

EFFECT OF STORAGE ON THE CONTENT OF SELECTED ANTIOXIDANTS AND QUALITY ATTRIBUTES IN CONVECTION AND FREEZE-DRIED PEARS (*PYRUS COMMUNIS* L.)

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ABSTRACT

Fresh, convection dried and freeze-dried pears were examined for selected quality parameters - vitamin C and E, total polyphenols, antioxidant activity, rehydration, and colour. Both products were analyzed immediately after drying and after long-term (12 months) storage at 2 ± 1 °C and 20 ± 2 °C. Retention in freeze-dried pears was superior to that in convection-dried products for vitamins and was similar for polyphenols and antioxidant activity. There were no significant differences in lightness between convection and freeze-dried products, either immediately after drying or throughout the storage period. 12-month storage led to a significant increase in the proportion of yellow color in both types of dried product compared to the raw material, and compared with the product after drying. The differences were significant in most cases except for the convection dried pear kept in cold store.

Keywords: fruit, drying, storing, antioxidants, rehydration, colour

1. INTRODUCTION

Fruits are recognized as a good or very good source of antioxidants in the human diet. These substances form a large group, which comprises polyphenols, vitamins, carotenoids and many others. Medical studies have shown a correlation between the consumption of antioxidants and decreased risk of cardiovascular disease and some cancer types (LILA, 2004; JOHN *et al.*, 1996; OLLSON *et al.*, 2004). In view of the seasonal availability most of the fresh fruits, there is a need to find relatively inexpensive methods of preservation that will give products with a similar nutritive value to that of the raw material.

Although dried fruits have long been a part of the human diet, there is little in the literature on the levels of antioxidant compounds they contain, not excluding even the popular fruit. One such species known is pear *Pyrus communis* (SANSAVINI, 2002). Pears are a good source of many valuable nutrients (CHEN *et al.*, 2007; KOMES *et al.*, 2013). It is a typical fruit of temperate zones. Due to its nutritive values and organoleptic properties, the pear is popular fruit among consumers. It is consumed as fresh fruit but also is popular as processed products, and it is used in juices, nectars, marmalades and purees, dried product, milk products (PARK *et al.*, 2003). Drying fruits allows their preservation by removing most of the free water content, and thus inhibiting microbial and fruit own enzymes activity. Dehydration also reduces the weight and volume of the raw material. This method gives the benefit due to the cost of packaging, transport and storage (BRENNAN and LANCASTER, 1994; GUINÉ and CASTRO, 2003).

Convection drying (using air circulation) is more widely used in industrial processing than freeze-drying due the high costs of the latter, both in terms of equipment and the process itself. Although convection drying is a cheaper process, the resulting product is less abundant in nutritive compounds and more difficult to rehydrate owing to the higher drying temperature and intensive aeration of the material among other factors (MICHALCZYK *et al.*, 2008). Apart from the drying method applied, the quality of the dried product may also be affected by the conditions and length of storage, two factors which have received little attention in the literature.

The aim of this paper was, therefore, to compare convection dried and freeze-dried pears in terms of the selected quality parameters, antioxidants, rehydration and colour, in each product and the extent to which quality is affected by the conditions and length of storage.

2. MATERIAL AND METHODS

2.1. Material

The experimental material consisted of whole and sound pears of the Conference cultivar, of uniform size gathered at consumption maturity. Fruits were obtained from the orchard experimental station of the University of Agriculture in Cracow (Garlica Murowana, Cracow district, 50°08'23.3N, 19°55'45.6E). Healthy and shaped fruit with a weight of 150.0-180.0 g were washed, peeled, removed the seeds, and sliced into eighths. Peeled and sliced pears were blanched in water containing 0.1 % sodium metabisulfite and 0.5% citric acid. Blanching time required to inactivate the peroxidase was 60 seconds at a temperature of 96-98 °C. After blanching the material is cooled by spraying cold water and allowed sieves for 30 minutes to drain any residual water and dried in a stream of air. Representative samples were then taken to determine the level of the selected indicators in the raw material. The remaining fruits were divided into two batches, one each for convection (CD) and freeze-drying (FD).

