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Food Chemistry 93 (2005) 395–401

Food Chemistry

www.elsevier.com/locate/foodchem

Nitrates, nitrites, and oxalates in products of spinach and New Zealand spinach

Effect of technological measures and storage time on the level of nitrates, nitrites, and oxalates in frozen and canned products of spinach and New Zealand spinach

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Received 26 May 2004; received in revised form 28 September 2004; accepted 28 September 2004

Abstract

The effects of blanching of raw materials before preservation, their freezing and sterilization and of the time of storage products on the contents of nitrates, nitrites and oxalates in spinach and New Zealand spinach were compared. In comparison with 2-min blanching, the cooking of the raw material for four minutes before preservation contributed to a distinctly greater decrease in the content of the analysed compounds. The pre-treatment raw materials contained less nitrates (by 4–14%), nitrites (by 0–16%), water-soluble oxalates (by 15–24%), and total oxalates (by 9–19%). With the two preservation methods, the level of nitrites increased by 8–78% after freezing and by 8–41% after sterilization. The production of canned vegetables additionally contributed to the reduction of oxalate content by 21–38% in water-soluble oxalates and by 5–26% in total oxalates. After a one-year storage, canned products contained smaller amounts of the determined compounds than frozen vegetables, except for total oxalates in New Zealand spinach. New Zealand spinach preserves contained less nitrites and oxalates and much more nitrates than the products of spinach.

Keywords: Spinach; New Zealand spinach; Nitrate; Nitrite; Oxalate; Frozen product; Canned product

1. Introduction

With respect to their utility, spinach and New Zealand spinach are classed as leafy vegetables but botanically they belong to different families, namely *Chenopodiaceae* and *Aizoaceae*, respectively. The two vegetables are characterized by high nutritive values. Works concerning common spinach are particularly numerous. This vegetable contains considerable amounts of vitamins, especially C, E, β-carotene, and folic acid and also mineral components and dietary fibre (Gupta & Wagle, 1988; Jaworska & Słupski, 2001; Watanabe, Uchiyama, & Yoshida, 1994). Among all vegetables it is also characterized by the highest antioxidative capacity. Unfortunately, as in other leafy vegetables, spinach and New Zealand spinach show a tendency to accumulate compounds unwanted in the human diet, above all of nitrates, nitrites, and oxalates (Jaworska, 2005; Takebe, Ishihara, Matsuno, Fujimoto, & Yoneyama, 1995).

Technological measures in vegetable processing, such as washing, blanching, shredding, freezing, or canning, can contribute to changes in the nutritional value, including the level of unwanted compounds (Bednar,

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doi:10.1016/j.foodchem.2004.09.035

Kies, & Carlson, 1991; Ezeagu & Fafunso, 1995). Processing with the use of water (washing, blanching) usually reduces the content of nitrates, nitrites and oxalates. However, the effect of preservation by freezing or sterilization, and the storage of products is not so explicit since literature data show both increases and decreases in the level of these compounds (Bednar et al., 1991; Gębczyński, 2002; Sistrunk & Cash, 1975).

The aim of the work was to determine the effect of blanching or cooking of the raw material, and its freezing or sterilization and storage period, on the contents of nitrates, nitrites and oxalates in preserved spinach and New Zealand spinach. The products compared in the work may be characterized as "convenience foods", processed to a similar degree and ready for consumption within 10 min of preparation.

2. Materials and methods

2.1. Conditions of harvesting the raw material

The investigated material were leaves of spinach cv. Markiza F_1, bred by Plantico Gołębiew in Poland, and usable parts (stems not exceeding 15 cm in length with leaves) of New Zealand spinach reproduced by Topstar, a Dutch breeding firm.

The vegetables were grown in southern Poland in the Krakow region on the experimental field of the investigators, on brown soil developed from loess formations of the mechanical composition of silt loam, in the second year after manure fertilization. The fore-crop was grass pea. The aim of the work was to investigate materials obtained in the shortest possible time interval. Therefore, the spinach was sown by the end of March and harvested early in June. The transplants of the New Zealand spinach were planted during the first 10 days of May and harvested four days later than the spinach. The level of fertilization was adjusted to nutritional requirements of plants and to the content of macro components in soil, amounting to 60 kg P_2O_5 ha^{-1}, 100 kg K_2O ha^{-1} and 40 kg N ha^{-1} before sowing or before transplanting, and to 20 kg N ha^{-1} as top dressing.

