

## Simulation of the process kinetics and analysis of physicochemical properties in the freeze drying of kale

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Received February 28, 2017; accepted October 27, 2017

**Abstract.** Investigations were performed to study the freeze-drying process of kale (*Brassica oleracea* L. var *acephala*). The process of freeze-drying was performed at temperatures of 20, 40, and 60°C for whole pieces of leaves and for pulped leaves. The kinetics of the freeze-drying of both kale leaves and kale pulp were best described by the Page model. The increasing freeze-drying temperature from 20 to 60°C induced an approximately two-fold decrease in the drying time. Freeze-drying significantly increased the value of the lightness, delta Chroma, and browning index of kale, and had little influence on the hue angle. The highest increase in the lightness and delta Chroma was observed for whole leaves freeze-dried at 20°C. An increase in the drying temperature brought about a slight decrease in the lightness, delta Chroma and the total colour difference. Pulping decreased the lightness and hue angle, and increased browning index. Freeze-drying engendered a slight decrease in the total phenolics content and antioxidant activity, in comparison to fresh leaves. The temperature of the process and pulping had little influence on the total phenolics content and antioxidant activity of dried kale, but significantly decreased the contents of chlorophyll *a* and chlorophyll *b*.

**Keywords:** kale, freeze-drying, temperature, colour, antioxidant activity

### INTRODUCTION

Greater vegetable consumption is increasingly being recommended as part of a healthy lifestyle. Several studies have shown that a diet rich in fruits and vegetables decreases the risk of developing the inflammation and oxidative stresses that are indicative of many diseases (Murador *et al.*, 2016). In particular, epidemiological studies have shown an

inverse relationship between the consumption of *Brassica* vegetables and the development of cancer and cardiovascular diseases (Steindal *et al.*, 2014). Such anticancer attributes have been linked to the contained glucosinolates and their degradation products, in addition to other compounds (Traka and Mithen, 2008; Verkerk *et al.*, 2009).

Curly kale (*Brassica oleracea* L. var *Acephala*) is a biannual leafy vegetable, a member of the cabbage family, and widely grown in all the East African countries and in many other parts of the world, including Europe, Asia and Latin America (Mwithiga and Olwal, 2005). Kale plants are robust and can tolerate cold temperatures, even -18°C (Steindal *et al.*, 2014). Its foliage is rich in nutrients and bioactive compounds such as vitamins, minerals, glucosinolates and phenolic compounds (Ayaz *et al.*, 2006; Armesto *et al.*, 2015). However, the foliage has a high moisture content (approximately 86% w.b.) at harvest and, therefore, it cannot be preserved for more than a few days under ambient conditions of 20-25°C (Korus, 2011; Mwithiga and Olwal, 2005).

Leaf senescence involves the loss of chlorophyll and other constituents, membrane deterioration and nutrient recycling (Guiboileau *et al.*, 2010). These changes are largely temperature-controlled in the harvested products (Albornoz and Cantwell, 2016). Furthermore, the high presence of naturally occurring microorganisms on fresh vegetables may lead to the rejection of the product by consumers because of spoilage, even though these are

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usually nonpathogenic for humans. Moreover, the damage of the fresh vegetable surfaces during peeling, cutting, and shredding may worsen the contamination with spoilage microorganisms (Mansur and Oh, 2015). Consequently, it may reduce the microbial and sensory shelf life of the end-product (Ragaert *et al.*, 2007). Therefore, we need to develop an effective preservation method that can enhance the shelf life of fresh-cut kale during storage.

To overcome this limitation, drying processes can be used as methods to increase the shelf life of this easily perishable food product. Drying is a mass transfer process consisting of the removal of water by evaporation from the material so as to increase the shelf life of vegetables. This process is important and often used as a final production step before selling or packaging products (Huang *et al.*, 2015). Vegetables are important source of phytochemicals known to provide health benefits (Van Duyn and Pivonka, 2000), but these compounds generally undergo significant degradation during drying because of their sensitivity to heat, oxygen and light (Oliveira *et al.*, 2015).

