POLISH JOURNAL OF FOOD AND NUTRITION SCIENCES

www.pan.olsztyn.pl/journal/
e-mail: joan@pan.olsztyn.pl

Pol. J. Food Nutr. Sci.
2007, Vol. 57, No. 4, pp. 441–446

TOCOTRIENOLS IN THREE RYE VARIETES: FROM THE GRAIN TO THE BREAD

Henryk Zieliński, Anna Michalska, Dorota Szawara-Nowak, Wiesław Wiczkowski, Mariusz K. Piskuła

Division of Food Science, Institute of Animal Reproduction and Food Research of Polish Academy of Sciences, Olsztyn

Key words: rye grain, rye flours, flour extraction rates, rye breads, vitamin E, tocotrienols

In this study the contribution of tocotrienols to the total tocols of three varieties of rye grain (Amilo, Warko and Dańkowskie Złote), their morphological fractions, milling products and breads made from them was shown. Tocotrienols (α-T3, β-T3, γ-T3) and tocopherols (α-T, β-T, γ-T, δ-T) were extracted with methanol and separated by HPLC. The study showed that the richest source of tocotrienols was the whole grain of Dańkowskie Złote followed by the whole grain of Warko and Amilo cultivars. The tocotrienols found in the whole grain of three rye cultivars were α-T3 and β-T3 while the pool of tocopherols was formed by α-T, β-T and small quantity of γ-T. Tocotrienols found in the whole grain or in endosperm with embryo fraction contributed to more than 50% of total tocols, however those noted in pericarb with testa fraction were about of 90% of total tocols. The highest level of tocotrienols (α-T3 + β-T3) was noted in rye flours with extraction rate of 100% of the three cultivars. The milling process decreased contents of tocotrienols, however flours with extraction rate from 100 to 90% kept the T3/T ratio above one, whereas for flour with extraction rate of 70% this ratio was less than one. The percentage contribution of α-T3 and β-T3 to the total tocols content in whole meal and brown flours was within a range of 23–35% but that noted for light flours was within a lower range. The baking process caused a significant decrease in the content of tocotrienols as well as tocopherols. The level of tocotrienols in whole meal rye breads was about five, three and two times higher when compared to the bread formulated on brown flours originated from Amilo, Warko and Dańkowskie Złote. Moreover, the level of tocotrienols found in breads formulated on light flour (extraction rate of 70%) was about 2–13% of that noted in breads based on whole meal flour.

INTRODUCTION

In nature, eight substances have been found to have vitamin E activity: α-, β-, γ- and δ-tocopherol; and α-, β-, γ- and δ-tocotrienols [Burton & Traber, 1990]. All of them consist of a chromanol ring and a hydrophobic side chain, which is a phytyl in tocopherols and an isoprenyl with three double bonds in tocotrienols. Tocopherols and tocotrienols are further separated into individual compounds depending on the number and position of methyl substitution on the chromanol ring. Generally, when the vitamin E activity of a particular food is evaluated, a sum of the all eight vitamers are usually quantified together taking into account their relative activities. Therefore, yet from of the 24.000+ papers on vitamin E listed in PubMed, only just over 200 relate to tocotrienols [Sen *et al.,* 2006]. As reflected in their structural similarity, tocopherol and tocotrienols are well recognized for their antioxidative effect [Kamal-Eldin & Appelqvist, 1996].

The abundance of α-tocopherol in the human body and the comparable efficiency of all vitamin E molecules as antioxidants, led biologists to neglect the non-tocopherol vitamin E molecules as topics for basic and clinical research. Recent developments warrant a serious reconsideration of this conventional wisdom [Schaffer *et al.,* 2005]. Most studies compare the activities of tocotrienols with those of tocopherols ("classical vitamin E"). However, some biological effects were found to be unique for tocotrienols. Although the absorption mechanisms are essentially the same for all vitamin E analogs, tocotrienols are degraded to a greater extent than tocopherols [Birringer *et al.,* 2002]. Tocotrienols possess excellent antioxidant activity *in vitro* and have been suggested to suppress reactive oxygen species (ROS) production more efficiently than tocopherols [Mutalib *et al.,* 2003]. In addition, tocotrienols show promising nonantioxidant activity in various *in vitro* and *in vivo* models. Most notable are the interactions of tocotrienols with the mevalonate pathway leading to the lowering of serum cholesterol levels [Qureshi *et al.,* 2002], the prevention of cell adhesion to endothelial cells [Chao *et al.,* 2002], and the suppression of tumor cell growth and glutamate-induced neurotoxicity [Khanna *et al.,* 2003].