2.2. Production of frozen and canned vegetables

The two vegetable species were processed directly after harvest. The aim of the technological process in producing frozen and canned vegetable was to obtain products of a similar degree of processing. It was assumed that the preparation of the products for consumption should include their warming and culinary seasoning. Hence, the two products compared in the work can be classed as convenience foods. Preliminary processing, prior to preservation, was adopted for the kind of product. The technological process of freezing included the washing of plants and, only in the case of New Zealand spinach, the cutting of shoots with leaves into halves, cooking the raw materials in boiling water for 4 min, with 2:1 proportions of water to plants, cooling, draining the water, and slightly shaking it out on sieves. The time of cooking, determined on the basis of preliminary experiments, was the same for the two vegetables. After the applied preliminary processing, the cooked vegetables reached the consumption consistency. The material was frozen in polystyrene unit boxes, 0.5 dm^3 in volume. Freezing was carried out in a 3226-51 type Feutron blast freezer with forced air circulation. Freezing at −40 °C to the storage temperature of −25 °C took 120 min. During freezing, the boxes were open; after freezing, the covered boxes were brought to a storage chamber at −25 °C. The preparation of materials, for the production of preserves in air-tight cans, included technological measures analogous to freezing procedures; the two spinach species were blanched for 2 min at 96–98 °C, the proportion of water to the vegetable being 5:1. Cans, 0.45 dm^3 in volume, were used, each containing 400 g of the blanched material and 50 g hot water. No salt was added since this addition affected the level of dry matter and ash, impeding the comparison of canned products with frozen ones. The following sterilization parameters were determined on the basis of preliminary technological tests: raising the temperature to 100 °C – 5 min, raising the temperature to 120 °C – 10 min, maintaining the temperature at 120 °C – 40 min, reducing the temperature to 100 °C – 10 min, reducing the temperature to 30 °C – 5 min. After preservation the cans were placed in a storage chamber at 4–6 °C where they were kept until the time of analyses.

2.3. Analysis of the levels of components

The raw material, the same material after preliminary processing, i.e. cooking or blanching and cooling, and frozen and canned products, were analysed after 1, 6 and 12 months of storage. It should be mentioned that the whole content of canned preserves (400 g of blanched material + 50 g brine) was analysed, since the preserve was a fairly uniform mass and in an opened can the brine and wet material could not have been separated. Hence the content of the investigated components was given in edible parts (the raw material and the raw material after blanching) or in a unit of the final product. The determinations concerned the level of dry matter (AOAC, 1984) and the content of nitrates and nitrites measured using the ISO method (ISO/6635, 1984), and also water-soluble oxalates (Wilson, Shaw, & Knight, 1982) and total oxalates (AOAC, 1984). All determinations were conducted, in four replications each, in two parallel samples. The results were statistically verified on the basis of the Snedecor F and Student *t* tests and of multifactor analysis of variance, using the Excel 97 programme. The least significant difference was calculated at the level of error probability, $\alpha = 0.01$.

3. Results and discussion

The contents of nitrates, nitrites, and oxalates in the raw material and in the raw material after preliminary processing are given in Table 1. Fresh spinach was characterized by a low content of nitrates, comparable to the content given by Takebe et al. (1995). Oguchi, Weerakkody, Tanaka, Nakazawa, and Ando (1996) showed that spinach leaves could accumulate even more than 7 g NO_3^- in 1 kg fresh matter. Gajda and Karłowski (1993) found that the level of nitrates in spinach varied from 29 to 6757 mg NO_3^- per kg fresh weight with almost 28% of samples showing a content below 180 mg. Bąkowski, Michalik, and Horbowicz (1996) report that spinach harvested in June – as in the present paper – contained 255–476 mg NO_3^- in 1 kg fresh matter, depending on the cultivar, this value being 3.6 and even to 8.5 times smaller than in the case of plants harvested in October. In New Zealand spinach, the level of nitrates may vary from 449 to 3472 mg (Jaworska, 2005; Jaworska & Słupski, 2001), hence the investigated raw material contained an average amount of these compounds. Field-grown fresh vegetables, produced with the use of proper agro-technical measures, show no tendencies to accumulation of nitrites. In the case of spinach, the reported content does not exceed 1.0 mg NO_2^- in 1 kg fresh matter (Siciliano, Krulick, Heisler, Schwartz, & White, 1975). The amounts found in the investigated vegetables did not exceed this, but it should be noted that, in spinach, the content of nitrites was three times greater than in New Zealand spinach.