Convective drying is one of the most important drying techniques used to dry vegetables. However, it often causes a high degradation of naturally heat-sensitive substances, such as antioxidants, vitamins, minerals, pigments, and other bioactive compounds (Araújo *et al.*, 2017). Oliveira *et al.* (2015) found that the antioxidant capacity losses from 52 to 70% with an increase in the air drying temperature increases from 35 to 85°C. They also found a degradation of chlorophyll a from 9 to 35%, and that of vitamin C, from 566.1 to 252.1 mg 100 g<sup>-1</sup> dry mass. Thus, increased attention should be given to the concerns regarding the quality degradation of kale during drying.

Freeze-drying, or 'lyophilization', has long been known as the best drying method for preserving the original properties of the raw material. This process is known to extend the shelf-life of foods by preventing microbial growth and retarding lipid oxidation (Nakagawa *et al.*, 2015). Freeze drying, in particular, preserves a higher level of bioactive compounds than does air-drying (Sogi *et al.*, 2013). Hence, this process is generally recommended for drying materials containing heat-sensitive components such as tocopherols, ascorbic acid, carotenoids, and plant phenolics (Shofian *et al.* 2011).

A few studies have been conducted regarding the freeze-drying of kale. Korus (2011) showed that freeze-dried kale leaves contained higher levels of antioxidants than did air-dried material: polyphenols, vitamin C, and antioxidant activity expressed as trolox equivalent were, respectively, 36, 15, and 33% higher. Moreover, Korus (2012, 2013) also pointed out that the levels of chlorophylls, carotenoids and individual amino acids content were higher in freeze-dried than in air-dried products, and from a practical point of view, she concluded that blanching was not a necessary procedure before drying kale leaves. Still, there is virtually no data in the literature on the freeze-drying kinetics

of whole and pulped kale leaves or the extent to which the temperature of this process impacts on the physicochemical properties of dried kale.

The aim of the present work was to study the influence of the freeze-drying temperature and the pulping on the drying characteristics and quality parameters of kale leaves.

## MATERIAL AND METHODS

The material investigated consisted of raw kale leaves (*Brassica oleracea* L. var *acephala*) cv. Lerchensungen. Fresh kale leaves (moisture content 866 g kg<sup>-1</sup> fresh weight) were harvested during the last five days of September from the University of Life Sciences in Lublin in 2015 and immediately used for the experiments. For the investigations, leaves without discoloration and damage were taken. The process of drying was preceded by a preliminary treatment of the leaves: removal of the main vein and washing. Two types of leaf samples were dried: whole pieces (WL) of leaves (about 5 cm long and 1 cm wide) and leaves after pulping (PL) into a homogeneous mass (30 s) by using a knife grinder (Braun, Model 2001, Germany) with a speed of 8.000 r.p.m.

Samples of the raw material were frozen at -35°C for 48 h by using a freezer (Panasonic, MDF-U5412-PE, Japan), and freeze-dried (a single layer of whole leaves and about 0.5 mm of pulping leaves). Frozen samples were immediately transferred to a freeze-drier. The same mass of sample (0.3 kg) was freeze-dried each time by using an ALPHA 1-4 laboratory freeze dryer consisting of drying chamber, a cold trap, a vacuum pump, and a measurement and control system. The freeze-drier was also equipped with a trap heating system linked to and co-operated with an LDC-1M driver (Martin Christ Company) and integrated with a weight system equipped with an electronic balance for measuring the mass changes of the samples during drying (Rudy *et al.*, 2015). The mass of the material was recorded continuously during the drying process (to an accuracy of ±0.1 g). The drying process was continued at 20, 40 and 60°C and with a constant pressure in the drying chamber of 52 Pa until the sample mass reached the equilibrium water content ( $u_r$ ) of approximately 40 g H<sub>2</sub>O/kg FW. The process at a decreased pressure in the freeze-drying chamber took approximately 120 s, and the cool traps were heated continuously to the set temperature level. The temperature of the traps was increased at the beginning of drying and reached an adequate level from 10 to 20 min.

Relying on the measurements of the mass loss taken during the experiment, drying curves were charted as functions of the moisture ratio ( $MR$ ) versus time, using the following equation:

$$MR = \frac{u - u_r}{u_0 - u_r}, \quad (1)$$

where:  $u$  denotes the water content in the course of drying ( $\text{kg H}_2\text{O kg}^{-1}$  DM) and  $u_0$  represents the initial water content ( $\text{kg H}_2\text{O kg}^{-1}$  DM). The seven semi-theoretical and empirical models were used to describe the drying kinetics of kale (Table 1).