Tocotrienols are found in abundance in plant foods such as rice bran or palm oil [Theriault *et al.,* 1999]. It has been stated that ratios of the individual tocopherols and tocotrienols play an important role in determining the hypocholesterolemic, antioxidative and antitumor properties of palm oil and rice bran [Qureshi *et al.,* 2002]. Cereals also contribute significantly to the dietary intake of tocotrienols [Slavin, 2000; Andlauer & Furst, 1999]. For example, barley contains all four tocopherols and four tocotrienols. Other cereals such as wheat, oats and rye also contain more tocotrienols than

Author's address for correspondence: Henryk Zieliński, Institute of Animal Reproduction and Food Research of Polish Academy of Sciences, Tuwima 10, 10-718 Olsztyn, Poland, tel.: (4889) 523 46 82; fax: (4889) 524 01 24; e-mail: haziel@pan.olsztyn.pl

tocopherols and thus have a potentially beneficial distribution of the vitamers [Piironen *et al.,* 1986; Peterson & Qureshi, 1993; Zielinski *et al.,* 2001]. Rye is second to wheat, the most commonly used grain in the production of bread [Bushuk, 2001]. Milling and baking are the most common techniques used in grain processing for food [Nilsson *et al.,* 1997]. Although the total production of rye has diminished, its use as food for humans has increased slightly over the 1990s. In 2005, according to the Faostat data, the rye production in the Europe was about 14 million metric ton whereas wheat production was fifteen times higher [Faostat, 2006].

Having all these evidences, the aim of this work was to show the contribution of tocotrienols to the total tocols in three varieties of rye grains, their morphological fractions, milling products and breads made from them. Moreover, changes in tocotrienols content occurring during milling and baking are discussed in the light of benefits for customers.

MATERIALS AND METHODS

Three varieties of rye grain (Amilo, Warko and Dańkowskie Złote) were selected from breeding materials grown in central Poland (DANKO, Plant Breeding Co., Laski) in 2004.

Preparation of the morphological fractions of grains. Whole-grain samples were dehulled using a laboratory dehuller and fractions of pericarb with testa and endosperm with embryo were separated manually by sieving through a set of sieves. All samples were ground in a WZ-1 laboratory mill (Factory of Machines and Mechanisms for the Food Industry, Żnin, Poland). Grounded samples were stored at 4°C until extraction.

Preparation of the milling product. Rye grains were tempered to 14.0% moisture and milled on a Quadrumat Senior laboratory mill (Brabender) to obtain a straight grade flour with extraction rates of 100%, 95%, 90% and 70%, respectively. Samples from three replications were taken for analysis. Flour samples were stored at 4°C until extraction.

Bread manufacture. Salt used in the formulation of bread dough was purchased from a local food manufacturer. Rye breads were baked using traditional fermentation generated by lactic acid bacteria without baker's yeast addition. The three-stage method was used to make dough. Sourdough starter, as the first stage, was prepared by mixing 36% of whole meal rye flour and 64 % of water (w/w). This mixture was left to ferment for 48 h at 28°C. In the second stage sour was prepared by mixing 300 g of sourdough starter, 300 g of rye flour and 300 mL of water. The mixture was left to ferment for 3 h at 28°C. In the third stage dough was prepared by mixing 800 g of sour, 600 g of rye flour with indicated extraction rate (100, 95, 90 and 70%), 300 g of water and 20 g of salt, and then the dough was left for final fermentation for 30 min at 28°C in a ferment chamber. Pieces of dough (350 g) were molded by hand, panned, and proofed for 45 min at 28°C (75% rh). Breads were baked in an electric oven at 230°C for 35 min. The breads were sliced (1 cm thick) and dried in an electric convection oven (40°C) for 24 h. The dried material was ground and sieved through a 60-mesh screen to obtain powdered bread ready for further analysis.