For convection drying, electric dryers designed for drying fruits, vegetables and mushrooms (Zorpot Zalmet, Poland) were used. The process was carried out at 60 °C for 10 hours to a moisture content of about 10%. For freeze-drying, pears were first frozen at -40 °C in a Feutron 3626-51 (ILKA Feutron, Germany) fast freezing chamber (KORUS, 2012). Next, sublimation was performed using a Gamma 1-16 LSC freeze dryer (Christ, Germany). The process was conducted under the following parameters: initial temperature of the frozen raw material: -30 °C; condenser temperature: -52 °C, shelf temperature: +20 °C; duration of secondary drying: 6 hours; shelf temperature: +30 °C. The overall time required to achieve a water content of less than 3% using this method was 20 hours.

Immediately after drying, the pears in each separate type of dried product (convection and freeze-dried) were thoroughly mixed, placed in airtight plastic containers, left for 7 days to allow for any equilibration of humidity, and mixed once more. Next, the containers were opened in conditions of low humidity (< 40%) in order to collect samples for analysis of indicators of chemical composition and to determine rehydration ability at the stage described in this work as "immediately after drying - 0 months storage". The remaining dried product was then packed in a twist off jars, divided into two groups and stored without exposure to light. One group was placed in chilled storage (2±1 °C) and the other stored at room temperature (20±2 °C).

2.1. Chemical analysis and colour evaluation

The content of vitamin C, E, total polyphenols and antioxidant activity were determined in the raw material, and in products immediately after drying and after 4, 8 and 12 months of storage. Additionally, rehydration ability and colour were determined immediately after drying and again after 12-month storage. Water content was established by the oven method (AOAC, 1984), vitamin C and E content using high-performance liquid chromatography (HPLC) (PN-EN, 2003; PN-EN, 2002). Total polyphenols were determined by the Folin-Ciocalteu spectrophotometric method (SINGLETON *et al.*, 1999) while total antioxidant activity was measured by means of the DPPH (2,2-diphenyl-1-picrylhydrazyl) (PEKKARINEN *et al.* 1999). Immediately after production and after 12-month storage, dried products were also examined for water absorption ability (PN, 1990) as well as for colour by an instrumental method with a Minolta CM-3500d spectroscope setting L*a*b* parameters. Analyses were made in four replications. The results were statistically evaluated using single-factor analysis of variance and LSD test (Statistica v. 12, StatSoft, Inc.). The standard deviation was calculated for the results obtained.

3. RESULTS AND DISCUSSIONS

Antioxidant levels in fresh fruits, including pears, have been discussed in the literature (PRIOR *et al.*, 1998; OMS-OLIU *et al.*, 2008; MARKOWSKI *et al.*, 2012). However, there are few works concerned exclusively with preserved products, including dried fruits (CHONG *et al.*, 2013; VEGA-GÁLVEZ *et al.*, 2012). Vitamin C, regarded as a fundamental antioxidant in fruits (SANTOS and SILVA, 2008), is susceptible to degradation by high pH, increased temperatures, exposure to light and the presence of oxygen, enzymes and such metals as iron and copper (MOSER and BENDICH, 1991). It has been observed that good L-ascorbic acid retention during technological treatment is accompanied by similar retention of other nutritive compounds (SANTOS and SILVA, 2008). The level of vitamin C may, therefore, be an indicator of the degradation of other biologically active substances.

Fresh pears contained 41.7 mg vitamin C/100 g dry matter (6.7 mg/100 g fresh matter) (Table 1). Similar values, less than 10 mg/100 g FM, gives SILVA *et al.* (2010) and TAVARINI *et al.* (2010), but OZTURKA *et al.* (2015) found in different cultivars of pears 9-30 mg/100 g FM.

Table 1. Effect of drying methods and storage temperature on the nutrient content in the dried pears.