The colour values ( $L^*$ ,  $a^*$  and  $b^*$ ) of fresh and dried kale were assessed using a Minolta CR-400 colorimeter (Konica-Minolta, Osaka, Japan), calibrated with a white standard tile. The analyses of the colour values were performed five times with each dried kale sample. From the data obtained, the values of delta Chroma ( $\Delta C$ ), hue angle ( $HU$ ), total colour difference ( $TDC$ ) and browning index ( $BI$ ) were calculated according to the following equations (Alibas, 2009):

$$\Delta C = \sqrt{(a^*)^2 + (b^*)^2}, \quad (2)$$

$$HU = \tan^{-1} \frac{b}{a}, \quad (3)$$

$$TDC = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2}, \quad (4)$$

where: the index '0' indicated the fresh unpulped leaves:

$$BI = \frac{100(x - 0.31)}{0.17}, \quad (5)$$

in which:

$$x = \frac{a^* + 1.75L^*}{5.645L^* + a^* - 3.012b^*}. \quad (6)$$

Quantitative chlorophyll determinations for fresh and dried kale samples were performed by reading absorbance at 665.2 ( $A_1$ ) and 652.4 ( $A_2$ ) nm in a spectrophotometer (Diode Array, Hewlett-Packard 8453, Waldbronn, Germany) according to the procedure described by Lichtenthaler (Oliveira *et al.*, 2015). The total chlorophyll was calculated as the sum of chlorophyll  $a$  ( $C_a$ ) and chlorophyll  $b$  ( $C_b$ ):

$$C_a = 16.72 A_1 - 9.16 A_2, \quad (7)$$

$$C_b = 34.09 A_2 - 15.28 A_1. \quad (8)$$

The chlorophyll contents were expressed in milligrammes per gramme of dry mass (DM).

For extract preparation, the ordered samples of kale (1 g DM) were extracted for 30 min with 20 ml of a methanol:water solution (1:1, v/v), pH = 1. The extracts were separated by decantation and the residues were extracted again with 20 ml of this solvent. Extracts were combined and stored in darkness at  $-20^\circ\text{C}$ . Total phenolics were estimated according to the Folin-Ciocalteu method (Singleton and Rossi, 1965). A 0.5 ml sample of the extract was mixed with 0.5 ml of  $\text{H}_2\text{O}$ , 2 ml of the Folin reagent (1:5  $\text{H}_2\text{O}$ ), and after 3 min, with 10 ml of 10 g  $100 \text{ ml}^{-1}$   $\text{Na}_2\text{CO}_3$ . After 30 min, the absorbance of the mixed samples was measured at a wavelength of 720 nm. The amount of total phenolics (corrected for the added ascorbic acid content) was expressed as a gallic acid equivalent (GAE) per g of dry mass.

The antioxidant activity (AA) was performed using an improved ABTS (2,20-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid)) decolorization assay (Re *et al.*, 1999). The ability of the extracts to quench the ABTS free radicals was determined using the following equation:

$$AA = \frac{A_C - A_A}{A_C} 100\%, \quad (9)$$

where:  $A_C$  denotes the absorbance of the control and  $A_A$  represents the absorbance of the sample.

The antiradical activity was expressed as  $\text{EC}_{50}$  – the extract concentration provided. Accordingly, there was 50% activity based on the dose-dependent mode of action.

**Table 1.** Equations applied to drying curves

Number	Name	Model	References
		Equation	
1	Newton	$MR = \exp(-k \tau)$	Demir <i>et al.</i> (2004)
2	Page	$MR = \exp(-k \tau^n)$	Sarimeseli (2011)
3	Henderson and Pabis	$MR = a \exp(-k \tau)$	Henderson and Pabis (1961)
4	Logarithmic	$MR = a \exp(-k \tau) + b$	Sarimeseli (2011)
5	Wang and Singh	$MR = 1 + a \tau + b \tau^2$	Wang and Singh (1978)
6	Logistic	$MR = b ((1 + a \exp(-k \tau))^{-1})$	Soysal <i>et al.</i> (2006)
7	Two-factor	$MR = a \exp(-k \tau) + b \exp(-k_i \tau)$	Arslan and Özcan (2008)

$k$ ,  $k_i$  – drying coefficients ( $\text{min}^{-1}$ );  $a$ ,  $b$  – coefficients of the equations;  $n$  – exponent;  $\tau$  – time (min).

