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EFFECT OF TEMPERATURE AND STORAGE PERIOD ON THE PRESERVATION OF VITAMIN C, THIAMINE AND RIBOFLAVIN IN FROZEN DILL (*ANETHUM GRAVEOLENS* L.)

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ABSTRACT

The aim of the present work was effect of temperature and storage period on the preservation of vitamin C, thiamine and riboflavin in leaves and whole plants (leaves with petioles and stems) of dill, harvested with a plant height of 25 cm. Changes in the level of these compounds in the process of freezing and refrigerated storage were also determined. The investigation concerned two kinds of the raw material (leaves and whole plants), various methods of preparation before freezing (non-blanching or blanching), different storage temperatures (-20°C and -30°C), and the 12-month storage period. Fresh dill leaves contained 116 mg vitamin C, 0.196 mg thiamine, and 0.638 mg riboflavin in 100 g fresh matter and whole plants 77 mg, 0.115 mg, and 0.433 mg, respectively. The treatment of blanching affected a decrease in the level of vitamin C by 35-48%, thiamine by 43-45%, and riboflavin by 27-33%. After blanching smaller losses were recorded in whole plants than in leaves. Freezing induced a decrease in the level of the investigated vitamins but only in non-blanching samples. During a 12-month refrigerated storage of the blanching material a decrease in the content of the analysed vitamins was smaller than in samples, which were non-blanching before freezing although in the case of thiamine, it was not small enough to equalize the losses affected by blanching. The lower storage temperature favourably affected only the preservation of vitamin C.

Key words: dill, freezing, storage, vitamin C, riboflavin, thiamine

INTRODUCTION

Dill is chiefly grown because of its specific aromatic qualities. It belongs to the group of leafy vegetables characterized by a high content of mineral compounds and some vitamins [1, 3, 6]. In spite of its provenance from southern Asia the plant has successfully spread over the entire Mediterranean region and, owing to its easy adaptability, also over central and even northern Europe and numerous regions of North America.

In Europe, the dill was at first grown as a pot herb. Because of its pharmacological effects the plant became interesting for folk medicine, and later for pharmaceutical and cosmetic industries [4]. The developing industry of food concentrates has considerably increased the demand for dried dill. The freezing industry can supply qualitatively good frozen dill products which, contrary to the dried herb, can be used not only for seasoning but also for preparing sauces and soups of specific taste and flavour. Freezing also differs from drying by the feasibility of using not only the leaves but also the remaining parts of young plants (petioles and stems) for semi-finished products if the appropriate preparation for freezing has been applied. However, it should be taken into consideration that all the technological measures with the use of high temperatures – as is the case in blanching raw material before freezing – can effect the degradation of nutrients, among them vitamins contained in plants. The storage of frozen products, including the level of temperature and the length of storage, are not irrelevant to the preservation of such sensitive compounds as vitamins [14, 15].

The aim of this study was to determine the level of vitamin C, thiamine, and riboflavin in leaves alone and in whole young plants of the dill. The preservation of these compounds in the process of freezing and storage of frozen goods and two storage temperatures were also taken into consideration.

MATERIALS AND METHODS

The investigated material was fresh and frozen dill cv. Amat. The raw material was harvested in the experimental field of our department carrying out the present investigation.

Seeds were sown on August 1, 2000. The sowing date was adjusted to ensure the harvest time on the turn of summer and autumn, this permitting shortening of the storage period of frozen dill to the new harvest and reducing the cost of refrigerated storage.

The harvest was carried out after 37 days, when the plants had reached about 25 cm in height, consisted of cutting plant tops about 5 cm above the soil. The harvested plants were therefore 20 cm in height. They were surveyed for removal of individuals of discoloured or unhealthy appearance. It should be mentioned that the plants were healthy, traces of yellowing appearing only on single stunted leaves at the plant base. The dill plants were harvested in the morning and the time from cutting to the beginning of analyses and processing the raw material did not exceed two hours. The first measure was to separate the leaves from the remaining parts of the plants. It was determined that the leaves constituted 51% of weight of whole plants.

