

## ANTHOCYANIN CONTENT IN LATVIAN CRANBERRIES DRIED IN CONVECTIVE AND MICROWAVE VACUUM DRIERS

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### Abstract

The current research focuses on the study of anthocyanin content changes in Latvia wild growing as well as cultivated cranberries during convective and microwave vacuum drying. The research was accomplished on fresh Latvian wild and cultivated cranberries. The berries before drying in a convective drier were pre-treated using perforating, steam-blanching and halving; berries dried in microwave vacuum drier – using steam-blanching and halving; part of berries was dried in microwave vacuum drier without pre-treatment (whole berries). For air drying experiments, a convective dryer “Memmert” (Model 100-800) was used. For drying experiments in microwave vacuum a dryer „Musson-1” was used. Anthocyanin was determined by means of spectrophotometric method. Data are expressed as mean  $\pm$  standard deviation; variance analysis, homogeneity were used for the evaluation of changes of anthocyanin in cranberries during drying depending on pre-treatment methods. The initial content of anthocyanin among wild and cultivated fresh cranberries was differing: very similar anthocyanin content was detected in cranberry cultivars ‘Pilgrim’ and ‘Early Black’, it was on average three times higher comparing to wild fresh cranberries. However, the lowest anthocyanin content was detected in wild fresh cranberries –  $306.81 \pm 4.19 \text{ mg} \oplus 100\text{g}^{-1}$  (in dry matter). With the probability of 95%, detected by means of the analysis of variance, it may be presumed, that pre-treatment method of cranberries influenced anthocyanin changes during convective and microwave vacuum drying ( $p=0.001$ ,  $< =0.05$ ). Halving is advisable as a pre-treatment method for berries processing in a convective or microwave drier, because decrease in anthocyanin content is smaller.

**Key words:** anthocyanin, cranberries, pre-treatment, convective drying, microwave vacuum drying.

### Introduction

The cranberry, *Vaccinium macrocarpon* Ait., accumulates some of the highest concentrations of phenolic compounds, with demonstrable human health related benefits including antioxidant status, antiviral, and anticancer properties. Studies on cranberries have focused mainly on the anthocyanin fraction due to the high concentration found in berries and importance as a berries’ quality (Vedenskaya and Vorsa, 2004). Recent studies have shown anthocyanin, proanthocyanidins from cranberries are active components in molecular mechanism behind various health benefits of cranberries (Lacombe et al., 2010).

Anthocyanins (from Greek anthos, a flower; and kyanos, dark blue) are the largest and most important group of water-soluble and vacuolar pigments in nature. They comprise a major flavonoid group that is responsible for cyanic colours ranging from salmon pink through red and violet to dark blue of most flowers, fruits and leaves of angiosperms commonly found in nature (Andersen and Jordheim, 2006; Delgado-Vargas and Paredes-López, 2003). The most significant function of anthocyanin is their ability to impart colour to the plants or plant products in which they occur (Kong et al., 2003).

The red colour of cranberries is due to the presence of four major anthocyanin pigments: cyanidin-3-galactoside (Cy-3Ga), peonidin-3-galactoside (Pn-3-Ga), cyanidin-3-araboside (Cy-3-Ar), peonidin-3-araboside (Pn-3-Ar) and two minor anthocyanin: cyanidin-3-glucoside and peonidin-3-glucoside (Sapers and Hargrave, 1987).

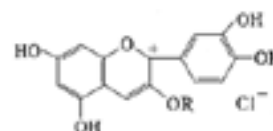


Figure 1. The structure of anthocyanin (Антоцианы, 2011).

