

INFLUENCE OF FOLIAR FERTILISATION WITH CALCIUM FERTILISERS ON THE FIRMNESS AND CHEMICAL COMPOSITION OF TWO HIGHBUSH BLUEBERRY CULTIVARS*

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Abstract

Maintaining the high quality of fruits after harvest, which amongst other things is determined by firmness, is the aim producers strive after. Calcium, which fruits can be enriched with also in an extraradicular manner, is mostly responsible for the mechanical resistance of fruits. In the research conducted at the Laboratory of Orchardring, West Pomeranian University of Technology in Szczecin, the influence of foliar calcium fertilisers on the quality of fruits from two cultivars of highbush blueberry was studied. The firmness, size and chemical composition of fruits were examined (the content of mineral and organic compounds, especially polyphenols). At the fruit growth stage, bushes were sprayed 4 times with calcium solutions every 10 days, starting from the first decade of June. All fertilisers caused an increase in calcium concentrations in fruits (0.12-0.15 g 100 g⁻¹), as compared with the control (0.09 g 100 g⁻¹). The weight of 100 fruits collected from bushes sprayed with the Lebosol, Folanx and Calcinit fertilisers was the highest and it ranged from 327 to 365 g, and the Sunrise cultivar fruits were larger. The firmest (391 and 415 G mm) and the most resistant to mechanical damage (132 and 114 G mm) were the fruits sprayed with the calcium chloride and Folanx fertilisers, while fruits sprayed with Folanx and Calcinit were characterised by the highest polyphenol content (300 and 313 mg 100 g⁻¹), and anthocyanins, among which delphinidin-3-galactoside predominated, constituted the largest group of compounds (77-80%).

The Calcinit and Lebosol Calcium Forte fertilisers had the greatest influence on the change of chemical composition of the fruits, while the Folanx fertiliser had the greatest influence on the increase in fruit firmness. All calcium-based fertilisers decreased the acidity of fruits and, except for calcium chloride, they increased the nitrite level.

Key words: anthocyanins, foliar fertilization, flavonols, macro- and microelements, *Vaccinium corymbosum*.

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INTRODUCTION

Highbush blueberry (*Vaccinium corymbosum* L.) is mostly grown for the fresh fruit market in Poland. Its bushes have specific habitat and soil requirements, for example acidic peat soils are the best, light sandy soils are possible if the demand for water and nutrients is satisfied. Highbush cultivars are derived from the genus *Vaccinium*, which grows wildy in soils characterised by a low nutrient content. As a result, fertilising requirements of highbush blueberry are relatively modest, as compared with other fruit crops. However, intensive cultivation influencing high yields and the use of organic litter determine the necessity of fertilisation to keep the content of micro- and macronutrients in the soil and the plants at a constant level (PORMALE et al. 2009).

Maintaining the high quality of fruits after harvesting, after the storage period as well as during marketing activities, is a goal that producers want to achieve. Firmness is one of the indicators of fruit freshness and attractiveness. Mechanical resistance of the skin and the flesh largely depends on the condition of cellular membranes and, in particular, the chemical composition of pectins binding plant cells together to form tissues. Calcium is mostly responsible as it contributes to the stabilisation of cellular membranes as a component of phospholipids, thus influencing their permeability (WHITE, BROADLEY 2003). Calcium deficits or calcium transport disorders cause a large number of physiological diseases, which lower the storage and commercial value of such fruits (SHEAR 1975). Plant roots absorb calcium from the soil solution in the form of the Ca^{2+} ion (WHITE 2001, CLARKSON 2003); however, the number of free calcium ions is limited by the high humus content, in which organic acids form chelated bindings with Ca^{2+} . The low pH of the substrate is also a problem, as it stimulates high Al^{3+} , Fe^{2+} , Mn^{2+} concentrations, which make it difficult to absorb calcium ions (HAYNES 1986). Thus, supply of calcium fertilisers by spraying the plants could be an alternative (WÓJCIK 2004). Calcium delivered to leaves by means of spraying increased the concentration of this nutrient in fruits by 17% (SAURE 2005, ROSEN et al. 2006). Therefore, the best results are observed when solution of a calcium preparation is applied directly onto the fruit surface. Young fruits are characterised by the highest calcium absorption (SCHLEGEL, SCHÖNHERR 2002), as the permeability of the cuticle is the highest at that time (PETIT-JIMENEZ et al. 2009), and properly functioning stomata are an easy route for Ca^{2+} absorption. The time of treatment is also very important. The movement of calcium salts largely depends on air humidity. An increase in humidity from 50% to 90% resulted in twice as high a rate of $\text{Ca}(\text{NO}_3)_2$ absorption through the cuticle layer (SCHÖNHERR 2001).

The influence of foliar application of calcium fertilisers with diverse chemical composition on the quality of highbush blueberry fruits, their size, firmness and chemical composition was studied.

MATERIAL AND METHODS

The studies were carried out in 2010-2012, in the Laboratory of Orchard- ing at the Department of Horticulture of the West Pomeranian University of Technology in Szczecin. The experiment was conducted at a 60 ha pro- duction plantation located in the area of Szczecin. Blueberry bushes were planted in the spacing of 1.2 x 2.0, in the podzolic soil of the VI valuation class. The experiment followed a randomised sub-block design (3 blocks, 15 plants in each block). The content analysis of the soil minerals showed a very high level of magnesium, medium levels of phosphorus and calcium, and a low level of potassium. In spring, the nitrogen fertilization was applied at a dose of 45 kg N ha⁻¹.

Within the growing period, the bushes were sprayed 4 times with cal- cium solutions (every 10 days from the first decade in June), starting from the fruit setting until the full wetting of the foliage. Liquid calcium fertili- zers, designed for foliar fertilization of plants and fruit, were used, together with the Silwet®Gold preparation enhancing the adhesion properties.