Determination of tocotrienols and tocopherols content. Tocotrienols (α-T3, β-T3, γ-T3) and tocopherols (α-T, β-T, γ-T, δ-T) were extracted with methanol (0.5 g of flour/7 mL) for one minute using a IKA Turrax homogeniser at full speed (15,000 rpm), at room temperature. The solvent was decanted after centrifugation (2000 × *g*, 10 min), and the extraction was repeated on the residue using the same volume of solvent. The combined supernatants were evaporated in a rotary evaporator under vacuum, and then evaporated extracts were redissolved in 2 mL of n-hexane. The tocols were separated by HPLC on Lichrospher Si 60 5-μm particle size, 4 × 250-mm column (Merck, Germany), according to the method described by Paterson & Qureshi [1993]. Twenty microliters of each sample was injected onto a column. The HPLC system consisted of a Shimadzu LC 10 AD pump, Shimadzu oven CTO-6A, and a Shimadzu RF-535 fluorescence detector. The mobile phase was 0.5% (v/v) isopropa-

TABLE 1. The content of tocotrienols (T3) and their percentage contribution to the total tocols content (T3 + T) in grains and their morphological fractions of the three rye cultivars (μg/g d.m.)

Cultivar/fraction	T3		Total T3	Total T	T3/(T3+T) (%)	αT3/(T3+T) (%)	βT3/(T3+T) (%)	T3/T
	α	β						
Amilo								
Whole grain	5.41±0.20^a	4.13±0.22^a	9.53±0.41^a	7.87±0.55^a	54.8	31.1	23.7	1.21
Endosperm with embryo	4.92±1.14^a	4.56±0.84^a	9.84±1.97^a	6.81±0.87^a	59.1	29.5	27.4	1.44
Pericarb with testa	4.92±1.14^a	7.20±0.39^b	19.96±1.03^b	2.43±0.09^b	89.1	57.0	32.1	8.21
Warko								
Whole grain	6.87±0.29^a	4.19±0.33^a	11.07±0.59^a	10.17±0.49^a	52.1	32.3	19.8	1.09
Endosperm with embryo	6.84±0.52^a	4.60±0.10^a	11.45±0.62^a	8.99±0.29^b	56.0	22.5	22.5	1.27
Pericarb with testa	13.54±2.10^b	7.01±1.16^b	20.55±3.22^b	2.84±0.32^c	87.9	57.9	0.0	7.24
Dańkowskie Złote								
Whole grain	7.47±0.17^a	6.49±0.07^a	13.96±0.14^a	9.82±0.47^a	58.7	21.4	27.3	1.42
Endosperm with embryo	6.23±0.30^b	6.00±0.30^a	12.23±0.59^b	7.46±0.24^b	62.1	31.9	30.5	1.64
Pericarb with testa	17.18±0.93^c	11.61±0.91^b	28.79±1.84^c	2.94±0.18^c	90.7	54.1	36.6	9.79

Data expressed as mean ± standard deviation (n=3). Within each column for the each rye variety, means with the same letter are not significantly different (p 0.05).

nol in hexane. Flow rate was 1 mL/min, and compounds were detected using an excitation wavelength of λ=295 nm and emission wavelength of λ=330 nm. The contents of tocols were calculated from the peak areas using standard curves of tocotrienols (α-T3, β-T3, γ-T3, δ-T3) and tocopherols (α-T, β-T, γ-T, δ-T) obtained from Merck and Sigma.

Statistical analysis. Data were subjected to multifactor analysis of variance (ANOVA) using the least-squared difference test with the Statgraphic 5.0 Program (Statistical Graphic, Rockville, Md., USA) for Windows.