All tests were performed in triplicate. The measurement scores were expressed as means  $\pm$  standard deviation. The measurement scores were subjected to a two-factor analysis of variance (ANOVA). When significant differences in ANOVA were detected, the means were compared using the Tukey test. Statistical analysis was performed at a significance level of  $\alpha = 0.05$ , by using the Statistica software (StatSoft, version 6.0). A regression analysis was also performed. The coefficient of determination  $R^2$ , root mean square error ( $RMSE$ ), and the reduced  $\chi^2$  values were calculated as follows:

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (MR_{i,p} - MR_{i,e})^2}{N}}, \quad (10)$$

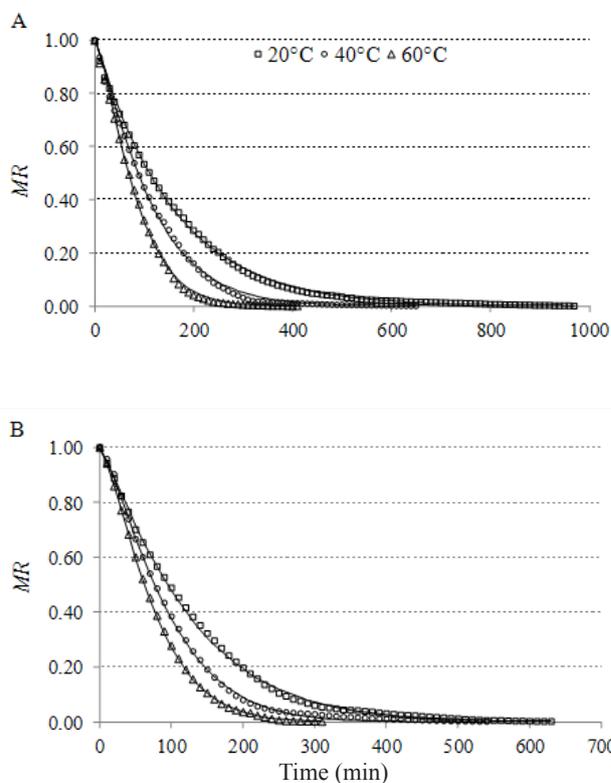
$$\chi^2 = \frac{\sum_{i=1}^N (MR_{i,p} - MR_{i,e})^2}{N - n}, \quad (11)$$

where:  $MR_{i,p}$  denotes the model-based value of the water ratio,  $MR_{i,e}$  represents the experimentally obtained value of the water ratio,  $N$  indicates the number of observations, and  $n$  stands for the number of constant parameters in the equation. Next, these parameters were served as a basis for the evaluation of suitability of the considered models. In general, the higher the  $R^2$  values and the lower the  $\chi^2$  and  $RMSE$  values indicate that the model is best fitted.

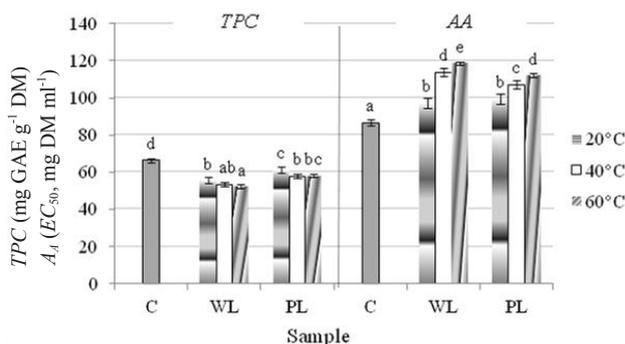
## RESULTS AND DISCUSSION

Drying curves as functions of the water content versus time are presented in Figs 1 and 2. Both the freeze-drying temperature and the pulping significantly increased the drying rate. The freeze-drying time for kale drying at 60°C was about three times and two times shorter for WL and PL lyophilized at 20°C, respectively. Pulping also decreased the drying time. However, the effect was of the most visibility for kale freeze-dried at the lowest temperature (20°C; decrease in the drying time of about 36%). Rudy *et al.* (2015) also pointed out that the pulping of cranberries before freeze-drying also reduced the drying time by approximately two-fold.