- Folanx® Ca29 – solution 1% (LANXESS Distribution GmbH);
- Calcium chloride – solution 0.5% (Inowrocławskie Zakłady Chemiczne Soda Małwy S.A.) CaCl₂ – 78-80%, NaCl – 3-3.5%;
- Lebosol Calcium Forte – solution 1% (Lebosol Dünger GmbH);
- Ca – 13.5%, Mn – 1.5%, Zn – 0.5%;
- Calcinit – solution 0.5% (Yara Poland) – Ca – 19.0%, N 15.5%, (NO₃ – 14.5%, NH₄ – 1.0%);
- control – spraying water.

Physical features of fruits (fruit size, firmness, puncture resistance of the skin) and soluble solids, titratable acidity, pH, total polyphenol, L-ascorbic acid and NO₃ were measured on fresh berries immediately after the harvest. Phenolics and mineral composition samples that were kept frozen (-32°C) in polyethylene bags (2 x 500 g) until analyzed.

Fruit diameter, firmness and puncture resistance of the skin were measured with a FirmTech2 apparatus (BioWorks, USA) on 100 randomly selected berries from each replicate, and the latter was expressed as a gram- force causing the fruit surface to sag by 1 mm. A puncture were made using a stamp with a diameter of 3 mm. The fruit weight (three replicates of 100 fruit) was measured on a RADWAG WPX 4500 electronic scales (0.01 g ac- curacy).

To obtain juice, berries (two replicates of 250 g) were macerated at 50°C for 60 minutes, with the addition of the PT 400 Pektopol enzyme at a dose of 400 mg kg⁻¹ of fruits. After the completion of the enzymatic processing, the pulp was pressed using a hydraulic press at a pressure of 3 MPa (OSZMIANSKI, WOJDYŁO 2005). Titratable acidity was determined by titration of the water extract of juice with 0.1 N NaOH to the end point of pH 8.1, measured with

a pH-meter Elmetron 501 (PN). The content of soluble solids was determined with an PAL1 KonicaMinolta refractometer. L-ascorbic acid and NO_3 concentrations were measured with a RQflex 10 reflectometer Merck (OCHMIAN et al. 2012).

In unwashed fruits, after mineralization in H_2SO_4 and H_2O_2 , the total N content was determined with the Kjeldahl method. The content of K and Ca was measured with atomic emission spectrometry, whereas the Mg content was determined with flame atomic absorption spectroscopy using an SAA Solaar. The phosphorus content was determined with the Barton method at the wavelength of 470 nm, whereas sulphur was assayed with the turbidimetric method at 490 nm employing a spectrophotometer Marcel s 330 PRO. The content of microelements (Cu, Zn, Mn, Fe), after mineralization in HClO_4 and HNO_3 , was measured with flame atomic absorption spectroscopy on an SAA Solaar (IUNG 1972).

The HPLC analyses of polyphenols were carried out with an HPLC apparatus consisting of a Merck-Hitachi L-7455 diode array detector (DAD) and quaternary pump L-119 7100 equipped with the D-7000 HSM Multisolvant Delivery System (Merck-Hitachi, Tokyo, Japan). The runs were monitored for phenolic acids at 320 nm, flavonols and luteolin glucoside at 360 nm, and anthocyanin glycosides at 520 nm. Retention times and spectra were compared to that of pure standards and total polyphenols content was expressed as mg per 100 g fruit tissue. Standards of anthocyanidin glycosides were obtained from Polyphenols Laboratories (Norway), while those for phenolic acids and flavonols were purchased from Extrasynthese (France).

In order to determine the significance of differences, a two-factor analysis of variance was carried out, followed by the assessment of the significance of differences using the Tukey's test. To determine the relation between the applied fertilizers and fruit firmness, chemical compositions and phenolic content, the results were subjected to an agglomerative cluster analysis and classified into groups in a hierarchical order by means of the Ward's method. The statistical analyses were performed using the Statistica software.

RESULTS AND DISCUSSION

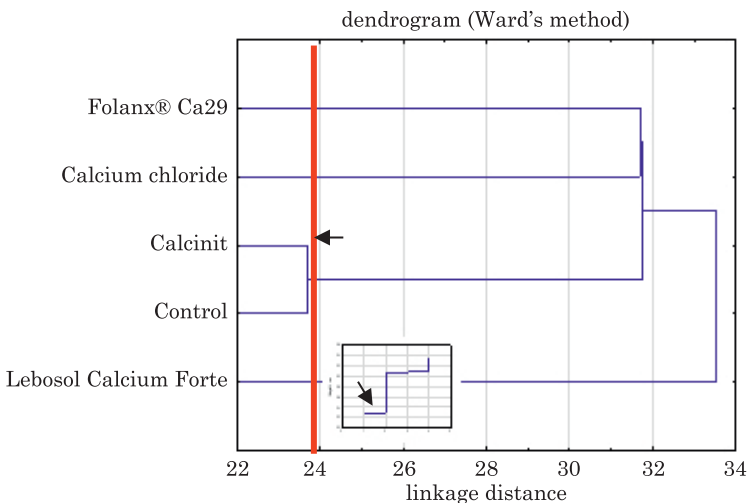
The firmness of fruits, and especially their size, is a very important factor determining the yield quality and its durability while on the market. The results showed high variability of this parameter after using calcium-based foliar fertilisers (Table 1). The foliar fertilisers, except for calcium chloride, allowed for obtaining larger fruits, as compared to the control. The largest fruits were collected from bushes sprayed with Lebosol (the average weight of 100 fruits was 365 g) and with Calcinit (333 g), the height of the fruits was 16.7 mm and 15.7 mm, respectively. Bushes treated with calcium chloride were characterised by the smallest fruits (the average height 14.0 mm,