RESULTS AND DISCUSSION

The analyzed individual vitamers were expressed as total tocotrienols and total tocopherols in order to calculate the contribution of either separate tocotrienol or total tocotrienols to the content of total tocols. Moreover, the tocotrienols/tocopherols ratio (T3/T), which is an index of different distributions of tocols within the kernel, was calculated [Panfili *et al.,* 2003].

The study showed that the richest source of tocotrienols was the whole grain of Dańkowskie Złote followed by the whole grain of Warko and Amilo cultivars (Table 1, Figure 1). The tocotrienols found in the whole grains of three rye cultivars were α-T3 and β-T3 while the pool of tocopherol was formed by α-T, β-T and small quantity of γ-T. Tocotrienols found in the whole grains or in endosperm with embryo fraction contributed more than 50% to total tocols, however those noted in pericarb with testa fraction were about of 90% of total tocols. This finding clearly demonstrates that tocotrienols are mainly distributed in the outer layer of the rye grain. It was supported by about six times higher T3/T ratio calculated for pericarb with testa when compared to the whole grain and endosperm with embryo fractions. On the basis of percentage contribution of α-T3 and β-T3 to the total tocols of different morphological fractions of the grain, the α-T3 was mainly localized in pericarb with testa whereas β-T3 was equally distributed in these three fractions. The content of tocotrienols in rye grain was similar to that reported by Holasova and co-workers [Holasova *et al.,* 1995]. The results provided in this study confirm differentiation of tocotrienol concentrations within grain kernels and their different morphological parts, and are in good agreement with published data [Piironen *et al.,* 1986; Holasova, 1997; Panfili *et al.,* 2003; Horvath *et al.,* 2006].

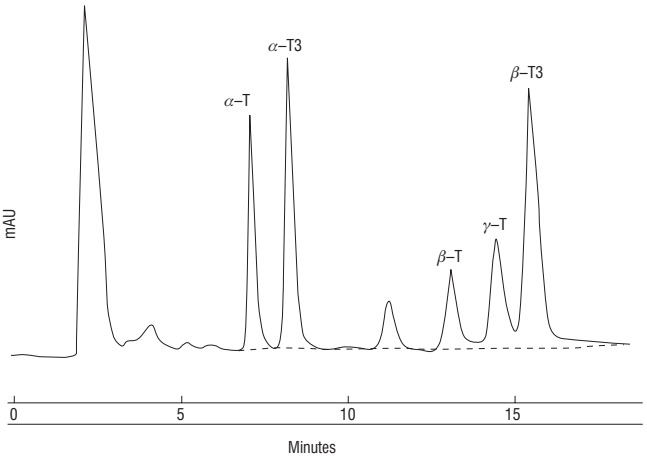

FIGURE 1. Typical chromatogram for tocotrienols and tocopherols in rye bread type W (100%)/ I.

Since pericarb with testa fraction is about 9.0–9.3% of the whole rye grain mass [Gasiorowski, 1994], it simply indicates a possible loss of tocotrienols during grain milling into different types of flours, especially light flour. On the other hand, the resulting rye bran may serve as a tocotrienol rich by-product of rye grain processing. It was shown that micromolar amounts of tocotrienol suppress the activity of 3-hydroxy-3-methylglutaryl CoA reductase (HMG-CoA), the hepatic enzyme responsible for cholesterol synthesis [Pearce *et al.,* 1992]. Moreover, nanomolar concentrations of α-T3 uniquely prevents inducible neurodegeneration by regulating specific mediators of cell death [Khanna *et al.,* 2003] but more research is needed in this field [Wilson *et al.,* 2002; Sen *et al.,* 2006].

In this study the results indicate the highest level of tocotrienols in rye flours with extraction rate of 100% of the three cultivars. As it was noted previously in respect to the whole grain, α-T3 and β-T3 formed the main pool of tocotrienols

TABLE 2. The content of tocotrienols (T3) and their percentage contribution to the total tocols content (T3 + T) in rye flours of the three rye cultivars (μg/g d.m.).