The investigation concerned: 1. Two kinds of the raw material: leaves alone and whole dill plants, i.e. leaves with petioles and stems. 2. Differentiated treatment before freezing, i.e. blanched and non-blanched samples. 3. Differentiated temperatures of refrigerated storage, i.e. at -20°C and -30°C . 4. Time of refrigerated storage throughout the year, frozen products being analysed at 3-month intervals.

Non-blanched leaves were cut into 5-7-mm sections. A sample representative of whole non-blanched plants was prepared by mixing leaves (previously cut into 5-7-mm sections) with the stem and petioles strained through a sieve of 2 mm sieve mesh. The preparation of blanched samples consisted of blanching in water at $94-96^{\circ}\text{C}$, the proportion of water to the blanched material being 1:5. The time of blanching was adjusted to that necessary for decreasing the activity of peroxidase to at least 95%. The planned decrease in activity was attained after 30 s in leaves and after 3 min in stems with petioles. After cooling in water and removing the remaining water by centrifugation to the weight equal to that before blanching, the leaves were cut into sections of 5-7 mm while stems with petioles were granulated as in the case of the non-blanched dill. In blanched and non-blanched samples the same proportion as in the raw material was maintained between the leaves and the stems with petioles.

Packing the dill in polythene bags 0.08 mm thick preceded its freezing. The content of a bag was 650 g of the material. The bags were pressed tightly to remove as much air as possible, then welded closely. Directly after closing, the product was frozen at -40 in a 3626-51 Feutron blast freezer with forced air circulation to a temperature of -20°C and to a temperature of -30°C. After freezing the bags were placed in storage chambers at -20°C and -30°C, respectively, and kept there until the time of evaluation.

Depending on the type of the material and pre-treatment, bags of the same weight had different volume. In the calculation per 1 kg of weight the volume of leaves was about 3.5 dm³ and of whole plants 2.0 dm³ in non-blanching samples and in blanching ones about 1 dm³ of both leaves and whole plants.

The average sample contained 650 g of the material and the manner of sampling ensured its being representative of the entire lot of the raw material. Analyses of the raw material were begun within 2 h of the harvest and of frozen products after the storage period appropriate to the method of the investigation. The samples for analysis were defrosted at 2-4°C during 17-18 h. Analyses concerned vitamin C content determined as the sum of ascorbic and dehydroascorbic acids by spectrophotometric method [11]. Thiamine content was determined by the thiochrome method, and riboflavin content by the fluorescence method [7].

Determination of the investigated components was carried out in four replications, average results of the determinations being calculated per 100 g fresh and 100 g dry matter. This form of presentation of results gives information concerning the level of a component in the product ready for consumption and can also be interesting in the cognitive aspect.

To determine the significance of differentiation in the content of the investigated components between the investigated combinations, statistical calculations were carried out using one-factor analysis for the material before freezing and two-factor analysis for the results including the whole experiment. Factor I was the usable part, pre-treatment, and the temperature of storage, factor II the period of storing frozen dill. Statistical analysis was carried out according to the Excel 5.0 program, using the Snedecor F test and the Student t test. The least statistical difference (LSD) was calculated for the probability level $p = 0.01$.