According to the literature, the limit values of the content of total oxalates varied from 250 to 1760 mg/100 g fresh matter in spinach (Yamanaka, Kuno, Shiomi, & Kikuchi, 1983; Oguchi et al., 1996) and from 506 to 1765 mg/100 fresh matter in New Zealand spinach (Jaworska, 2005; Savage, Vanhanen, Mason, & Ross, 2000). Grevsen and Kaack (1996) investigated the value of 12 spinach cultivars in the processing industry, determining the content of 605–806 mg oxalic acid in 100 g fresh matter. Potassium and sodium salts of oxalic acid are classed as water-soluble oxalates while calcium, magnesium and zinc salts as insoluble ones. The proportion of water-soluble oxalates in total oxalates was 59% for spinach and 81% for New Zealand spinach. A similar share of soluble oxalates of their total content is given by Takebe et al. (1995) and Yamanaka et al. (1983) for spinach, while Watanabe et al. (1994) and Savage et al. (2000) recorded much higher values, namely 80% and 87%. The same authors give a 21% proportion only for New Zealand spinach.

In order to obtain products characterized as convenience foods, the raw materials were soft-boiled for 4 min before freezing and or blanched for half that time before preservation in air-tight cans. Preliminary processing effected a statistically significant decrease in the level of the analysed compounds, except for nitrites. Sistrunk and Cash (1975) and Michalik (1984) observed that the longer the time of blanching in water the greater was the decrease in the content of nitrites in spinach after this treatment. Hence, as expected, the losses of the analysed components were greater after cooking the raw materials than after a 2-min blanching. After blanching, the raw materials contained less nitrates (by 23–36%) in fresh matter and (by 26–28%) in dry matter than did raw vegetables; after cooking, the respective figures were 26–45% and 35–42%. The above results confirm the opinion of Garcia and Bosch (1988) that the losses of nitrates during cooking in water are as much the function of the time of cooking as of the type of the vegetable. The level of losses determined in the two vegetables should be regarded as relatively low. Michalik (1984) determined a decrease (by 54–86%) in the content of these compounds after 2-min of blanching; Amal (2000) (by almost 74%) after a 3-min treatment, and Gawęcka (1974) (even by 88–92%) after 5 min. The content of nitrites was practically unchanged

Table 1
Contents of nitrates, nitrites and oxalates in spinach and New Zealand spinach after preliminary processing

Index	Species	Raw material		Raw material after blanching		Raw material after cooking		LSD $\alpha = 0.01$	
		f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m.	d.m.
Nitrates (g/kg)	S	0.11 ± 0.005	1.02 ± 0.039	0.07 ± 0.002	0.75 ± 0.018	0.06 ± 0.003	0.59 ± 0.026	0.010	0.067
	NZ	1.63 ± 0.011	31.1 ± 0.193	1.26 ± 0.024	22.5 ± 0.378	1.21 ± 0.005	20.2 ± 0.077	0.035	0.572
Nitrites (mg/kg)	S	0.84 ± 0.150	7.76 ± 1.36	0.79 ± 0.069	8.27 ± 0.730	0.66 ± 0.030	7.04 ± 0.276	ns	ns
	NZ	0.27 ± 0.024	5.18 ± 0.448	0.27 ± 0.056	4.85 ± 0.986	0.27 ± 0.053	4.45 ± 0.888	ns	ns
Soluble oxalates (g/100 g)	S	0.56 ± 0.013	5.19 ± 0.160	0.39 ± 0.007	4.12 ± 0.072	0.33 ± 0.009	3.56 ± 0.120	0.023	0.278
	NZ	0.41 ± 0.012	7.74 ± 0.237	0.34 ± 0.012	6.09 ± 0.214	0.26 ± 0.013	4.39 ± 0.215	0.028	0.510
Total oxalates (g/100 g)	S	0.94 ± 0.030	8.73 ± 0.328	0.78 ± 0.011	8.16 ± 0.124	0.71 ± 0.010	7.51 ± 0.092	0.044	0.481
	NZ	0.51 ± 0.007	9.62 ± 0.138	0.37 ± 0.014	6.64 ± 0.252	0.30 ± 0.018	5.04 ± 0.301	0.031	0.552