The biosynthesis of anthocyanin has been characterized in great detail. The basic anthocyanin molecule is comprised of two aromatic rings and oxygen containing heterocyclic ring (Figure 1). One of the aromatic rings is derived from phenylalanine and the second ring from the action of chalcone synthase (CHS), condensing one molecule of p-coumaroyl-coA with three molecules of malonyl-coA to produce tetrahydroxy chalcone (Winkel-Shirley, 2001; Grotewold, 2006; Yu et al., 2006). CHS is the first committed enzyme in the anthocyanin biosynthetic pathway. The regulation of anthocyanin biosynthesis has also been studied thoroughly and comprises basic-helix-loop-helix (bHLH) transcription factors, interacting with R2R3 MYB (LhMYB6 and LhMYB12) transcription factors to activate either all or part of the anthocyanin genes (Allan et al., 2008).

According to Lee (2009), anthocyanin constitutes pigments with a wide range of biological activities including antioxidant (Tsuda et al., 2003), anti-inflammatory (Wang and Mazza, 2002; Youdim et al., 2002), anticancer (Hou, 2003), antimutagenic (Peterson and Dwyer, 1998) and

$\alpha$ -glucosidase inhibition (Matsui et al., 2001).

Drying is one of the oldest methods of food preservation, and it is a food processing operation mainly because undesirable changes in quality (Wang and Xi, 2005).

Many authors have studied the influence of temperature in the anthocyanin stability from different sources proving that heating has a detrimental effect on the anthocyanin content (Ikeda et al., 2009; Jimenez et al., 2010; Lin et al., 2009; Ochoa et al., 1999; Rodrigues et al., 2009; Sadilova et al., 2009). Anthocyanin is highly unstable and easily susceptible to degradation whose colour stability is strongly affected by pH, temperature, anthocyanin concentration, oxygen, light, enzymes, and other accompanying substances such as ascorbic acid, sugars, sulphites, co-pigments, metallic ions, among others (Wilska-Jeszka, 2007).

Different drying methods are used for drying fruits, berries and vegetables. Air-drying is the most common method in the drying of foodstuffs. However, this method leads to serious injuries such as worsening of the taste, colour and nutritional content of the product, decline in the density and water absorbance capacity and shifting of the solutes from the internal part of the drying material to the surface due to the long drying period and high temperature. Microwave drying has the specific advantage of rapid and uniform heating due to the penetration of microwaves into the body of the product. Microwave energy is capable of polarizing substances. The electrons in the polarized substance are in motion due to the conversion of electromagnetic energy embedded in the substance into kinetic energy. Electrons bump into each other during this electron movement and their energy is converted to heat energy as a result of friction. Thus, the moisture was removed from the product in the microwave drying (Alibas, 2007).

Compared with convective atmospheric drying, vacuum drying has some distinctive characteristics such as higher drying rate, lower drying temperature and oxygen deficient processing environment etc., these characteristics may help to improve the quality and nutritive value of the dried products. Presently, vacuum drying has been applied to dry various food materials, the vacuum drying kinetics of many fruits and vegetables has been investigated and the effect of vacuum drying conditions on the drying process and the qualities of dried products have been evaluated (Wu et al., 2007).

For the better water evaporation during drying process there are known many vegetable and fruit pre-treatment methods such as halving or slicing (Hui et al., 2006), blanching in hot water (Mayer-Miebach and Spieß, 2003), steam-blanching in order to inactivate enzymes activity (Llano, 2003) and perforation with needle (of 1 mm diameter) (Shi et al., 1997).

The current research focuses on the study of anthocyanin.

## Materials and Methods

The research was accomplished on fresh in Latvia wild growing (*Vaccinium oxycoccus* L.) and cultivated (*Vaccinium macrocarpon* Ait.) cranberries harvested in Kurzeme region in the first part of October, 2010 and immediately used in current drying experiment. Cranberry cultivars were: 'Early Black', 'Ben Lear', 'Stevens', 'Bergman' and 'Pilgrim'.

Three methods were used for pre-treatment of berries: perforation, halving and steam-blanching. The berries before drying in a convective drier were pre-treated using all three methods and berries dried in microwave vacuum drier – using two pre-treatment methods – steam-blanching and halving. Part of berries was dried in microwave vacuum drier without pre-treatment (whole berries).