Rye variety / flour extraction rate	T3		Total T3	Total T	T3/(T3+T) (%)	αT3/(T3+T) (%)	βT3/(T3+T) (%)	T3/T
	α	β						
A/100%	4.96±1.00^{a}	4.82±0.50^{a}	9.78±1.43^{a}	6.19±0.90^{a}	61.2	31.1	30.2	1.58
A/95%	2.84±0.35^{b}	4.08±0.45^{b}	6.92±0.53^{b}	5.43±0.58^{a}	56.0	23.0	33.0	1.27
A/90%	2.77±0.46^{b}	3.75±0.07^{b}	6.52±0.46^{b}	5.53±0.64^{a}	54.1	23.0	31.1	1.18
A/70%	0.49±0.01^{c}	1.93±0.15^{c}	2.42±0.15^{c}	3.08±0.19^{b}	45.7	8.9	36.4	0.79
W/100%	6.22±0.29^{a}	3.98±0.12^{a}	10.19±0.40^{a}	8.41±0.38^{a}	54.8	33.4	21.4	1.21
W/95%	4.41±2.60^{a}	4.11±0.09^{a}	8.52±2.52^{ad}	7.94±0.66^{a}	51.8	26.8	25.0	1.07
W/90%	4.57±0.75^{a}	3.64±0.47^{a}	8.21±1.18^{bd}	7.26±1.07^{a}	53.1	29.5	23.5	1.13
W/70%	1.14±0.05^{b}	2.12±0.11^{b}	3.26±0.15^{c}	4.01±0.27^{b}	44.8	15.7	29.2	0.81
DZ/100%	9.31±1.39^{a}	6.72±0.93^{a}	16.02±2.29^{a}	10.14±1.75^{a}	61.2	35.6	25.7	1.58
DZ/95%	8.45±0.54^{a,b}	6.80±0.49^{a}	15.25±1.02^{a}	9.41±0.68^{a}	61.8	34.3	27.6	1.62
DZ/90%	7.44±0.44^{b}	6.34±0.33^{a}	13.77±0.76^{a}	8.31±0.34^{a}	62.4	33.7	28.7	1.66
DZ/70%	1.99±0.07^{c}	3.26±0.09^{b}	5.24±0.16^{b}	6.21±0.13^{b}	45.8	17.4	28.5	0.84

Data expressed as mean ± standard deviation (n=3). Within each column for the each rye variety, means with the same letter are not significantly different (p 0.05).

(Table 2). Milling process decreased contents of tocotrienols, however milling into flours with extraction rate from 100 to 90% kept the T3/T ratio above one whereas for flour with extraction rate of 70% this ratio was less than one. These findings clearly show the beneficial content of tocotrienols in whole meal rye flour (extraction rate of 100%) and brown flours (extraction rate of 95 and 90%) but not in the light flour (extraction rte of 70%). The percentage contribution of α-T3 and β-T3 to the total tocols content in whole meal and brown flours was within a range of 23–35% but that noted for light flours was within a lower range. The contents of tocotrienol are in agreement with recent report by Ryynanen *et al.* [2004] who studied T3 contents in ten rye varieties and whole meal flour. Additionally, these authors, apart from α-T3 and β-T3, detected trace amounts of γ-T3 and δ-T3 (below 0.2 μg/g) [Ryynanen *et al.,* 2004]. As lipophilic substances, tocols are intimately associated with lipid components of the sample matrix. For this reason, the methods of extraction for tocopherols and tocotrienols analysis fall into two categories: nonsaponification (solvent extraction) and saponification methods (alkaline hydrolysis). More recently, the use of supercritical fluid extraction has been proposed as an alternative method for the determination of vitamin E from food [Fratianni *et al.,* 2002]. This method was recently compared to hot saponification followed by solvent extraction and extraction without saponification [Panfili *et al.,* 2003]. It was shown that the percentage of tocopherols and tocotrienols recovery from cereals was higher after hot saponification followed by solvent extraction when compared to only methanol extraction. For this reason, the presented data express only tocols extractable with methanol. The data provided here point to the need of using whole meal or brown rye flours by bakeries in order to keep the higher tocotrienol level.

