dry weight	mg·100 g^{-1} fresh weight	mg·100 g $^{-1}$ dry weight	mg·100 g^{-1} fresh weight	mg·100 g^{-1} dry weight
Protocatechuic	29.63 ± 4.36	36.54 ± 5.38	97.21 ± 30.48	119.89 ± 37.60	34.22 ± 1.48	42.20 ± 1.82	161.06	198.64
p-OH-Benzoic	18.41 ± 0.60	22.71 ± 0.74	14.01 ± 2.42	17.28 ± 2.99	13.34 ± 0.92	16.45 ± 1.13	45.76	56.44
Vanillic	15.88 ± 0.42	19.59 ± 0.52	4.53 ± 0.60	5.59 ± 0.74	17.95 ± 0.56	22.14 ± 0.70	38.36	47.28
Caffeic	0.00 ± 0.00	0.00 ± 0.00	5.74 ± 1.25	7.08 ± 1.54	0.00 ± 0.00	0.00 ± 0.00	5.74	7.08
p-Coumaric	63.63 ± 2.99	78.47 ± 3.69	81.00 ± 17.71	99.90 ± 21.84	2.29 ± 0.20	2.83 ± 0.24	146.92	181.2
Ferulic	39.51 ± 6.08	48.72 ± 7.50	53.50 ± 17.57	65.98 ± 21.67	1.76 ± 0.64	2.17 ± 0.79	94.77	116.87
Total	167.06	206.03	255.99	315.72	69.56	85.79	492.61 ± 10.13	607.54 ± 25.00

Protocatechuic acid is the dominant phenolic acid in lingonberry fruit with the content of 306.13 mg·100 g^{-1} d.m. (40.5% of all the acids). *p*-Coumaric acid was present in the amount of 175.37 mg·100 g^{-1} d.m. (23.2%), and ferulic acid – 147.88 mg·100 g^{-1} d.m. (19.5%) – Table 3. The ratio of these acids changed after lyophilisation: the content of protocatechuic acid decreased to 198.64 mg·100 g^{-1} d.m. (32.7%) and that of ferulic acid to 116.87 mg·100 g^{-1} d.m. (Table 3, Table 4, Figure 2).

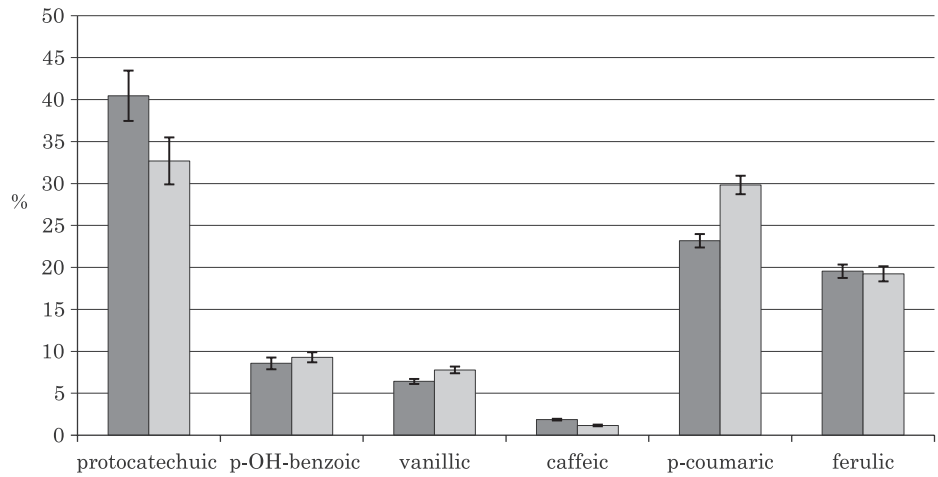

Fig. 2. The percentage of phenolic acids in fruit lingonberry cold storage and freeze-dried

The content of *p*-coumaric acid increased to 181.2 mg·100 g^{-1} d.m. (29.8%). The content of caffeic acid was the lowest: 14.05 mg·100 g^{-1} d.m. (1.9%) in cold-stored fruit and 7.08 mg·100 g^{-1} d.m. in lyophilised fruit (1.2%) (Table 3, Table 4, Figure 2).

The anti-oxidative activity of phenolic compounds in cold-stored and frozen lingonberry fruit was similar: 5.36 µM $DPPH^{\cdot}$ scavenged by 1 mg of phenolic compounds for cold-stored fruit and 5.31 µM $DPPH^{\cdot}$ scavenged by 1 mg of phenolic compounds in frozen fruit. The figure was lower by approx. 36% for the lyophilised fruit: 3.43 µM $DPPH^{\cdot}$ scavenged by 1 mg of phenolic compounds (Table 5).