Perforation of berries ( $3.000 \pm 0.001$  kg) was realised manually by a needle (1 mm diameter) about 20 pricks equally on all berry surface; halving ( $3.000 \pm 0.001$  kg) was realised manually by knife; steam-blanching ( $3.000 \pm 0.001$  kg) was realised using "TEFAL VC4003 VITAMIN+" (Tefal, China) vessel at temperature  $+94 \pm 1$  °C.

Drying conditions were selected in accordance to results of previous experiments for maximal biological compounds preservation in berries during processing in elevated temperatures (Dorofejeva et al., 2010).

For air drying experiments, a convective dryer "Memmert" Model 100-800 (Memmert GmbH Co. KG, Germany) was used; drying parameters were as follows: temperature  $50 \pm 1$  °C and air flow velocity  $1.2 \pm 0.1$  m  $\oplus$  s<sup>-1</sup>. Berries were placed on a perforated sieve (diameter – 0.185 m), with the diameter of the holes – 0.002 m.

For drying experiments in vacuum, a microwave dryer „Musson-1" (OOO Ingredient, Russia) was used (at 2450 MHz frequency and length of waves – 12.5 cm) (Vacuum microwave drier MUSSON-1, 2007). The power of installed magnetrons each of four is 640 W. The necessary amount of microwave energy (magnetron minutes) was calculated. The following drying conditions for processing of cranberries in microwave vacuum drier were selected: the first drying stage at 4 magnetrons – energy of 2100 kJ, the second stage at 3 magnetrons – energy of 2520 kJ, the third stage at 2 magnetrons – 1260 kJ and the fourth stage at 1 magnetron – 756 kJ. Temperature in microwave vacuum drier was  $36 \pm 2$  °C.

Anthocyanin were determined by means of "Spectrophotometer Anthocyanin Determination Method" (Bordignon-Luiz et al., 2007) using a device 6705 UV/VIS Spectrophotometer YENWAY.

Data are expressed as mean  $\pm$  standard deviation; variance analysis, homogeneity were used for the evaluation of changes of anthocyanin in cranberries during drying depending on pre-treatment methods. Each experiment was carried out in triplicate.

**Results and Discussion**

During the current research it was established that the initial content of anthocyanins in wild and cultivated fresh cranberries was different, which mainly depended on varieties' individuality and growing conditions.

Very similar anthocyanin content was detected in cranberry cultivars 'Pilgrim' and 'Early Black',  $898.66 \pm 12.69 \text{ mg } 100\text{g}^{-1}$  and  $839.59 \pm 8.53 \text{ mg } 100\text{g}^{-1}$  in dry matter respectively (Table 1); the anthocyanin content in analysed berries was on average three times higher compared to

wild fresh cranberries. However, the lowest anthocyanin content was detected in wild fresh cranberries –  $306.81 \pm 4.19 \text{ mg } 100\text{g}^{-1}$  (in dry matter) (Table 1).

Low anthocyanin content in wild cranberries could be explained mainly by growing conditions of berries, ie., in berries grown in greenwood bog in a sunny place without pronounced wind (air temperature was elevated); as a result, smaller amount of anthocyanin was formed. It is possible that fertilizer presence positively influenced anthocyanin formation in cultivated berries during growing process too.

Table 1

**Anthocyanin content in dry matter of fresh cranberries**

No.	Cranberry cultivar	Content of anthocyanin, $\text{mg } 100\text{g}^{-1}$
1	Wild	$306.81 \pm 4.19$
2	'Stevens'	$612.98 \pm 6.69$
3	'Bergman'	$674.34 \pm 6.79$
4	'Ben Lear'	$492.56 \pm 4.74$
5	'Pilgrim'	$898.66 \pm 12.69$
6	'Early Black'	$839.59 \pm 8.53$

For the shelf life extension, cranberries were dried using convective or microwave vacuum drying methods.