SZ: spinach; NZ; New Zealand spinach; f.m.: content in fresh matter; d.m.: content in dry matter; SD: standard deviation.

after preliminary processing. Amal (2000) and Ezeagu and Fafunso (1995) observed an increase in the content of these compounds in blanched or cooked leafy vegetables. The losses of total oxalates reached 17–27% after blanching and 24–41% after cooking, always being higher in the case of New Zealand spinach. After 2-min of cooking in tap water Savage et al. (2000) recorded a 53% decrease in the content of total oxalates in spinach and a 25% decrease in New Zealand spinach; the recorded losses of soluble oxalates varied from 65% to 66%. In the present experiment, decreases in the level of soluble oxalates were much smaller, varying over the range 18–41%. Considerable differences between the levels of losses in oxalate content given by the above quoted authors and the present work might have been caused by differences in water hardness. In the present experiment the hardness of tap water used in all the treatments was high (14°N). Owing to the applied treatments the raw material after cooking contained less nitrates (by 4–14%), nitrites (by 0–16%), water-soluble oxalates (by 15–24%), and total oxalates (by 9–19%) in comparison with the raw material after blanching.

After freezing, a significant increase in the content of nitrates was found in fresh matter of spinach while, in New Zealand spinach, the content decreased (Table 2). After freezing, a significant increase in the level of nitrates was determined in broccoli by Huarte-Mendicoa, Astiasarán, and Bello (1997) and in spinach by Michalik (1984) while Gębczyński (2002) reported a usually statistically non-significant decrease in Brussels sprouts and Michalik (1984) in carrot. Lisiewska (1985) observed that raw materials with a rich content of nitrates contained smaller amounts of these compounds after freezing while, in the case of the smaller contents, an increase was usually recorded. In relation to the material after preliminary processing in canned products of New Zealand spinach, the content of nitrates was smaller by 29% and in canned spinach no changes were determined. On comparison of results obtained on a dry matter basis, the level of nitrates increased by 4–24% in the two final products of spinach and decreased by 8–19% in New Zealand spinach. Irrespective of the preservation method, the content of nitrites decreased by 8% in spinach. In New Zealand spinach it increased by 41–78% although it was still very low, not exceeding 0.48 mg NO$_2^-$/kg fresh matter.

After freezing, small statistically non-significant changes were found in the level of oxalates (Table 3).

Table 2
Contents of nitrates and nitrites in frozen and canned spinach and New Zealand spinach

Index	Species	Product	Time of storage (months)						LSD α = 0.01	
			1		6		12			
			f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m.	d.m.
Nitrates (g/kg)	S	F	0.07 ± 0.002	0.73 ± 0.018	0.07 ± 0.004	0.71 ± 0.043	0.07 ± 0.005	0.69 ± 0.043	0.010	0.092
		C	0.07 ± 0.004	0.78 ± 0.066	0.06 ± 0.005	0.67 ± 0.056	0.05 ± 0.003	0.62 ± 0.031		
	NZ	F	1.12 ± 0.078	18.5 ± 1.29	1.12 ± 0.016	18.24 ± 0.373	1.12 ± 0.012	18.2 ± 0.229	0.072	ns
		C	0.90 ± 0.031	18.2 ± 0.622	0.90 ± 0.004	18.34 ± 0.155	0.88 ± 0.007	17.9 ± 0.177		
Nitrites (mg/kg)	S	F	0.71 ± 0.065	7.6 ± 0.709	0.90 ± 0.063	9.6 ± 0.741	0.90 ± 0.029	9.77 ± 0.360	0.132	1.512
		C	0.85 ± 0.093	10.1 ± 1.08	0.81 ± 0.071	9.7 ± 0.817	0.82 ± 0.050	9.8 ± 0.552		
	NZ	F	0.48 ± 0.000	7.94 ± 0.012	0.62 ± 0.068	10.0 ± 1.08	0.68 ± 0.057	11.1 ± 0.893	0.087	1.506
		C	0.38 ± 0.045	7.73 ± 0.908	0.51 ± 0.034	10.4 ± 0.700	0.64 ± 0.000	13.0 ± 0.057		

S: spinach; NZ; New Zealand spinach; F: frozen product; C: canned product; f.m.: content in fresh matter; d.m.: content in dry matter; SD: standard deviation.