The results of the regression analyses for the seven considered models used to describe the freeze drying kinetics of the WL and PL are presented in Table 2. Note that, for six of the models, a good fit for the experimental data was observed. Only for the Wang and Singh model were relative lower values of  $R^2$  and  $RMSE$  obtained. All the calculated  $R^2$  values fell in the 0.836-0.999 range, whereas the  $RMSE$  changed from 0.0069 to 0.0980. Both for WL and PL, the highest values of  $R^2$  and the lowest values of  $RMSE$  were obtained when the Page model was used to describe the drying kinetics of kale. The drying curve presented in Figs 1 and 2 show a comparison of the experimental data and the predicted data based on the Page model. The calculated coefficients for the relevant equations are listed in Table 3. Similarly, Marques and Freire (2005) and Kirmaci *et al.*



**Fig. 1.** Drying curves of freeze-dried kale with experimental and predicted data based on the Page model; A – whole leaves, B – pulped leaves, and  $MR$  – moisture ratio.



**Fig. 2.** Total phenolics content ( $TPC$ ) and antioxidant activity ( $AA$ ) of kale before and after freeze-drying; C – fresh leaves, WL – whole dried leaves, and PL – pulped dried leaves; values designated by the different letters are statistically significantly different ( $\alpha = 0.05$ ).

(2008) found that the best equation to represent the drying kinetics for the freeze-drying of pineapple, guava, mango pulps and strawberries was that of the Page model.

During the thermal processing of plant materials, the structural characteristics of natural plant pigments are often modified and the colour of the products usually changes. Colour has to be considered as a special parameter that seems to be one of the first attributes of quality that a consumer perceives (Darvishi *et al.*, 2014). The average

**Table 2.** Statistical analysis of models describing the kinetics of freeze-drying of whole and pulped kale leaves

Model name	Drying temperature (°C)								
	20			40			60		
	R <sup>2</sup>	RMSE	χ <sup>2</sup>	R <sup>2</sup>	RMSE	χ <sup>2</sup>	R <sup>2</sup>	RMSE	χ <sup>2</sup>
Whole kale leaves									
Newton	0.999	0.0077	0.00006	0.992	0.024	0.0006	0.982	0.0394	0.0016
Page	0.999	0.0069	0.00005	0.998	0.011	0.0001	0.999	0.0094	0.00009
Henderson and Pabis	0.999	0.0077	0.00006	0.994	0.021	0.0005	0.987	0.0328	0.0011
Logarithmic	0.999	0.0074	0.00006	0.994	0.0189	0.0004	0.991	0.0268	0.0008
Wang and Singh	0.836	0.0980	0.00980	0.915	0.0772	0.0061	0.969	0.0514	0.0028
Logistic	0.999	0.0077	0.00006	0.994	0.021	0.0005	0.987	0.0328	0.0012
Two-factor	0.999	0.0077	0.00006	0.992	0.024	0.0006	0.982	0.0394	0.0016
Pulped kale leaves									
Newton	0.994	0.0216	0.0005	0.985	0.0342	0.0012	0.979	0.0447	0.0021
Page	0.994	0.0081	0.00007	0.999	0.007	0.00005	0.9999	0.0032	0.00001
Henderson and Pabis	0.994	0.0175	0.0003	0.992	0.0251	0.0007	0.987	0.0347	0.0013
Logarithmic	0.990	0.0109	0.0001	0.993	0.0233	0.0006	0.993	0.0249	0.0007
Wang and Singh	0.945	0.0637	0.0042	0.923	0.0771	0.0062	0.990	0.0306	0.0010
Logistic	0.996	0.0175	0.0003	0.992	0.0251	0.0007	0.987	0.0347	0.0013
Two-factor	0.993	0.0087	0.0002	0.992	0.024	0.0006	0.982	0.0394	0.0016

**Table 3.** Coefficient values in the models describing the freeze drying of whole (WL) and pulped (PL) kale leaves – Page model

Drying temperature (°C)	Sample	k (min <sup>-1</sup> )	n
20	WL	0.0055	1.0278
40		0.0036	1.1806
60		0.0025	1.3314
20	PL	0.0035	1.1586
40		0.0024	1.3076
60		0.0026	1.3509

values for the colour parameters of fresh kale leaves were as follows:  $L^* = 37.7$ ,  $DC = 17.1$ ,  $HU = 112.3$  and  $BI = 43.3$ . Pulping induced a significant decrease in lightness (up to 29.6), and slightly decreased the hue angle (up to 107.7), and increased  $BI$  up to 60.41. The freeze-drying of kale significantly increased lightness,  $\Delta C$  and  $BI$ , and had negligible impact on  $HU$ . The highest increase in  $L^*$  and