The temperature in convective dryer for maximum preservation of biologically active compounds was established of  $50 \pm 1 \text{ }^\circ\text{C}$  (Doymaz, 2008; Dorofejeva et al., 2010).

Anthocyanin are highly unstable molecules and easily susceptible to degradation through factors such as light, pH, temperature, sulphite, ascorbic acid, enzymes, among others (Wesche-Ebeling and Argaiiz-Jamet, 2002). In scientific literature it was found that the stability of anthocyanin and

all pigment content in foods decreased during processing and storage as temperature increases (Bobbio and Mercadante, 2008).

The mechanical and thermal pre-treatment of berries was used because the berries' waxy skin presents a high resistance to water vapour transfer. In the present research it was found out that there was no pronounced correlation between changes in content of anthocyanin, cranberry cultivar and pre-treatment method of cranberries, when microwave vacuum drying was applied (Figure 2).

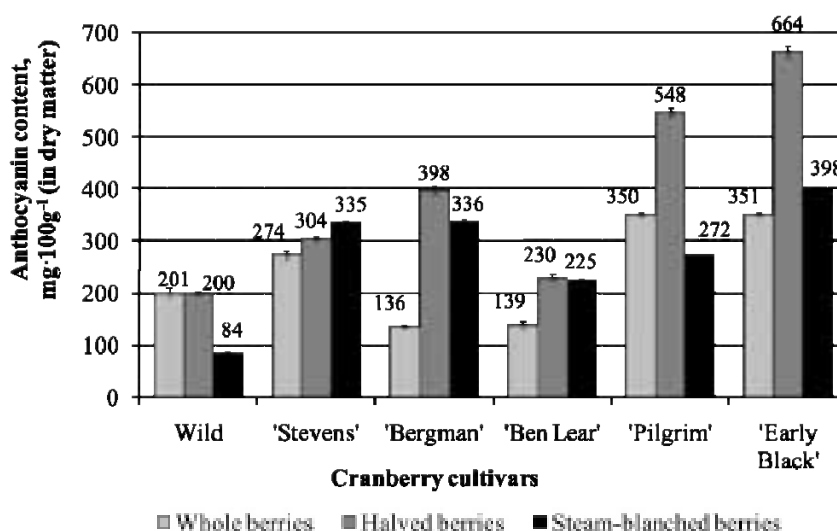


Figure 2. Anthocyanin content in microwave vacuum dried cranberries of different cultivars depending on the pre-treatment method.

The results of present experiments demonstrate that for maximum preservation of anthocyanin in berries during microwave vacuum drying pre-treatment of berries is necessary. Smaller loss of anthocyanin was found only if wild cranberries dried as whole berries: the anthocyanin content decreased 1.53 times (by 65%) comparing to anthocyanin content in fresh wild cranberries. The halving of berries prior to drying reduces the loss of anthocyanin in cranberry cultivars 'Bergman', 'Pilgrim' and 'Early Black' during microwave vacuum drying (Figure 2), i.e. anthocyanin content decreased by 1.69, 1.64 and 1.26 times (by 59%, 61% and 79%) respectively comparing to fresh berries (Table 1). The decrease of anthocyanin content in cranberry cultivars 'Stevens' and 'Ben Lear' pre-treated by

halving or by steam-blanching was very similar (Figure 2), therefore for drying process optimisation the halving is advisable as pre-treatment method for berries. It is necessary to observe minimal juice losses during berries halving, mainly because berries tightness. During short time steaming only micro crevices are formed on berries surface for better moisture migration in future drying process. With the probability of 95%, detected by means of the analysis of variance, it may be presumed that pre-treatment method of cranberries influenced anthocyanin decrease (the anthocyanin content decrease –  $\text{mg} \cdot 100\text{g}^{-1}$  was used as the dependent variable) in berries during microwave vacuum drying ( $p=0.00 < =0.05$ ).