Table 3
Contents of oxalates in frozen and canned spinach and New Zealand spinach

Index	Species	Product	Time of storage (months)						LSD α = 0.01	
			1		6		12			
			f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m. ± SD	d.m. ± SD	f.m.	d.m.
Soluble oxalates (g/100 g)	S	F	0.32 ± 0.014	3.45 ± 0.156	0.31 ± 0.005	3.29 ± 0.063	0.31 ± 0.012	3.30 ± 0.105	0.019	0.214
		C	0.24 ± 0.009	2.85 ± 0.102	0.24 ± 0.008	2.81 ± 0.113	0.22 ± 0.003	2.58 ± 0.061		
	NZ	F	0.26 ± 0.015	4.29 ± 0.246	0.26 ± 0.010	4.17 ± 0.197	0.26 ± 0.013	4.20 ± 0.205	ns	0.403
		C	0.27 ± 0.003	5.47 ± 0.069	0.26 ± 0.009	5.28 ± 0.171	0.26 ± 0.011	5.18 ± 0.244		
Total oxalates (g/100 g)	S	F	0.69 ± 0.011	7.33 ± 0.102	0.68 ± 0.008	7.32 ± 0.072	0.68 ± 0.008	7.32 ± 0.144	0.016	0.227
		C	0.58 ± 0.006	6.95 ± 0.089	0.59 ± 0.005	7.01 ± 0.060	0.59 ± 0.008	6.98 ± 0.163		
	NZ	F	0.30 ± 0.011	4.88 ± 0.176	0.29 ± 0.016	4.74 ± 0.213	0.29 ± 0.011	4.69 ± 0.191	0.023	0.397
		C	0.35 ± 0.010	7.15 ± 0.202	0.35 ± 0.012	7.12 ± 0.251	0.35 ± 0.007	7.11 ± 0.111		

S: spinach; NZ; New Zealand spinach; F: frozen product; C: canned product; f.m.: content in fresh matter; d.m.: content in dry matter; SD: standard deviation.

In relation to the raw material after blanching, their content was distinctly smaller in canned products – by 21–39% of water-soluble oxalates and by 5–25% of total oxalates. In comparison with frozen products, canned spinach contained less soluble oxalates (by 25%) and less total oxalates (by 16%); however, in canned New Zealand spinach, the content of these compounds was greater (by 4–17%).

The one-year storage period did not practically affect changes in the level of nitrates or oxalates in the investigated products. Michalik (1984) stressed the lack of changes in the concentration of nitrates during the storage of frozen spinach. However, Amal (2000) and Gębczyński (2002) showed that the contents of these compounds were diminished. During the storage period the content of nitrites in frozen products increased by 27–42% and in canned New Zealand spinach by 68%. It should be stressed that, after the storage period, in no sample did the content of these compounds exceed 1 mg NO_2^-/kg. Numerous authors have observed increases in the content of nitrites during the storage of final products (Amal, 2000; Huarte-Mendicoa et al., 1997; Jaworska & Słupski, 2001). In comparison with the raw material, the contents of nitrates, soluble oxalates, and total oxalates were smaller in products after the one-year storage, while the content of nitrites increased except for the canned spinach (Fig. 1).