Table 1
The firmness and size of highbush blueberry in relation to the fertilisation and cultivars (average values for the years 2010-2012)

Fertilizer (AxB)	Cultivar (A)	Mass of 100 fruits (g)	Measured on height axis		Measured on diameter axis		
			height (mm)	firmness (G mm)	diameter (mm)	firmness (G mm)	puncture (G mm)
Folanx® Ca29	Brigitta	302	14.4	435	20.9	236	134
Calcium chloride		255	14.1	407	18.5	217	115
Lebosol Calcium Forte		369	15.3	341	21.1	174	101
Calcinit		321	14.8	384	20.3	208	122
Control		299	14.3	389	18.8	193	109
Mean		309	14.6	391	19.9	206	116
Folanx® Ca29	Sunrise	352	14.4	394	22.0	196	129
Calcium chloride		292	13.8	375	18.9	177	113
Lebosol Calcium Forte		361	18.0	322	22.0	151	82
Calcinit		345	16.6	319	21.8	164	89
Control		311	15.7	359	20.4	168	94
Mean		332	15.7	354	21.0	171	101
Folanx® Ca29	The mean for fertilizer (B)	327	14.4	415	21.5	216	132
Calcium chloride		274	14.0	391	18.7	197	114
Lebosol Calcium Forte		365	16.7	332	21.6	163	92
Calcinit		333	15.7	352	21.1	186	106
Control		305	15.0	374	19.6	181	102
LSD _{q,0.05}		A-22; B-27; AxB-33	A-0.8; B-1.1; AxB-1.3	A-28; B-32; AxB-37	A-0.7; B-0.9; AxB-1.2	A-25; B-29; AxB-36	A-16; B-19; AxB-22

and the diameter 18.7 mm). The firmness of fruits determines, amongst other things, the resistance to mechanical damage. It is assumed that this phenomenon occurs to a lesser extent in fruits with a good calcium content (CARL, SAMS 1993, FALLAHI et al. 1997). Reports concerning the influence of calcium on the firmness of blueberry fruits do not render unambiguous results. Fruits soaked in a calcium solution after harvesting were less susceptible to crushing (HANSON et al. 1993). Also, fruits from the 'O'Neal' cultivar treated with calcium were firmer than fruits from the control bushes. However, this relationship was not confirmed by 'Bluecrop' fruits (ANGELETTI et al. 2010). The results obtained are also ambiguous, which is confirmed by an analysis of concentrations, the activity of the Calcinit fertiliser did not affect fruit firmness (Figure 1). Fruits sprayed with the Lebosol fertiliser had the highest calcium content (Table 2); however, they were the least firm. Undoubtedly, their size had an influence on this, large fruits are less firm. However, blueberries treated with the Folanx fertiliser contained a lot of calcium and were characterised by high firmness, both in the diameter and in the height and fruit resistance to mechanical damage (129-134 G mm). Regardless of the fertilisers used, fruits of the tested cultivars were characterised by a lower firmness as compared to fruits from the 'Sierra' (440) and 'Patriot' cultivars (512 G mm) (OCHMIAN et al. 2007, 2009b).

The chemical composition of fruits is an equally important parameter determining fruit quality. It affects both the taste and the health promoting properties of fruits. The analyses showed that cv. Brigitta fruits were characterised by a higher content of organic acids and a lower extract content (Table 3). Moreover, it was shown that all foliar fertilisers used, regardless of the cultivar, had an influence on the reduction of fruit acidity (from 0.35



The vertical line indicate the cut-off used to form the groups

Fig. 1. Dendrogram of cluster analysis for fertilizers based on average for firmness

Table 2

The influence of calcium-based fertilisers on the macronutrient content in highbush blueberry fruits(g 100 g⁻¹f.w.)

Fertilizer (AxB)	Cultivar (A)	Content in fruits (g 100 g ⁻¹ f.w.)					
		Ca	N	P	K	Mg	
Folanx® Ca29	Brigitta	0.16	0.53	0.11	0.45	0.06	
Calcium chloride		0.15	0.36	0.11	0.49	0.03	
Lebosal Calcium Forte		0.18	0.39	0.09	0.67	0.04	
Calcinit		0.15	0.74	0.07	0.65	0.04	
Control		0.11	0.35	0.08	0.54	0.03	
Mean		0.15	0.47	0.09	0.56	0.04	
Folanx® Ca29	Sunrise	0.11	0.85	0.14	0.62	0.07	
Calcium chloride		0.09	0.52	0.14	0.50	0.04	
Lebosal Calcium Forte		0.12	0.60	0.11	0.71	0.06	
Calcinit		0.09	1.19	0.09	0.62	0.06	
Control		0.06	0.51	0.09	0.50	0.04	
Mean		0.09	0.73	0.11	0.59	0.05	
Folanx® Ca29	The mean for fertilizer (B)	0.14	0.69	0.12	0.54	0.07	
Calcium chloride		0.12	0.44	0.12	0.49	0.04	
Lebosal Calcium Forte		0.15	0.49	0.10	0.69	0.05	
Calcinit		0.12	0.96	0.08	0.64	0.05	
Control		0.09	0.43	0.09	0.52	0.04	
LSD _{α,0.05}		A-0.03, B-0.04 AxB-0.06	A-0.19, B-0.23 AxB-0.28	A-0.04, B-0.05 AxB-0.08	A-0.07, B-0.10 AxB-0.12	A-0.01, B-0.02 AxB-0.04	