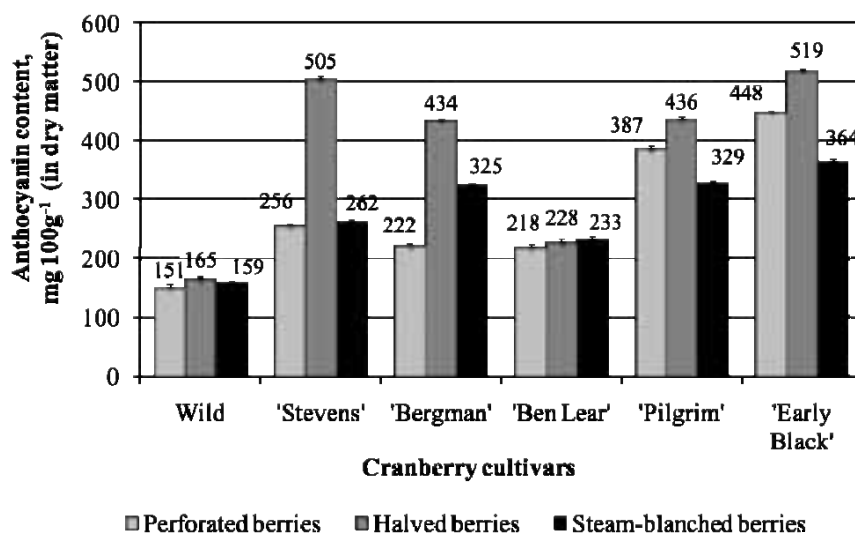


Figure 3. Influence of pre-treatment method on the anthocyanin content in several cultivars of convective dried cranberries.

In the present research it was found that there is no pronounced correlation between changes in content of anthocyanin, cranberry cultivars and pre-treatment method of cranberries, when drying in a convective drier was applied (Figure 3).

In present experiments it was established that pre-treatment does not significantly influence loss of anthocyanins in wild cranberries and cranberry cultivar 'Ben Lear' – the loss of anthocyanins was very similar, i.e., approximately 50% decrease compared to initial anthocyanin content in fresh cranberries was observed. Anthocyanin losses in berries pre-treated by perforating and steam-blanching were significant (Figure 3) for cranberry cultivars 'Stevens', 'Bergman', 'Pilgrim' and 'Early Black' compared to anthocyanin content in berries pre-treated by other methods. Therefore, the pre-treatment methods such as perforating and steam-blanching of berries are not recommendable for preservation of anthocyanin during convective drying of cranberries. Such pre-treatment processes are difficult and labour-consuming and the possible economical effect is not beneficial. Halving,

as a pre-treatment method for anthocyanin preservation in berries during convective drying is more recommendable for cranberry cultivars 'Stevens', 'Bergman', 'Pilgrim' and 'Early Black'; i.e. anthocyanin content in berries decreased during drying by 1.21, 1.55, 2.06 and 1.62 times (by 82%, 64%, 49% and 62%) respectively compared to the initial content of anthocyanin in fresh berries.

As in experiments of berries drying in microwave vacuum drier, with the probability of 95%, detected by means of the analysis of variance, it may be presumed, that pre-treatment method of cranberries influenced anthocyanin decrease (the anthocyanin content decrease –  $\text{mg} \cdot 100\text{g}^{-1}$  was used as the dependent variable) during berries convective drying ( $p=0.001 < =0.05$ ).

As a result, halving is advisable as a pre-treatment method for berries processing before both convective and microwave vacuum drying, because decreases in anthocyanin content (Figure 4) are smaller. It could be explained by anthocyanin location in the skin of berries, i.e., if berries are dried whole or perforated, the skin of berries reduce the water evaporation, therefore the temperature on

the skin increases. As a result, anthocyanin destroys. If berries are halved, the moisture evaporation from the inside of berries is easier; thus, the temperature on the surface of a berry does not increase and loss of anthocyanin is smaller.