RESULTS AND DISCUSSION

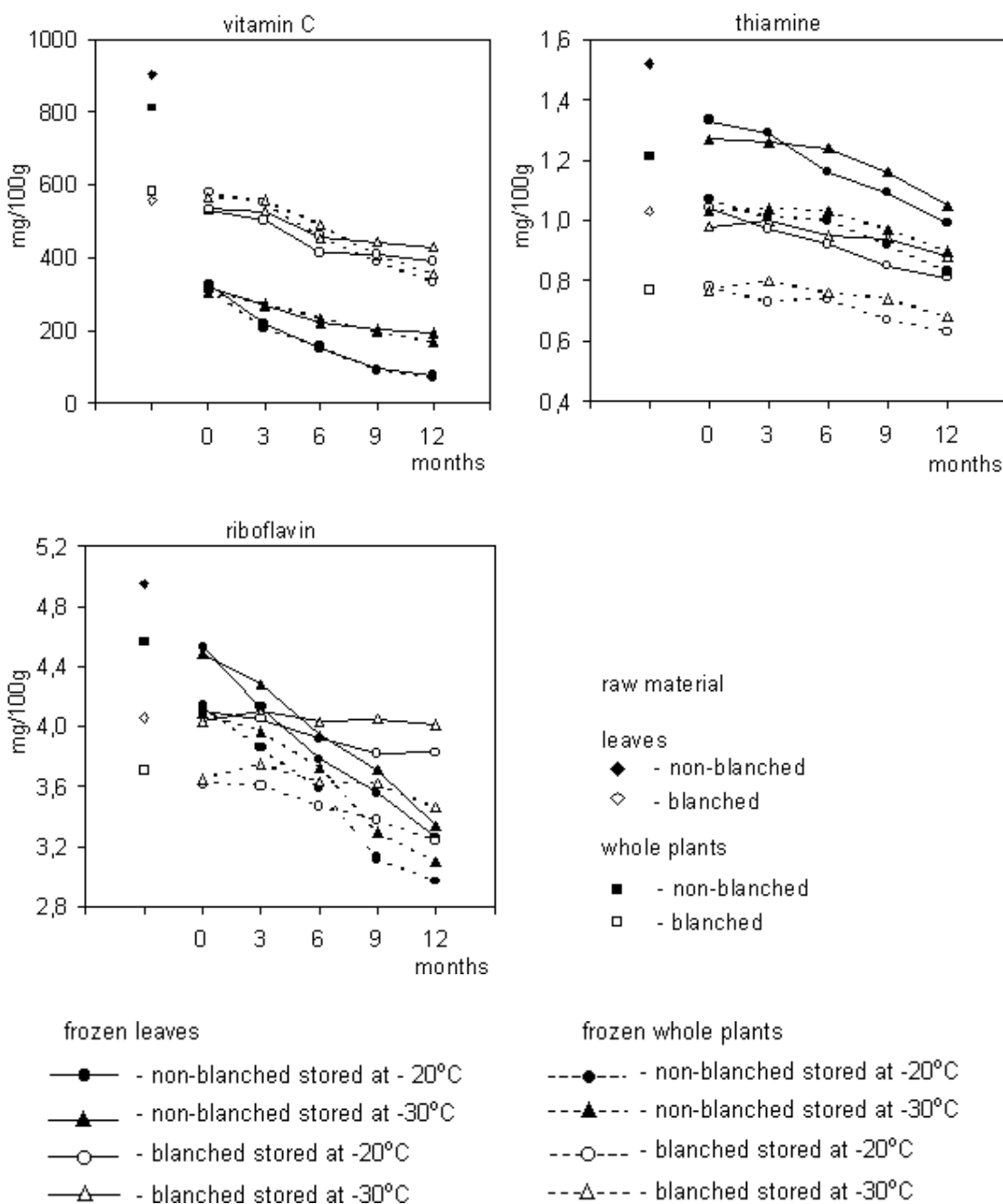
Separate parts of plants can considerably differ in their chemical composition, this particularly concerning differences between leaves, petioles, or stems [18, 23]. Ishida et al. [10] found that the leaves of sweet potato contained 78-130% more vitamin C, four to eight times more thiamine, and five to seven times more riboflavin than the shoots. According to Ottosson [20], kale and parsley leaves contain much more vitamin C than shoots. In the presented work the content of vitamin C in 100 g fresh matter of dill leaves was 116 mg and in whole plants significantly less, i.e. 77 mg, the difference reaching 51% in favour of the leaves. However, the difference in the level of vitamin C in leaves and whole plants was distinctly smaller in dry matter, reaching only 10% ([Table 1](#), [Fig. 1](#)). In whole plants L-ascorbic acid constituted 88% of the total content of vitamin C while it was higher in leaves, reaching 92% ([Table 2](#)). According to Ajayi et al. [2] who investigated the level of vitamin C and L-ascorbic acid in six species of leafy vegetables, L-ascorbic acid constituted almost 100% of the vitamin. The recorded content of vitamin C can be estimated as high. This is confirmed by Agte et al. [1] who claimed that the content of this vitamin in 24 species of leafy vegetables considerably exceeds its level in other groups of these crops.