Table 3

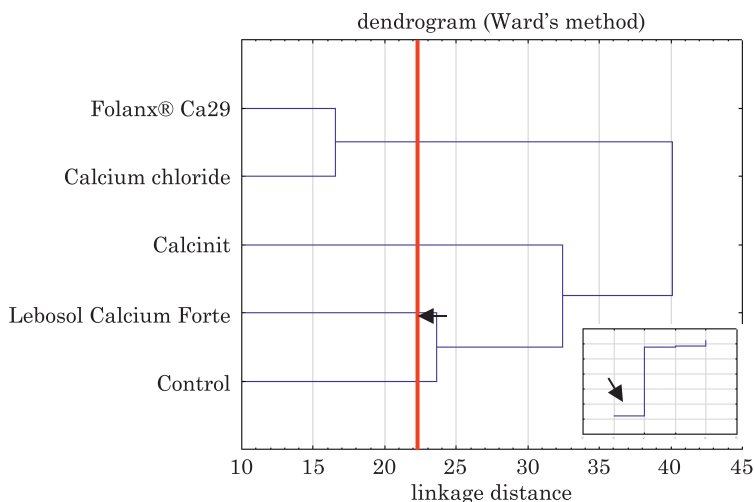
Some characteristics of the fruits of highbush blueberry in dependence on fertilizing and cultivar (mean for 2010–2012)

Fertilizer (AxB)	Cultivar (A)	Titrateable acidity (g 100 mL ⁻¹)	Soluble solids (%)	NO ₃ (mg 1000 mL ⁻¹)	L-ascorbic acid (mg 1000 mL ⁻¹)	Juice pH
Folanx® Ca29	Brigitta	0.78	14.7	39.6	95	3.86
Calcium chloride		0.87	13.9	29.2	102	3.75
Lebosol Calcium Forte		0.85	13.6	42.4	120	3.84
Calcinit		0.74	14.9	47.8	84	3.81
Control		0.96	13.8	31.5	126	3.67
Mean		0.84	14.2	38.1	105	3.79
Folanx® Ca29	Sunrise	0.35	15.7	32.7	71	3.85
Calcium chloride		0.42	15.2	18.3	107	3.89
Lebosol Calcium Forte		0.44	15.1	31.0	92	3.94
Calcinit		0.38	15.2	34.3	68	3.97
Control		0.55	15.5	17.3	84	3.82
Mean		0.43	15.3	26.7	84	3.89
Folanx® Ca29	The mean for fertilizer (B)	0.57	15.2	36.2	83	3.86
Calcium chloride		0.65	14.6	23.8	105	3.82
Lebosol Calcium Forte		0.65	14.4	36.7	106	3.89
Calcinit		0.56	15.1	41.1	76	3.89
Control		0.76	14.7	24.4	105	3.75
LSDa _{0.05}			A-0.08 . B-0.09 AxB-0.11	A-0.4 . B-0.5 AxB-0.7	A-4.3 . B-5.6 AxB-7.9	A-13 . B-19 AxB-24

to $0.87 \text{ g } 100 \text{ mL}^{-1}$), as compared with the control (cv. Sunrise 0.55 and Brigitta $0.96 \text{ g } 100 \text{ mL}^{-1}$, respectively) and a slight increase in the pH of the juice. These parameters are similar to those obtained by DUAN et al. (2011). The influence of the fertilisers used on the extract content was diverse. The extract content in the cultivar Sunrise fruit was at a similar level (15.1 - 15.7%), while in cv. Brigitta fruits, the extract content was the highest in bushes sprayed with the Calcinit and Folanx fertilisers (14.9 and 14.7%). In studies by other authors, the extract content in fruits from the cultivars under analysis ranged from 10% to 14.6% (PRIOR et al. 1998, SKUPIEŃ 2006, DUAN et al. 2011).

The use of calcium fertilisers did not increased the L-ascorbic acid content, and in fruits collected from bushes sprayed with the Calcinit and Folanx fertilisers, it was found to be at a level (76 and $83 \text{ mg } 1000 \text{ mL}^{-1}$) lower than the control ($105 \text{ mg } 1000 \text{ mL}^{-1}$). The use of Calcinit, Lebosol and Folanx fertilisers, on the other hand, had an influence on a higher nitrate content (on average $36.2241.1 \text{ mg } 1000 \text{ mL}^{-1}$) in fruits from both cultivars, as compared to control fruits ($24.4 \text{ mg } 1000 \text{ mL}^{-1}$). Nevertheless, these are levels which are allowed for consumption even by children, according to the Polish standards. Similar levels were identified by other authors: from 15.5 to $34.7 \text{ mg } \text{NO}_3$ in 1000 g fruits (OCHMIAN et al. 2009a, b, 2010). To show similarities in the action of fertilisers, an analysis of concentrations was performed between the fertilisers used and the content of SS, TA, NO_3 and L-ascorbic acid (Figure 2). All of the fertilisers affected the analysed features, and the action of Folanx and Calcinit was similar.