$\Delta C$  was observed for WL (average from 37.7 to 61.9, and from 17.1 to 39.58, respectively) freeze-dried at 20°C. An increase in the drying temperature brought about a slight decrease in  $L^*$ ,  $\Delta C$ , and  $TDC$ . This tendency was observed for both PL and WL (Table 4). Araújo *et al.* (2016) studied the colour changes of air dried kale and found that the  $L^*$  value slightly increased after convective drying (from 35.6 for fresh leaves to 41.3), but significantly decreased, even up to 20.8, when different methods of pretreatment, such as blanching, steaming or submerging in different solvents were used. In our study, during the freeze-drying of both WL and PL, an increase in  $L^*$  and  $BI$  was observed.  $BI$  ranged from 43.3 for fresh unpulped kale leaves, to 66.8 for PL freeze-dried at 20°C. The lowest changes in  $BI$  were found for WL samples freeze-dried at 60°C (average 51.9).  $BI$  corresponds to a quantification of the brown colour resulting from thermal processing, and increases of this parameter reflects the development of the brown colour in kale during the drying process, as a result of the pigments formed by the effect of the enzymatic and non-enzymatic reactions (Serratosa *et al.*, 2011). Araújo *et al.* (2016) found that  $BI$  increased from 200 to 300% after air drying. In our study, freeze-drying only increased of  $BI$  from 20 to 55%.

**Table 4.** Colour parameters of fresh and dried kale at different drying temperatures

Sample	Drying temperature (°C)	Colour parameter				
		<i>L*</i>	$\Delta C$	<i>HU</i>	<i>TDC</i>	<i>BI</i>
C	–	37.70±1.79b	17.11±2.12a	112.33±0.88c	–	43.30±0.51a
CPK	–	29.61±0.42a	18.30±0.34a	107.70±0.79a	5.97±0.21	60.41±0.92c
WL	20	62.37±0.35f	39.58±0.31f	112.41±0.35c	32.49±0.63	66.71±0.85f
PL	20	56.91±0.19de	37.77±0.41e	111.52±0.41c	27.28±0.54	66.83±0.68f
WL	40	61.52±0.52f	36.59±0.45d	112.39±0.30c	29.51±0.38	62.58±0.48d
PL	40	56.27±0.22d	35.92±0.26d	110.63±0.28b	25.82±0.25	63.66±0.87d
WL	60	57.09±0.51e	34.55±0.3c	109.85±0.34b	23.32±0.31	51.87±0.35b
PL	60	52.56±0.33c	31.56±0.41b	108.04±0.33a	21.90±0.23	64.10±0.60e

C – control sample (fresh leaves), CPK – fresh pulped kale, WL – whole dried leaves, PL – pulped dried leaves, *L\** – lightness,  $\Delta C$  – delta chroma, *HU* – hue angle, *TDC* – total colour difference, *BI* – browning index. The values designated by the different letters in the columns of the table are significantly different ( $\alpha = 0.05$ ).

**Table 5.** Chlorophyll *a* and chlorophyll *b* content (mg g<sup>-1</sup> DM) depending on temperature of the heating plates and the pretreatment of the raw material

Drying temperature (°C)	Chlorophyll <i>a</i>		Chlorophyll <i>b</i>	
	WL	PL	WL	PL
20	491.8±4.4a*A**	450.8±6.8B	271.2±5aC	251.4±6.3aD
40	442.0±3.0bA	375.6±5.4bB	236.8±6.7bC	225.6±3.8bD
60	314.2±4.5cA	299.6±6.5cB	203.6±5.1cC	186.4±6.3cD

DT – drying temperature, WL – whole leaves, PL – pulped leaves. The values designated by the different: small letters in the columns and capital letters in the lines; of the table are significantly different ( $\alpha = 0.05$ ).

This change could have come about by a limitation of the oxidative changes of the metabolites taking place because the oxygen concentration was very low during the freeze-drying process. Moreover, we observed that a higher drying temperature initiated lower changes in *BI*. These changes were particularly visible during the freeze-drying of WL. The lowest increase in *BI* was observed for WL freeze-dried at 60°C (average 51.9), whereas the highest values of this index were obtained when WL and PL were lyophilized at 20°C. These results reveal that at a higher temperature of lyophilization, the colour changes are limited.