After mathematical data processing, it was established that halving of cranberry cultivar 'Ben Lear' (Figure 4) influences the changes in anthocyanin content similar

in microwave vacuum or convective driers and there is not found any substantial difference ( $p=0.807, < =0.05$ ). However, there is found substantial difference ( $p=0.001, < =0.05$ ) in anthocyanin content loss in wild, 'Stevens', 'Bergman', 'Pilgrim' and 'Early Black' using different drying methods.

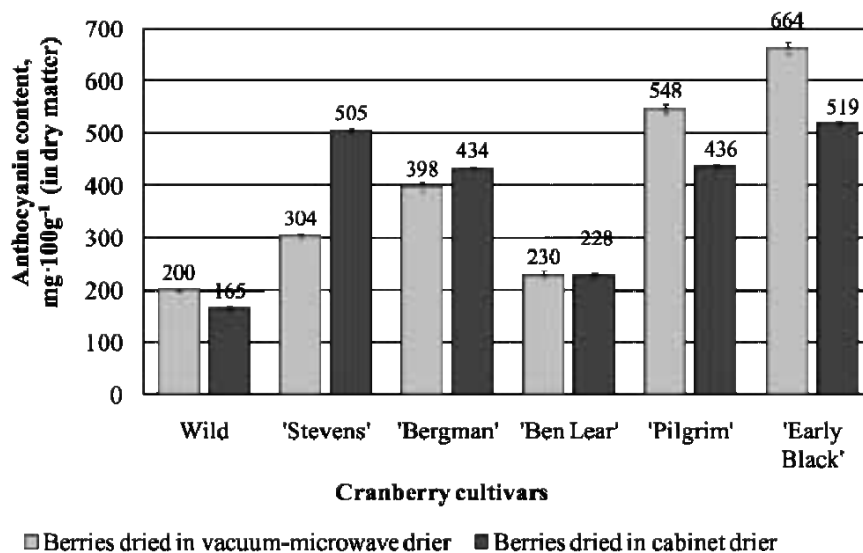


Figure 4. Anthocyanin content in halved convective and microwave vacuum dried cranberries.

During current experiments it was proved, that halving of wild, 'Ben Lear', Pilgrim' and 'Early Black' cranberry cultivars do not significantly influence the anthocyanin content loss during drying process in microwave vacuum dryer whereas halving of cranberry cultivars 'Stevens' and 'Bergman' does not significantly influence the anthocyanin content loss during drying in convective dryer that mainly depends on variety individuality and chemical composition of berries.

### Conclusions

The highest anthocyanin content was detected in fresh cranberry cultivars 'Pilgrim' and 'Early Black' ( $898.66 \pm 12.69$  and  $839.59 \pm 8.53$  mg 100 g<sup>-1</sup> in dry matter respectively); the lowest – in wild fresh cranberries ( $306.81 \pm 4.19$  mg 100 g<sup>-1</sup> in dry matter) Halving of berries reduces the loss of anthocyanin in cranberry cultivars 'Bergman', 'Pilgrim' and 'Early Black' during microwave vacuum drying – anthocyanin content decreased by 59%, 61% and 79% respectively compared to initial content in fresh cranberries. The loss of anthocyanin in cranberry cultivars 'Stevens' and 'Ben Lear' pre-treated by halving or by steam-blanching was very similar.

The perforating and steam-blanching pre-treatment methods do not preserve the anthocyanin in convective dried cranberries. Halving, as a pre-treatment method influence the anthocyanin preservation in convective dried cranberry cultivars 'Stevens', 'Bergman', 'Pilgrim' and 'Early Black' – anthocyanin content decreased by 82%,

64%, 49% and 62% respectively compared to the initial content of anthocyanin in fresh berries.

During current experiments it was proved that halving of wild, 'Ben Lear', Pilgrim' and 'Early Black' cranberry cultivars do not significantly influence the anthocyanin content loss during drying in microwave vacuum dryer whereas halving of cranberry cultivars 'Stevens' and 'Bergman' variety does not significantly influence the anthocyanin content loss during drying in convective dryer.

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