Owing to a high content of phenolic compounds as well as other biologically active substances, dark fruits are valued as products with pro-health

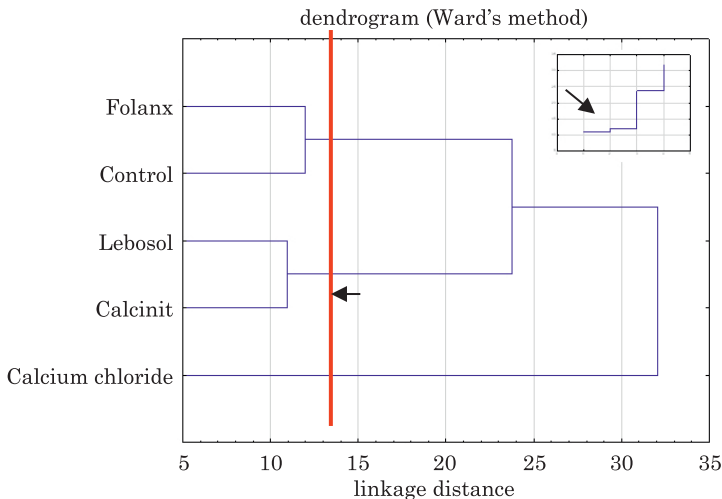


The vertical line indicate the cut-off used to form the groups

Fig. 2. Dendrogram of cluster analysis for fertilizers based on average for chemical compositions

properties. Polyphenols are products of the secondary synthesis which protect from ultraviolet radiation and pathogens (DE GARA et al. 2003, HODGES et al. 2004). Their content largely depends on the cultivar (MIKKONEN et al. 2001) and fruit ripeness (WANG, JIAO 2001). In the authors' research, fruits from cv. Sunrise were richer in polyphenolic compounds (on average $314 \text{ mg } 100 \text{ mL}^{-1}$) than from cv. Brigitta ($241 \text{ mg } 100 \text{ mL}^{-1}$) – Table 4. Those levels were similar to those reported by MOYER et al. (2002): 274 mg , and PRIOR et al. (1998): 305 mg , but lower than in fruits tested by OCHMIAN et al. (2009b, c): 375 mg , and BUNEA et al. (2011): $424 \text{ mg } 100 \text{ g}^{-1}$.

It was found that the fertilisers did not have the same influence on this feature. The lowest polyphenolic content was found in cv. Brigitta fruits, control and sprayed with Folanx fertiliser, and in berries from the cultivar Sunrise collected from objects sprayed with calcium chloride. Fruits of both cultivars sprayed with Lebosol and Calcinit were characterised by the highest content of these compounds. A similar influence of these fertilisers was confirmed by an analysis of concentrations (Figure 3). In highbush blueberry fruits, anthocyanins made up approx. 80% of all determined phenolic compounds. Among anthocyanins, the amount of delphinidin-3-galactoside was the highest, especially in fruits sprayed with Lebosol and Calcinit fertilisers (Table 5). In total, delphinidins made up approx. 50% of all determined anthocyanins. In research by LOHACHOOMPOL et al. (2008), this group of compounds constituted 34-36% of all anthocyanins. In fruits collected from these bushes, a large amount of chlorogenic acid, which is a strong natural antioxidant, was also determined. The largest amounts of flavonoids, on the other hand, were found in cv. Brigitta fruits sprayed with calcium chloride and in cv. Sunrise' fruits sprayed with Lebosol.



The vertical line indicate the cut-off used to form the groups

Fig. 3. Dendrogram of cluster analysis for fertilizers based on average for phenolic compositions

Table 4
The influence of calcium-based fertilisers on the polyphenol content in highbush blueberry fruits(mg 100 g⁻¹ f.w.)

Fertilizer (AxB)	Cultivar (A)	Que-3-gal	Que-3-glu	Que-3-ram	Kem-3-rut	Total flavonols	Neochlorogenic acid	Total anthocyanins (Table 5)	SUME
Folanx® Ca29	Brigitta	9.0	3.32	0.87	0.45	13.7	26.8	171	212
Calcium chloride		16.4	1.47	1.62	0.89	20.4	38.1	183	242
Lebosal Calcium Forte		10.2	3.54	1.94	1.32	17.0	33.8	211	262
Calcinit		9.3	1.87	0.99	1.11	13.2	43.5	206	263
Control		10.8	1.73	1.35	0.57	14.5	29.5	184	228
Mean		11.1	2.39	1.35	0.87	15.7	34.3	191	241
Folanx® Ca29	Sunrise	10.7	3.85	1.51	2.05	18.1	40.4	238	297
Calcium chloride		12.0	1.92	2.35	1.53	17.8	32.8	205	256
Lebosal Calcium Forte		19.2	5.00	2.11	2.44	28.7	54.6	255	338
Calcinit		12.9	2.60	3.48	1.69	20.6	60.1	282	363
Control		17.7	3.14	1.86	0.97	23.7	46.7	247	317
Mean		14.5	3.30	2.26	1.74	21.8	46.9	245	314
Folanx® Ca29	The mean for fertilizer (B)	9.9	3.59	1.19	1.25	15.9	33.6	204	254
Calcium chloride		14.2	1.70	1.99	1.21	19.1	35.4	194	249
Lebosal Calcium Forte		14.7	4.27	2.03	1.88	22.9	44.2	233	300
Calcinit		11.1	2.24	2.24	1.40	16.9	51.8	244	313
Control		14.2	2.44	1.61	0.77	19.1	38.1	215	273

LSD_{0.05} for: total flavonols A-2.6; B-3.1; AxB-3.6; neochlorogenic acid A-3.7; B-4.2; AxB-4.9; total anthocyanins A-16; B-19; AxB-26; SUME A-17; B-21; AxB-25

The results of the analyses confirmed the influence of the fertilisers used on the content of some macro- and micronutrients in fruits (Tables 2 and 6). Generally, fruits from the Brigitta cultivar contained more calcium ($0.15 \text{ g } 100 \text{ g}^{-1}$) than fruits from the Sunrise cultivar ($0.09 \text{ g } 100 \text{ g}^{-1}$). All the tested foliar fertilisers increased its concentration in fruits from both cultivars (Table 2). The fruits of cv. Brigitta sprayed with Lebosol had the highest calcium content ($0.18 \text{ g } 100 \text{ g}^{-1}$). In other experiments, the use of foliar fertilisation with calcium also increased the level of this component in fruits (STÜCKRATH *et al.* 2008, ANGELETTI *et al.* 2010). The content of this component obtained in this study was at a comparable level to that found by EICHHOLZ *et al.* (2011), while being much higher than reported by HANSON (1995), who determined it as $0.04 \text{ g } 100 \text{ g}^{-1}$.