Table 1. Content of vitamin C, thiamine and riboflavin in raw and frozen dill, mg in 100 g of fresh matter

Component	Usable part	Method of pretreatment	Before freezing	Storage temperature	After storage time in months				
					0	3	6	9	12
Vitamin C	leaves	non-blanching	116 ± 5	-20°C	42 ± 3	28 ± 1	20 ± 1	12 ± 1	10 ± 1
			116 ± 5	-30°C	41 ± 2	35 ± 2	29 ± 2	26 ± 1	25 ± 2
		blanching	59 ± 3	-20°C	56 ± 3	53 ± 2	44 ± 2	44 ± 2	42 ± 2
			59 ± 3	-30°C	56 ± 3	55 ± 2	48 ± 3	47 ± 1	46 ± 2
	whole plant	non-blanching	77 ± 4	-20°C	30 ± 2	20 ± 2	15 ± 1	9 ± 1	7 ± 1
			77 ± 4	-30°C	29 ± 2	26 ± 1	22 ± 2	19 ± 1	16 ± 1
		blanching	50 ± 3	-20°C	49 ± 2	47 ± 2	40 ± 2	34 ± 1	29 ± 1
			50 ± 3	-30°C	48 ± 3	47 ± 2	42 ± 2	35 ± 1	31 ± 2
LSD (p=0.01) for material before freezing: 7.9			for whole experiment:		factor (I) factor (II) interaction (IxII)		1.6 1.4 4.0		
Thiamine	leaves	non-blanching	0.196 ± 0.011	-20°C	0.172 ± 0.010	0.166 ± 0.007	0.151 ± 0.009	0.142 ± 0.010	0.129 ± 0.007
			0.196 ± 0.011	-30°C	0.163 ± 0.009	0.162 ± 0.010	0.160 ± 0.009	0.150 ± 0.011	0.136 ± 0.008
		blanching	0.108 ± 0.006	-20°C	0.110 ± 0.009	0.103 ± 0.010	0.099 ± 0.009	0.092 ± 0.007	0.087 ± 0.005
			0.108 ± 0.006	-30°C	0.103 ± 0.004	0.104 ± 0.007	0.100 ± 0.009	0.100 ± 0.006	0.094 ± 0.005
	whole plant	non-blanching	0.115 ± 0.007	-20°C	0.101 ± 0.005	0.097 ± 0.006	0.096 ± 0.005	0.089 ± 0.006	0.081 ± 0.005
			0.115 ± 0.007	-30°C	0.098 ± 0.004	0.099 ± 0.006	0.097 ± 0.003	0.093 ± 0.005	0.087 ± 0.005
		blanching	0.066 ± 0.004	-20°C	0.067 ± 0.003	0.063 ± 0.004	0.064 ± 0.004	0.058 ± 0.004	0.055 ± 0.003
			0.066 ± 0.004	-30°C	0.066 ± 0.004	0.067 ± 0.004	0.065 ± 0.004	0.064 ± 0.006	0.059 ± 0.003
LSD (p=0.01) for material before freezing: 0.0178			for whole experiment:		factor (I) factor (II) interaction (IxII)		0.0059 0.0051 0.0145		
Riboflavin	leaves	non-blanching	0.638 ± 0.038	-20°C	0.584 ± 0.017	0.532 ± 0.025	0.491 ± 0.032	0.463 ± 0.042	0.426 ± 0.025
			0.638 ± 0.038	-30°C	0.576 ± 0.022	0.549 ± 0.022	0.510 ± 0.027	0.479 ± 0.046	0.435 ± 0.026
		blanching	0.427 ± 0.013	-20°C	0.432 ± 0.021	0.430 ± 0.025	0.420 ± 0.015	0.411 ± 0.024	0.413 ± 0.024
			0.427 ± 0.013	-30°C	0.424 ± 0.017	0.428 ± 0.021	0.424 ± 0.023	0.429 ± 0.025	0.427 ± 0.025
	whole plant	non-blanching	0.433 ± 0.026	-20°C	0.391 ± 0.022	0.369 ± 0.020	0.346 ± 0.021	0.303 ± 0.019	0.289 ± 0.017
			0.433 ± 0.026	-30°C	0.390 ± 0.027	0.377 ± 0.020	0.351 ± 0.015	0.316 ± 0.012	0.299 ± 0.018
		blanching	0.318 ± 0.019	-20°C	0.309 ± 0.014	0.310 ± 0.018	0.301 ± 0.021	0.294 ± 0.016	0.283 ± 0.017
			0.318 ± 0.019	-30°C	0.311 ± 0.016	0.316 ± 0.012	0.310 ± 0.017	0.312 ± 0.016	0.299 ± 0.018
LSD (p=0.01) for material before freezing: 0.0614			for whole experiment:		factor (I) factor (II) interaction (IxII)		0.0202 0.0175 0.0496		