Table 5

The antioxidant activity of phenolic compounds present in the studied fruits lingonberry

Specification	Fruits stored in refrigerator	Frozen fruits	Lyophilized fruits
µM $DPPH^{\cdot}$ / 1 mg phenolic	5.31±0,11	5.38±0,06	3.43±0,20

Conclusions

An analysis of the findings showed that lingonberry fruit, like other berry fruit, is a rich source of phenolic compounds. Anthocyanins were found to account for approx. 21% and phenolic acids for 20% of the phenolic compounds in fresh lingonberry fruit. The greatest portion of phenolic acids present in fresh lingonberry fruit was bound by ester bonds and the smallest portion occurred as free phenolic acids (15%). Protocatechuic acid was the dominant phenolic acid (40.5% of all the acids) present in lingonberry fruit. Lyophilisation reduced the content of all the phenolic compounds under analysis in lingonberry fruit and especially reduced the content of anthocyanins. The content of phenolic compounds was found to decrease by 37%, those of phenolic acids – by 20% and anthocyanins – by 97%. Lyophilisation cleft ester and glycosidic bonds in lingonberry, thereby increasing the content of free phenolic acids. Moreover, the study found that lyophilisation decreased the antioxidative activity of the phenolic compounds present in lingonberry fruit by 36%.

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References

AOAC. 1974. *Official Methods of Analysis*, 12th ed. Association Of Official Analitical Chemists, Washington DC, 9, 110.

CIOŁKOWSKA-PALUCH G. 2000. *Borówka brusznica – surowiec o właściwościach leczniczych i odżywczych*, Wiadomości Zielarskie, 42(4): 10.

EK S., KARTIMO H.,MATTILA S.,TOLONEN. 2006. *Characterization of phenolic compounds from lingonberry (Vaccinium vitis-idaea).* J. Agric. Food Chem., 54(26): 9834–9842.

GAWLIK-DZIKI U. 2004. *Fenolokwasy jako bioaktywne składniki żywności*. Żywność. Nauka. Technologia. Jakość, 4(41): 29–40.

GIUSTI M.M., WROLSTAD R.E. 2001. *Characterization and measurement of anthocyanins by UV-Visible spectroscopy*. In: Current protocols in food analytical chemistry, (F): F1.2– F1.2.13.

HOKKANEN J., MATTILA S., JAAKOLA L., PIRTTILÄ A.M., TOLONEN A. 2009. *Identification of phenolic compounds from lingonberry (Vaccinium vitis-idaea* L.*), bilberry (Vaccinium myrtillus* L.*) and hybrid bilberry (Vaccinium x intermedium Ruthe* L.*) leaves.* J. Agric. Food Chem., 57(20): 9437–9447.

HO KY., TSAI C.C., HUANG J.S. 2001. *Antimicrobialactivity of tannin components from Vacciniu vitis-idaea* L. J. Pharm. Pharmacol., 53(2): 187–191.

IERI F., MARTINI S., INNOCENTI M., MULINACCI N. 2013. *Phenolic distribution in liquid preparations of Vaccinium myrtillus* L. *and Vacciniu mvitisidaea* L. Phytochem. Anal., 24(5): 467–475.

KÄHKÖNEN M.P., HOPIA A.I., HEINONEN M. 2001. *Berry Phenolics and Their Antioxidant Activity.* J. Agric. Food Chem., 49: 4076–82.

LEE J., FINN C.E. 2012. *Lingonberry (Vaccinium vitis-idaea* L.*) grown in the Pacific Northwest of North America: Anthocyanin and free aminoacid composition.* J. Funct. Foods, 4: 213– 218.

MAZUR B., BOROWSKA E. 2007. *Produkty z owoców żurawiny błotnej – zawartość związków fenolowych i właściwości przeciwutleniające*. Bromat. Chem. Toksykol., 3: 239–243.

MOURE A., CRUZ J.M., FRANCO D., DOMINGUEZ J. M., SINEIRO J., DOMINGUEZ H. 2001. *Natural antioxidants from residual sources.* Food Chem.,72: 145–171.

PLISZKA K. 2003. Żurawina i borówka brusznica, Wyd. Działkowiec, Warszawa.

Przetwory owocowe i warzywne. Przygotowanie próbek i metody badań fizykochemicznych. Oznaczenie zawartości suchej masy metodą wagową. PN-90-A-75101-03.

SHAHIDI F., NACZK M. 1995. *Methods of analysis and quantification of phenolic compounds.* Food phenolics: sources, chemistry, effects and applications. Eds. F. Shahidi, M. Naczk. Technomic Publishing Company, Inc., Lancaster, Pennsylvania, U.S.A., pp. 287–293.

SZAJDEK A., BOROWSKA E.J. 2008. *Bioactive compounds and health-promoting properties of berry fruits: A review*. Plant Foods Hum. Nutr., 63: 147–156.

VOLLMANNOVA A., TOMAS J.,URMINSKA D., POLAKOVA Z., MELICHACOVA S., KRIZOVA L. 2009. *COntent of Bioactive Components in Chosen Cultivars of Cranberries* (*Vaccinium vitis-idaea* L.). Czech J. Food Sci., 27 Special Issue.

ZADERNOWSKI R. 1987. *Studia nad związkami fenolowymi mąk rzepakowych i rzepikowych*, Acta Acad. Agric. Tech. Olst. Technol. Aliment., (21F): 3–55.

ZADERNOWSKI R., OSZMIAŃSKI J. 1994. *Wybrane zagadnienia z przetwórstwa owoców i warzyw.* Wyd. ART Olsztyn.