A considerable increase in nitrogen levels was observed in fruits from both tested cultivars collected from bushes sprayed with Calcinit fertiliser. The composition of the fertiliser had undoubtedly some influence, as it contains nitrogen. It is also reflected by elevated nitrate levels (Table 3). However, no influence of the fertilisers on the phosphorus content in fruits was observed. Phosphorus levels ranged from 0.07 to $0.14 \text{ g } 100 \text{ g}^{-1}$. In contrast, the use of Lebosol and Calcinit fertilisers resulted in increased levels of potassium in fruits (0.69 and $0.64 \text{ g } 100 \text{ g}^{-1}$). The content of this ingredient in fruits sprayed with calcium chloride or Folanx fertiliser was at a similar level as in the control (from 0.49 to $0.54 \text{ g } 100 \text{ g}^{-1}$). An increased level of magnesium was observed only in fruits which were sprayed with Folanx fertiliser ($0.07 \text{ g } 100 \text{ g}^{-1}$), and it was at a similar level in the other fruits (0.04 - $0.05 \text{ g } 100 \text{ g}^{-1}$). The macronutrient content, except for nitrogen, in the analyzed fruits was at a similar level as in fruits from the cultivars Sierra and Patriot examined by OCHMIAN *et al.* (2009*a,b*, 2010).

Fruits from the Sunrise cultivar contained more copper, zinc and manganese than fruits from the Brigitta cultivar (Table 6). It was found that the influence of the fertilisers used on the micronutrient content varied. The largest amount of copper was found in fruits collected from bushes sprayed with calcium chloride, while the zinc content was the highest when Lebosol was used. Calcinit and Folanx, on the other hand, increased the manganese levels; additionally, fruits treated with Calcinit were characterised by the highest iron content. SKUPIEŃ (2004) found a considerably lower content of copper and zinc in highbush blueberry fruits (1.08 - 1.30 and 0.17 - $0.30 \text{ mg } 100 \text{ g}^{-1}$).

CONCLUSIONS

The application of foliar calcium fertilisers affected the quality of highbush blueberry fruits; however, the results depended on the fertiliser used. The main purpose of calcium supplementation is to fortify the mechanical resistance of fruits. Not all fertilisers contributed to the achievement of this effect, despite

Table 5

The influence of calcium-based fertilisers on the anthocyanin content in highbush blueberry fruits(mg 100 g^{f.w.})

Fertilizer (AxB)	Cultivar (A)	Del-3-ara	Del-3-gal	Del-3-glu	Cy-3-ara	Cy-3-gal	Cy-3-glu	Pet-3-ara	Pet-3-gal	Pet-3-glu	Peo-3-ara	Peo-3-gal	Peo-3-glu	Mal-3-ara	Mal-3-gal	Mal-3-glu
Folanx® Ca29	Brigitta	20.9	50.9	4.27	2.89	9.32	4.99	7.60	10.59	3.47	0.97	26.6	17.8	6.74	2.01	1.54
Calcium chloride		31.8	56.6	2.46	3.78	5.06	8.33	5.27	11.66	5.70	1.40	20.1	16.7	10.92	0.89	2.06
Lebosol Calcium		24.4	62.8	1.61	2.86	11.21	11.57	4.22	16.61	6.80	0.53	35.9	19.0	12.41	1.01	0.31
Calcinit		44.0	60.9	4.55	5.69	14.74	7.26	11.60	8.05	5.26	0.86	15.6	12.3	12.14	2.86	0.58
Control		23.2	56.0	4.48	3.18	10.16	5.48	7.29	9.53	3.89	1.07	29.2	19.6	7.42	2.21	1.69
Mean		28.9	57.5	3.47	3.68	10.10	7.53	7.20	11.29	5.03	0.97	25.5	17.1	9.93	1.79	1.24
Folanx® Ca29	Sunrise	55.4	64.9	3.73	4.20	7.62	9.26	5.85	12.96	6.33	1.56	26.3	18.6	12.14	8.59	0.32
Calcium chloride		25.8	62.2	4.98	3.53	11.29	6.09	8.10	10.59	4.32	1.19	32.5	21.8	8.24	2.45	1.88
Lebosol Calcium		46.8	81.0	3.81	4.79	16.16	7.72	13.89	12.74	10.44	0.36	19.4	15.5	15.33	6.20	0.73
Calcinit		52.0	89.1	5.50	5.27	17.61	8.49	17.09	11.47	11.69	0.40	20.3	17.1	16.86	7.82	0.80
Control		62.9	67.2	1.65	3.82	15.58	8.42	6.10	14.40	5.66	1.42	23.9	16.9	11.03	7.81	0.29
Mean		48.6	72.9	3.93	4.32	13.65	8.00	10.21	12.43	7.69	0.98	24.5	18.0	12.72	6.57	0.80
Folanx® Ca29	The mean for fertilizer (B)	38.2	57.9	4.00	3.54	8.47	7.12	6.72	11.78	4.90	1.26	26.5	18.2	9.44	5.30	0.93
Calcium chloride		28.8	59.4	3.72	3.65	8.18	7.21	6.69	11.13	5.01	1.29	26.3	19.3	9.58	1.67	1.97
Lebosol Calcium		35.6	71.9	2.71	3.83	13.68	9.65	9.06	14.68	8.62	0.45	27.6	17.3	13.87	3.60	0.52
Calcinit		48.0	75.0	5.03	5.48	16.18	7.88	14.35	9.76	8.48	0.63	17.9	14.7	14.50	5.34	0.69
Control		43.1	61.6	3.06	3.50	12.87	6.95	6.69	11.97	4.77	1.24	26.6	18.3	9.22	5.01	0.99