Object		Vitamin C [mg/100 g dry matter]		Vitamin E [mg/100 g dry matter]		Total polyphenol [mg/100 g dry matter]		Antioxidant activity [µM Trolox /1g dry matter]	
Raw material		41.7±1.9		0.94±0.03		597±27		100±3	
Dried fruits, time and temperature of storage									
[months]	[°C]	CD	FD	CD	FD	CD	FD	CD	FD
0	-	12.9±0.7	18.5±0.9	0.50±0.03	0.79±0.05	528±20	555±21	71±3	91±4
4	2±1	11.6±0.5	17.6±0.8	0.31±0.02	0.51±0.01	505±18	527±22	61±3	61±4
	20±2	10.7±0.5	16.2±0.6	0.25±0.02	0.48±0.01	486±19	501±21	54±3	56±4
8	2±1	10.7±0.5	16.6±0.6	0.44±0.01	0.42±0.03	485±24	494±18	57±4	61±3
	20±2	9.9±0.5	14.5±0.7	0.20±0.03	0.34±0.01	472±21	453±22	50±3	49±2
12	2±1	10.3±0.4	15.6±0.4	0.22±0.01	0.36±0.02	463±16	473±17	54±3	56±3
	20±2	9.6±0.6	12.5±0.7	0.14±0.01	0.27±0.01	439±16	427±18	45±2	45±3
LSD (α = 0.05)		1.10		0.031		28.8		4.5	

CD - convection drying, FD - freeze-drying.

Drying caused significant vitamin C loss in both convection and freeze dried pears: 69% and 56% respectively. This confirms the earlier findings for strawberry and American cultivars of blackberry, in which freeze-drying resulted in better L-ascorbic acid retention than other drying methods. This being attributed to lack of oxygen and lower temperature of the process (ASAMI *et al.*, 2003). Reduction of vitamin C losses can be achieved by using neutral gas instead of air in the convection drying (RAMESH *et al.*, 1999). Vitamin C content fell steadily throughout the 12 month period of storage at both storage temperatures. Although at every stage of evaluation. The freeze-dried product contained significantly more vitamin C than convection dried. In addition, vitamin C levels were higher in products stored at the lower temperature. After 12 months of storage vitamin C retention, compared with the raw material, was 23-25% in the convection dried product and 30-37% in the freeze-dried product; and 74-79% and 68-84% respectively compared with the product immediately after drying (the two values refer to the higher and lower storage temperature respectively).

Vitamin E, which comprises a number of tocopherol- and tocotrienol-derived compounds, is subject to degradation from exposure to oxygen and UV radiation and the presence of iron (LIN *et al.*, 2006). Vitamin E content in fresh pears was 0.94 mg/100g dry matter (0.157 mg/100 g FM) (Table 1). According to LIN *et al.* (2006), the edible part of the pears had about 0.2 mg vitamin E per 100 g FM.

The drying process caused significant though but moderate losses in vitamin E content compared with the raw material: 47% in the convection dried product and 26% in the freeze-dried product. Examination of vitamin content in apricots after microwave and radiation drying showed that the shorter exposure to high temperature in microwave drying resulted in better vitamin E retention (KARATAS and KAMIŞLI, 2007). DAOOD *et al.* (1996) comparing natural drying of paprika under ambient conditions with forced-air

dehydration, showed that the former method led to higher losses of α -tocopherol. Vitamin E loss after 12 months' storage was significant; their levels in convection and freeze-dried products were 15-22% and 28-38% respectively of those found in the raw material and 28-44% and 34-46% of those in the product immediately after drying (the two values refer to higher and lower storage temperature respectively). Industrially dried peaches, pears, and plums contained respectively 75, 76, and 48% of the vitamin E levels in fresh fruits, although there is no information concerning the conditions and length of storage (CHUN *et al.*, 2007). In the convection dried and comminuted paprika observed falls in α -tocopherol content were 70%, 90% and 100% in products stored for 30, 60 and 90 days respectively (DAOOD *et al.*, 1996).