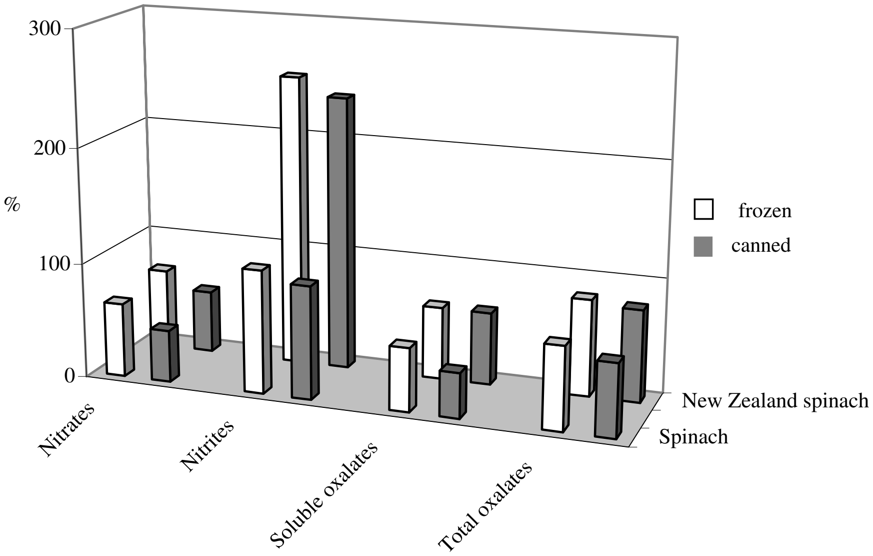

Fig. 1. Effect of technological processing and a 12-month storage period on the content of nitrates, nitrites and oxalates in frozen and canned products of spinach and New Zealand spinach (the level of the compounds in the raw material = 100%).

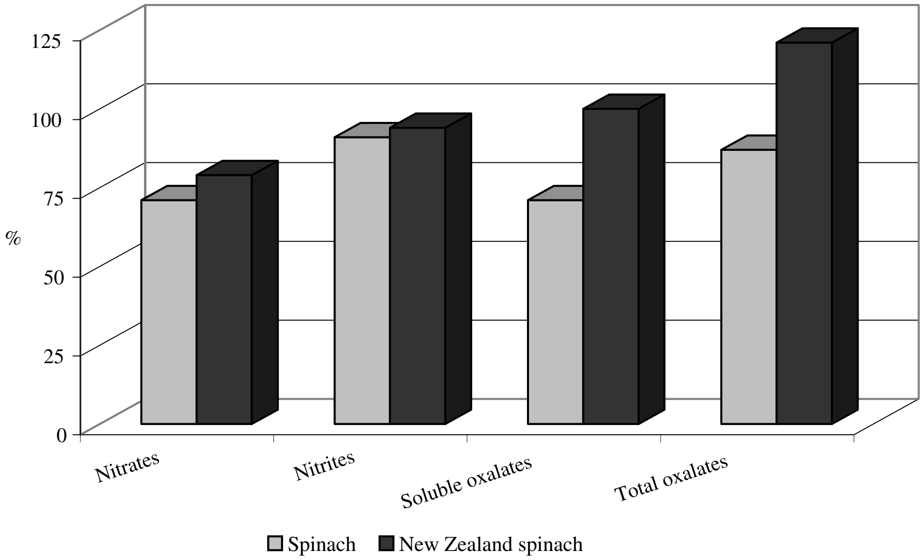

Fig. 2. Comparison of the content of nitrates, nitrites and oxalates between frozen and canned products after a 12-month storage (content in frozen products = 100%).

According to Siciliano et al. (1975), canned products are usually characterized by a smaller content of nitrates and nitrites than frozen vegetables. This opinion was corroborated in the present paper, particularly with respect to products stored for at least 6 months. Canned spinach also contained less oxalates than frozen preserves. In canned New Zealand spinach, the content of these compounds was greater or comparable. However, it should be noted that the compared results concerned the content of compounds in 100 g of the preserve; hence 11 g of the brine fell to each 100 g of the canned product. If the content of compounds in 100 g fresh matter of the material were taken into consideration, sterilized vegetables would have contained less nitrates by 12–14% and slightly more nitrites, by 206%, in comparison with frozen products. With respect to oxalates, canned spinach contained less total oxalates (by 3%) and less soluble oxalates (by 19%), while in canned New Zealand spinach these contents were greater (by 34% and 12%, respectively) (Fig. 2).

4. Conclusion

In relation to blanching, the cooking contributed to statistically significant decrease in the contents of nitrates and oxalates. However, the size of losses was also affected by the species of the preserved vegetable. With respect to compounds analysed in the present work, the production of canned vegetables is a better preservation method than freezing. After a 12-month storage, canned products contained less nitrates (by 21–40%), nitrites (by 6–9%), water soluble oxalates (by 0–29%) and, in canned spinach only, less nitrites (by 13%) (Fig. 2). After the storage period, in relation to products of spinach, final products of New Zealand spinach contained less nitrites and total oxalates (by 22–24% and 41–58%, respectively). However, the content of nitrites was 16–18 times greater in them owing to the exceptionally small content of these compounds in fresh spinach.

Acknowledgement

The investigation was supported by a grant from the State Committee for Scientific Research (KBN) in Warsaw (No. 3 P06T 037 24).

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