Table 6
The influence of calcium-based fertilisers on the micronutrient content in highbush blueberry fruits (mg 100 g⁻¹)

Fertilizer (AxB)	Cultivar (A)	Content in fruits (mg 100 g ⁻¹ f.w.)				
		Cu	Zn	Mn	Fe	
Folanx® Ca29	Brigitta	1.54	4.55	18.79	40.33	
Calcium chloride		2.35	5.33	9.43	31.48	
Lebosol Calcium Forte		1.36	8.47	23.62	21.94	
Calcinit		1.52	5.02	11.55	53.07	
Control		1.82	3.74	7.37	25.61	
Mean		1.72	5.42	14.15	34.48	
Folanx® Ca29	Sunrise	2.10	7.56	41.52	23.27	
Calcium chloride		3.21	8.86	20.79	27.83	
Lebosol Calcium Forte		1.86	14.08	25.50	43.86	
Calcinit		2.08	8.34	52.18	56.45	
Control		2.26	5.65	14.83	24.70	
Mean		2.30	8.90	30.97	35.22	
Folanx® Ca29	The mean for fertilizer (B)	1.82	6.06	30.15	31.81	
Calcium chloride		2.78	7.10	15.13	29.65	
Lebosol Calcium Forte		1.61	11.28	24.57	32.90	
Calcinit		1.80	6.68	31.86	54.73	
Control		2.04	4.70	11.09	25.15	
LSD _{α,0.05}		A-0.19; B-0.22; AxB-0.31	A-2.17; B-2.34; AxB-3.46	A-13.2; B-16.5; AxB-19.0	A-9.4; B-13.1; AxB-17.7	

increasing the calcium content in fruits, especially ones sprayed with Lebosol fertiliser. Bushes sprayed with Lebosol and Calcinit fertilisers were characterised by the largest fruits; however, these fertilisers did not improve fruit firmness as compared to the control. They were, however, characterised by the highest content of valuable polyphenols. Fruits collected from bushes sprayed with Folanx fertilisers and calcium chloride were the firmest and the most resistant to mechanical damage. The latter fertiliser, however, had the least advantageous effect on the fruit size. All calcium-based fertilisers reduced the acidity of fruits and nearly all, except for calcium chloride, contributed to the accumulation of larger amounts of harmful nitrates.

REFERENCES

- ANGELETTI P., CASTAGNASSO H., MICELI E., TERMINIELLO L., CONCILLON A., CHAVES A., VINCENTE A.R. 2010. *Effect of preharvest calcium applications on postharvest quality, softening and cell wall degradation of two blueberry (Vaccinium corymbosum) varieties*. Post. Biol. Tech., 58: 98-103.
- BUNEA A., RUGINĂ D., PINTEA A., SCONTA Z., BUNEA C., SOCACIU C. 2011. *Comparative polyphenolic content and antioxidant activities of some wild and cultivated blueberries from Romania*. Not. Bot. Hort. Agrobot., 39(2): 70-76.
- CARL C.E., SAMS W.S. 1993. *Firmness and decay of apples following postharvest pressure infiltration of calcium and heat treatment*. J. Am. Soc. Hort. Sci., 118(5): 623-627.
- CLARKSON D.T. 2003. *Roots and the delivery of solutes to the xylem*. Philos. Trans. R. Soc. London, Ser B., 341: 5-17.
- DE GARA L., DE PLNTO., M.C., TOMMASI F. 2003. *The antioxidant systems vis-à-vis reactive species during plantpathogen interaction*. Plant Physiol. Biochem., 41: 863-870.
- DUAN J., RUYI W., STRIK B., YANYUN Z. 2011. *Effect of edible coatings on the quality of fresh blueberries (Duke and Elliott) under commercial storage conditions*. Postharv. Biol. Technol., 59(1):71-79.
- EICHHOLZ I., HUYSKENS-KEIL S., KROH L.W., ROHN S. 2011. *Phenolic compounds, pectin and antioxidant activity in blueberries (Vaccinium corymbosum L.) influenced by boron and mulch cover*. J. Appl. Bot. Food Qual., 84: 26-32.
- FALLAHI E., CONWAY W.S., HICKEY K.D., SAMS C.E. 1997. *The role of calcium and nitrogen in postharvest quality and disease resistance of apples*. Hort. Sci., 32: 831-835.
- HANSON E., BEGGS J., BEAUDRY R. 1993. *Applying calcium chloride postharvest to improve highbush blueberry firmness*. Hort. Sci., 28(10): 1033-1034.
- HANSON E. 1995. *Preharvest calcium sprays do not improve highbush blueberry (Vaccinium corymbosum L.) quality*. Hort. Sci., 30(5): 977-978.
- HAYNES R.J. 1986. *Laboratory study of soil acidification and leaching of nutrients from a soil amended with various surface-incorporated acidifying agents*. Nutrient Cycling Agroecosyst., 2: 165-174.
- HODGES D.M., LESTER G.E., MUNRO K.D., TOIVONEN P.M.A. 2004. *Oxidative stress: importance for postharvest quality*. Hort. Sci., 39: 924-929.
- IUNG. 1972. *Laboratory analytical methods in agricultural chemistry stations*. Part II. *Analyses of plant material*. IUNG Puławy: 25-83.
- LOHACHOOMPOL V., MULHOLLAND M., SRZEDNICKI G., CRASKE J. 2008. *Determination of anthocyanins in various cultivars of highbush and rabbiteye blueberries*. Food Chem., 111(1): 249-254.