Polyphenols form one of the principal groups of plant secondary metabolites. Pear fruits are characterized by moderate polyphenol content (NACZK and SHAHIDI, 2006). In fresh pears total polyphenols amounted to 597 mg/100 g dry matter (96 mg/100 g FM). The content of this substances can vary over a wide range, for example, catechin can range from 40-544 mg/kg FM although considerably lower levels of 525 mg/100 g and 429 mg/100 g FM (OZTURKA *et al.*, 2015). Total phenols can vary from 30 mg in Italian Coscia cultivar (TAVARINI *et al.*, 2010) up to 232 mg/100 g FM in unidentified Thai cultivar of *Pyrus pyrifolia* (CHONG *et al.*, 2013).

Convection and freeze-drying caused moderate though still significant reductions in polyphenol content of 47 and 26% respectively compared with the raw material. CHONG *et al.* (2013) reported losses in dried pears of 13-66%, depends on the used drying methods. Further slight losses in total polyphenols were observed throughout the 12-month storage period, becoming significant after 8 months. The effect of both the drying method and lower temperature was not always proved statistically. After 12 months' storage polyphenol retention in convection and freeze-dried products was 74-78% and 72-79% respectively compared with the raw material, and 82-88% and 77-85% compared with the product immediately after drying (the two values refer to storage at 20 ± 2 °C and 2 ± 1 °C respectively).

The level of antioxidant activity depends on the fruit species, cultivation conditions, the length of storage and method of measurement (CONNOR *et al.*, 2002; KALT *et al.*, 1999). Antioxidant activity in fresh pears was 100 μ M Trolox eq/1 g dry matter (16.1 μ M Trolox eq/1 g FM). CHONG *et al.* (2013) using an identical method, reported a value of 16.6 μ M Trolox eq/g, while KEVERS *et al.* (2011) who applied the oxygen radical absorbance capacity (ORAC) method, recorded 27.5 μ M Trolox eq/g in an extract of Conference pear, and 14.6-42.5 μ M Trolox eq/g FM for five other cultivars. Convection drying and freeze-drying caused 29 and 9% reductions in antioxidant activity. Storage of products, however, led to larger losses, becoming significant after 4 and 12 months in air-dried product and after first 4 and 8 months in freeze-dried ones. Antioxidant activity was not significantly higher in freeze-dried than in convection-dried products at all stages of storage experiment. The lower storage temperature was found to have a beneficial effect. After 12 months of storage, antioxidant activity in convection and freeze-dried products was lower by 46-55 %, and by 44-55% compared to the raw material, and by 63-76% and by 49-62% compared to the product immediately after drying (the two values refer to storage at 20 ± 2 °C and 2 ± 1 °C respectively).

The content of vitamin C and polyphenols in fresh berry fruits was positively correlated with the level of antioxidant activity (CONNOR *et al.*, 2002; KALT *et al.*, 1999; KEVERS *et al.*, 2007). In comparison with other fruit species, extracts of pears had moderate amounts of polyphenols and lower amounts of vitamin C (GARCIA-ALONSO *et al.*, 2004). Hence, WANG *et al.* (1996) reported that vitamin C did not account for more than 15% of total antioxidant activity. Our results showed that for dried pear products stored for 12 months the correlation coefficients calculated between antioxidant activity and polyphenols, and

vitamin C were 0.89 and 0.80 respectively, regardless of the drying method or storage temperature.

The water content in the raw material affects the yield of the dried product, its quality and tendency to go mouldy. Fresh pears contained 83.97 g water per 100 g. Convection drying removed water to the level of 9.13 g/100 g immediately after production. In freeze-drying, the respective value was 2.89 g/100 g. Therefore, both products conformed to the methodical assumptions of this research with water contents after 12-month storage of 9.58-9.66 g in the convection dried product and 2.95-2.97 g/100 g in the freeze-dried product. Good rehydration properties are an essential characteristic of quality in dried products (RATTI, 2001). When apples, bananas, carrots, and potatoes were dried using five different methods, freeze-drying resulted in the highest porosity and natural drying in the lowest [KROKIDA and MAROULIS, 1997]. This statement agrees with our observations because the higher water absorption ability of FD pears could be explained, above all, by higher porosity. Immediately after drying, 100 g of convection dried pears absorbed 360 cm³ of water, while freeze-dried ones absorbed 19% more (Table 2).