Chlorophylls are pigments abundantly found in green vegetables and are strongly related to the colour characteristics. Hence, they are an important quality parameter, reflecting a certain aspect of the final dried product and thus playing a crucial role in the overall consumer acceptability (Korus, 2013). The average contents of chlorophyll *a* and chlorophyll *b* in fresh kale leaves were 510.2 and 282.4 mg 100 g<sup>-1</sup> DM, respectively. The effect of the freeze-drying temperature and the pulping on the chlorophyll content in kale is presented in Table 5. The freeze-drying engendered

a decrease in both chlorophyll *a* and chlorophyll *b*. This tendency was more noticeable with an increase in the drying temperature. Slightly higher degradation was observed for pulped leaves. These degradations are induced by the oxidation brought about by the contact of the pulped kale with air. An increase in the freeze-drying temperature decreased the contents of both forms of chlorophyll; the highest decrease was observed when the drying temperature was 60°C (an average of approximately about 40 and 31%, respectively). The lowest drying temperature (20°C) caused only a slight decrease in chlorophylls (an average of 8% for both forms of chlorophyll). In general, when a higher freeze-drying temperature was applied, a higher degradation of chlorophyll *a* was observed, in comparison to chlorophyll *b*. The chlorophyll *b* form was more resistant to heat treatment because of the lower susceptibility of this pigment to pheophytin formation (Araújo *et al.*, 2016; Cui *et al.*, 2004). Lefsrud *et al.* (2008) compared different methods and temperatures of kale drying and they found that the highest stability of carotenoids was obtained for freeze-dried kale and at a drying temperature of < 25°C.

Results of *TPC* and *AA* in fresh and dried kale are presented on Fig. 2. The highest value of *TPC* and *AA* (the lowest values of  $EC_{50}$ ) were obtained for kale leaves before drying (66.3 mg GAE/g DM and 86.7 mg DM ml<sup>-1</sup>, respectively). Freeze-drying caused a slight decrease in both *TPC* and *AA*. The process temperature had, however, little influence on *TPC* and *AA*. Slightly lower values of *TPC* and higher values of  $EC_{50}$  were obtained for kale dried at a higher temperature. Most importantly, the pulping of leaves before freeze-drying had no negative effects on both *TPC* and *AA*, and similar or even slightly higher values of these parameters were obtained for PL, as compared to WL. Korus (2011) compared the different drying methods of kale drying and found that the higher levels of *TPC* and *AA* were obtained for freeze-dried leaves than for the air-dried ones. Further, Oliveira *et al.* (2015) found that the convective drying of kale generated a slight decrease in *TPC* and a significant decrease in *AA* (approximately two-fold), particularly when the air temperature exceeded 50°C. In our study, we showed that the freeze-drying temperature (range 20-60°C) has little influence on both *TPC* and *AA*.

#### CONCLUSIONS

1. The freeze-drying kinetics of kale was the best described by the Page model. The model exhibited a very good fit to experimental data, mainly because of the high values of the coefficient of determination, and the lowest values of root mean square error, along with a decrease in the  $\chi^2$  test.

2. Increasing the freeze-drying temperature from 20 to 60°C decreased the drying time by approximately two-fold. The pulping of kale also decreased the drying time. However, the effect was most visible for material dried at temperature 20°C (a decrease in the drying time of approximately 36%).

3. The freeze-drying of kale significantly increased the lightness, delta Chroma and browning index, and had little influence on hue angle. The highest increase in the lightness and delta Chroma was observed for whole pieces freeze-dried at 20°C. Increasing the drying temperature slightly decreased the lightness, delta Chroma and total phenolics content. Furthermore, pulping significantly decreased lightness and browning index and slightly decreased hue angle.

4. Freeze-drying caused a slight decrease in both total phenolics content and antioxidant activity, in comparison to samples before drying. The process temperature and the pulping of kale before drying had little influence on total phenolics content and antioxidant activity. Lyophilization decreased both chlorophyll *a* and chlorophyll *b*. This tendency became noticeable with an increase in the drying temperature.

5. The best quality freeze-dried kale was obtained at temperature 20°C and for unpulped leaves.

**Conflict of interest:** The Authors do not declare conflict of interest.

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