(x ± SD) – mean value of three samples and standard deviation

Fig. 1. Changes in the level of vitamin C, thiamine and riboflavin during freezing and storage of frozen dill, in dry matter



The content of thiamine and riboflavin found in the presented investigation was within the limits of these vitamins given by Mosha et al. [16] for the leaves of five species of leafy vegetables. Fresh dill leaves contained 0.196 mg thiamine and 0.638 mg riboflavin in 100 g fresh matter (Table 1). In whole plants the content was statistically lower, i. e. by 41% and 32%, respectively, in fresh matter and in dry matter lower by 20% and 8% (Fig. 1).

The chief reasons of losses in the content of the analysed vitamins are the solubility in water, thermic destruction, and enzymatic oxidation during the technological process [21]. The treatment of blanching in water applied before freezing dill brought about a significant decrease in the level of vitamin C; in leaves it amounted to 52% fresh matter and in whole plants to 65%. The losses in thiamine content were 55% and 57%, respectively, and of riboflavin 67% and 73%. If calculated per dry matter the losses were distinctly smaller. These pronounced decreases in the content of vitamins, particularly if referred to fresh matter, can be attributed

to the fact that, contrary to other vegetables, dill has a large surface in relation to weight. A considerable decrease in the level of thiamine and riboflavin effected by hot water was also shown by Villanueva et al. [22] in two species of vegetables. However, Mosha et al. [16] found a considerable decrease or increase in the content of riboflavin, depending on the species of leafy vegetables. Kimura et al. [13] emphasised that the prolonged time of preliminary treatment of spinach increased the losses of thiamine. It should be stressed that the time of dill blanching was so adjusted as to reduce the level of catalase and peroxidase to a level corresponding to the quantity given for leafy vegetables as the residual content [5,24]. The results concerning the effects of blanching were more unequivocal with respect to vitamin C. The losses effected by blanching in the content of this vitamin in leafy vegetables ranged from 47% even to 80% [2,15,19]. According to Ajayi et al. [2] L-ascorbic acid constituted 68-96% of vitamin C in six species of leafy vegetables treated with blanching. In the investigated dill plants, the level of L-ascorbic acid decreased to 84-86% after blanching (Table 2).