This tendency remained unchanged after 12 months of storage. Although absorption power decreased by 12-14% and 9-11% in convection and freeze-dried products respectively (the two values refer to storage at 20±2 °C and 2±1 °C respectively).

Table 2. The ability of water absorption by dried pears immediately after drying and after 12 months of storage, ml/100 g dried fruits.

Dried material after storage time [months]	Storage temperature [°C]	Convention drying	Freeze-drying
0	-	360±12	428±10
12	2±1	318±13	398±8
	20±2	308±10	380±8
LSD ($\alpha = 0.05$)		12.3	

Colour is a crucial factor determining the sensory attractiveness of fruits. Changes in colour may indicate deterioration in the quality of a product due to processing and storage. Colour is determined by the presence of natural pigments and the degree of their decomposition as well as the interactions and degradation of other components in fruit, which occur, for example, during the process of enzymatic and non-enzymatic browning (CHONG *et al.*, 2013; PASŁAWSKA, 2005). In the present work, the colour of the raw material and dried products was determined according to the CIE (L*a*b*) system (Table 3). The drying process caused significant increase of lightness (the L* value increased by 15-17% in convection and freeze-dried pears). Only freeze-drying resulted in a significant change in a* value, i.e., the decrease in the red colour, as compared to the raw material. This occurrence can be explained by the use of blanching before drying. This operation in aqueous solution could cause rinsing of the ingredients responsible for a* parameter in fresh fruits, e.g., water-soluble polyphenols. Then, low FD drying temperatures and lack of oxidation enzymes in the blanched material caused that the darkening no took place. In turn, the CD pears were dehydrated at a temperature that could induce Maillard reactions (VEGA-GALVEZ *et al.*, 2012) and thus increase a*. The above explanation also seems to confirm minor changes in b*. Positive values of b* parameter (b* > 0) correspond to the yellow colour formed mainly by water-insoluble carotenoids (GUINÉ and BARROCA, 2012). However, it should be noted that the values of parameters a* and b* were small, with a* close to zero and parameter L* was over 80, which translated into the colour of

fresh and dried pears similar to white or cream-white. Conversely, the b^* value determined in the convection dried product was 14% higher than in the raw material, while in the freeze-dried product this difference was insignificant.

Table 3. Effect of drying method and storage temperature on changes of colour parameters $L^*a^*b^*$ in the dried pears.

Object		L^*		a^*		b^*	
Raw material		76.66±4.14		4.46±1.31		17.49±2.04	
Dried fruits, time and temperature of storage							
[months]	[°C]	CD	FD	CD	FD	CD	FD
0		88.01±4.50	89.92±4.72	3.46±0.19	-0.52±0.19	20.05±2.23	18.03±1.88
12	2 ± 1	85.97±4.09	80.98±3.98	-1.97±0.09	0.96±0.08	19.74±1.95	20.59±2.24
	20 ± 2	85.23±4.17	80.59±4.02	-1.38±0.07	0.96±0.09	21.55±2.37	20.31±2.21
LSD ($\alpha = 0.05$)		4.511		0.561		1.193	

CD - convection drying, FD - freeze-drying.

4. CONCLUSIONS

Retention rates in dried products stored for 12 months were similar for vitamin C and vitamin E, 23-37% and 15-38% respectively, and over 70% total polyphenols. Retention rates for antioxidant activity against the DPPH radical were between these values, 45-56%. Retention in freeze-dried products was superior to that in convection-dried products for both vitamins and was similar for total polyphenols and total antioxidant activity. In addition, retention rates were almost ever significantly higher at the lower storage temperature. Average losses of vitamin C and total polyphenols were higher during drying than over the 12-month storage period, while for vitamin E and antioxidant activity the losses were lower, slightly in the case of the former, and distinctly so for the latter.

There were no significant differences in L^* value between convection and freeze-dried products, either immediately after drying or throughout the storage period. 12-month storage led to a significant increase in the proportion of yellow colour in both types of dried product compared to the raw material; however, compared with the product immediately after drying, the differences found were significant in most cases except for the convection dried product kept in chilled storage.

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