- MIKKONEN T.P., MAATTA K.R., HUKKANEN A.T., KOKKO H.I., TORRONEN A.R., KARENLAMPI S.O., KARJALAINEN R.O. 2001. *Flavonol content varies among black currant cultivars*. J. Agric. Food. Chem., 49(7): 3274-3277.
- MOYER R.A., HUMMER K.E., FINN C.E., FREI B., WROLSTAD R.E. 2002. *Anthocyanins, phenolic, and antioxidant capacity in diverse small fruits: Vaccinium, Rubus, and Ribes*. J. Agric. Food Chem., 50: 519-525.
- OCHMIAN I., GRAJKOWSKI J., MIKICIUK G., OSTROWSKA K., CHELPIŃSKI P. 2009a. *Mineral composition of high blueberry leaves and fruits depending on substrate type used for cultivation*. J. Elem., 14(3): 509-516.
- OCHMIAN I., GRAJKOWSKI J., OSTROWSKA K., MIKICIUK G. 2007. *Growth, yielding and fruit firmness of two highbush blueberry cultivars cultivated on three different organic substrates*. Zesz. Nauk. Inst. Sadow. Kwiac., 15: 47-54. (in Polish).
- OCHMIAN I., GRAJKOWSKI J., SKUPIEŃ K. 2009b. *Influence of substrate on yield and chemical composition of highbush blueberry fruit cv. 'Sierra'*. J. Fruit Ornament. Plant. Res., 17(1): 89-100.
- OCHMIAN I., GRAJKOWSKI J., SKUPIEŃ K. 2010. *Effect of substrate type on the field performance and chemical composition of highbush blueberry cv. Patriot*. Agric. Food Sci., 19(1): 69-80.
- OCHMIAN I., GRAJKOWSKI J., SMOLIK M. 2012. *Comparison of some morphological features, quality and chemical content of four cultivars of chokeberry fruits (Aronia melanocarpa)*. Not. Bot. Hort. Agrobot., 40(1): 253-260.
- OCHMIAN I., OSZMIAŃSKI J., SKUPIEŃ K. 2009c. *Chemical composition, phenolics, and firmness of small black fruits*. J. Appl. Bot. Food Qual., 83: 64-69.
- OSZMIAŃSKI J., WOJDYŁO A. 2005. *Aronia melanocarpa phenolics and their antioxidant activity*. Eur. Food Res. Tech., 221: 809-813.
- PETIT-JIMENEZ D., GONZALEZ-LEON A., GONZALEZ-AGUILAR G., SOTELO-MUNDO R., BAEZ-SANUDO R. 2009. *Permeability of cuticular membrane during the ontogeny of Mangifera indica L.* Acta Hort., 820: 213-220.
- PORMALE J., OSVALDE A., NOLLENDORFS V. 2009. *Comparison study of cultivated highbush and wild blueberry nutrient status in producing plantings and woodlands*. Latvian J. Agron., 12: 80-87.
- PRIOR R.L., CAO G., MARTIN A., SOFIC E., MCEWEN J., O'BRIEN C., LISCHNER N., EHLENFELDT M., KALT W., KREWER G., MAINLAND C.M. 1998. *Antioxidant capacity as influenced by total phenolic and anthocyanin content, maturity, and variety of Vaccinium species*. J. Agric. Food Chem., 46: 2686-2693.
- PN-90/A-75101/04. *Processed fruit and vegetable products. Preparation of samples and methods of physicochemical analyses. Determination of total acidity*.
- ROSEN C.J., BIERMAN P.M., TELIAS A., HOOVER E.E. 2006. *Foliar and fruit-applied strontium as a tracer for calcium transport in apple trees*. Hort. Sci., 41: 220-224.
- SAURE M.C. 2005. *Calcium translocation to fleshy fruit: its mechanism and endogenous control*. Sci. Hort., 105: 65-89.
- SCHLEGEL T.K., SCHÖNHERR J. 2002. *Stage of development affects penetration of calcium chloride into apple fruits*. J. Plant Nutr. Soil Sci., 165: 738-745.
- SCHÖNHERR J. 2001. *Cuticular penetration of calcium salts: effect of humidity, anions, and adjuvants*. J. Plant Nutr. Soil Sci., 164: 225-231.
- SHEAR. C. B. 1975. *Calcium-related disorders of fruits and vegetables*. Hort. Sci., 10: 361-365.
- SKUPIEŃ K. 2006. *Evaluation of chemical composition of fresh and frozen blueberry fruit (Vaccinium corymbosum L.)*. Acta Sci. Pol., Hort. Cult., 5(1): 19-25.
- SKUPIEŃ K. 2004. *The content of selected minerals in four cultivars highbush blueberry (Vaccinium corymbosum L.) fruit*. J. Elementol., 9(1): 43-49.
- STÜCKRATH R., QUEVEDO R., DE LA FUENTE L., HERNANDEZ A., SEPULVEDA V. 2008. *Effect of calcium*

-
- foliar application on the characteristics of blueberry fruit during storage.* J. Plant. Nutr., 31: 849-866.
- WANG S.Y., JIAO H.J. 2001. *Changes in oxygen-scavenging systems and membrane lipid peroxidation during maturation and ripening in blackberry.* J. Agric. Food Chem., 49(3): 1612-1619.
- WHITE P.J. 2001. *The pathways of calcium movement to the xylem.* J. Exp. Bot., 358: 891-899.
- WHITE P.J., BROADLEY M.R. 2003. *Calcium in plants.* Ann. Bot., 92: 487-511.
- WÓJCIK P. 2004. *Uptake of mineral nutrients from foliar fertilization.* J. Ornam. Plant Res., 12: 201-218.