Table 2. Share of L-ascorbic acid in vitamin C, in percent

Usable part	Method of pretreatment	Before freezing	Storage temperature	After storage time in months				
				0	3	6	9	12
Leaves	non-blanching	92	-20°C	90	86	80	75	70
		92	-30°C	93	89	83	77	76
	blanching	86	-20°C	86	85	84	82	79
		86	-30°C	84	85	85	83	80
Whole plant	non-blanching	88	-20°C	87	85	73	67	63
		88	-30°C	90	81	77	68	71
	blanching	84	-20°C	84	81	80	79	69
		84	-30°C	85	81	81	80	81

For non-blanching samples the losses of vitamin C brought about only by freezing decisively exceeded the total losses effected by blanching and freezing (Table 1). Howard et al. [8] and Katsaboxakis and Papanicolaou [12] confirmed that the freezing of blanching vegetables only slightly reduced the level of vitamin C. However, Niedzielski and Mokrosińska [17] found that, depending on the freezing method, the losses reached 10%.

Howard et al. [8] showed a linear decrease in vitamin C content during refrigerated storage of vegetables. According to Ibanez et al. [9], the greatest reduction occurred in the initial stage of storage life of frozen products. Selman [21] postulates that the losses of vitamin C reaching 10% can be expected during one-year storage at -20 to 25°C while a still lower temperature stabilizes the level of this vitamin. During the refrigerated storage of dill a gradual decrease in the level of vitamin C was observed in all the samples (Table 1, Fig. 1). In comparison with the content directly after freezing, the refrigerated products of non-blanching dill preserved 23-61% of vitamin C after a 12-month storage, depending on the sample, while blanching dill preserved 59-82%. If the samples kept at storage temperatures of -20°C and -30°C are taken into consideration, the above values are 23-75% and 55-82%, respectively. After a 12-month storage the content of vitamin C in 100 g of frozen dill leaves was 10-46 mg and in 100 g of frozen whole plants of dill 7-31 mg. The content of L-ascorbic acid decreased faster than that of vitamin C since its share in vitamin C was 81-89% after three months of refrigerated storage. After the full storage period it was 63-81%, being slightly higher at the lower storage temperature at all the dates of analyses (Table 2).

Selman [21] stressed that during the refrigerated storage vitamins B are more stable than vitamin C and the losses depend on the species of the frozen raw material. In non-blanching dill only the freezing effected a decrease in the content of thiamine and riboflavin by 12-17% and 8-10%, depending on the frozen sample (Table 1). During refrigerated storage the rate of decreases in the content of thiamine was slower in blanching samples than in non-blanching ones. Although after 12-months of refrigerated storage, dill leaves which were not blanching before freezing contained by 45-48% more thiamine than the blanching ones, similar behaviour of this vitamin being recorded in frozen intact plants of dill. The preservation of thiamine did not depend on the storage temperature. The losses in the content of the discussed vitamins in dry matter were in the same order of magnitude as those in fresh matter (Fig. 1).

Contrary to the effect on thiamine, the blanching showed distinctly protective effects on the content of riboflavin during the refrigerated storage. However, the total losses brought about by blanching and refrigerated storage approximated those observed in non-blanching samples during storage. Hence, after 12-month storage frozen samples treated or not treated with blanching showed a similar content of riboflavin. As in the case of thiamine neither the kind of the usable part of the plant nor the storage temperature had a significant effect on the magnitude of losses in the content of riboflavin.

CONCLUSIONS

Fresh dill leaves contained 116 mg vitamin C, 0.196 mg thiamine, and 0.638 mg riboflavin in 100 g fresh matter and whole plants 77 mg, 0.115 mg, and 0.433 mg, respectively. The treatment of blanching affected a decrease in the level of vitamin C by 35-48%, thiamine by 43-45%, and riboflavin by 27-33%. After blanching smaller losses were recorded in whole plants than in leaves. Freezing induced a decrease in the level of the investigated vitamins but only in non-blanching samples. During a 12-month refrigerated storage of the blanched material a decrease in the content of the analysed vitamins was smaller than in samples, which were non-blanching before freezing although in the case of thiamine, it was not small enough to equalize the losses affected by blanching. The lower storage temperature favourably affected only the preservation of vitamin C.

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