The baking process (230°C, 35 min) decreased significantly the content of tocotrienols and tocopherols. It was interesting to find out that approximately 2–3 fold decrease was seen in brown breads when compared to the tocotrienols content in the respective breads from whole meal flours. A significant decrease of tocotrienols, approximately about 10 times, was noted in the remaining breads. Similar phenomenon was also noted in respect of the total tocopherols content of the four types of breads. The similar reduction in tocols content was previously observed during extrusion cooking of different cereal grains, including also rye grain [Zielinski *et al.,* 2001].

The main rye bread tocotrienol's fraction was formed by α-T3 and β-T3. The content of tocotrienols in the four types of bread based on flours from the three rye cultivars is shown in Table 3. The content of tocotrienols (α-T3 + β-T3) in rye breads formulated on whole meal flour (extraction rate of 100%) was within the range from 3.16 to 3.38 μg/g d.m. and it contributed to about 50% of total tocols. The level of tocotrienols noted in this type of breads was about five, three and two times higher when compared to the bread formulated on brown flours originated from Amilo, Warko and Dańkowskie Złote. Moreover, the level of tocotrienols found in breads formulated on light flour (extraction rate of 70%) was about 2–13% of that noted in breads based on whole meal flour. The results from this study showed that breads based on whole meal flours were the richest source of both tocotrienols and tocopherols, in spite of the fact that the better distribution was found in the breads based on brown flour wit extraction rate of 95%. It should be also pointed out that using flours with decreasing extraction rates down to 70% in bread making changed the share of α-T3 but not β-T3 to the total tocols of breads to a substantial extent.

The data showed that the content of tocotrienols, despite losses due to the baking process, strongly depends on the type of flour used for bread making. It can also be suggested that tocotrienols found in whole meal flour are better protected against degradation due to the thermal treatment than in brown and light rye flours.

Tocotrienols show significant inhibition of lipid peroxidation in several model systems. Whether antioxidant activity is measured *in vitro* or *in vivo*, it is evident that tocotrienols have stronger antioxidant activity than tocopherols [Serbinova *et al.,* 1993; Suzuki *et al.,* 1993; Nesaretnam *et al.,* 1993]. Similar results were observed in rat liver mitochondria and the strongest effect was observed with γ-T3 [Kamat & Devasagayam, 1995]. In the other study, α-T3 was shown to be 40 times more effective than α-T in protecting rat liver microsomal membranes against lipid peroxida-

TABLE 3. The content of tocotrienols (T3) and their percentage contribution to the total tocols content (T3 + T) in rye breads of the three rye cultivars (μg/g d.m.).

Rye bread	T3		Total T3	Total T	T3/(T3+T) (%)	αT3/(T3+T) (%)	βT3/(T3+T) (%)	T3/T
	α	β						
A (100%) / I	1.68±0.14^a	1.65±0.16^a	3.33±0.24^a	3.29±0.26^a	50.3	25.4	24.9	1.01
A (95%) / II	0.16±0.02^b	0.55±0.06^b	0.71±0.06^b	0.44±0.04^b	61.7	13.9	47.8	1.61
A (90%) / III	0.17±0.01^b	0.44±0.03^b	0.61±0.03^b	0.82±0.01^b	42.7	11.9	30.8	0.74
A (70%) / IV	n.d.	0.07±0.02^c	0.07±0.02^c	0.14±0.02^b	33.3	0	33.3	0.50
W (100%) / I	1.85±0.08^a	1.53±0.14^a	3.38±0.18^a	3.42±0.06^a	49.7	27.2	22.5	0.99
W (95%) / II	0.41±0.04^b	0.65±0.04^b	1.06±0.08^b	1.01±0.06^b	51.2	19.8	31.4	1.05
W (90%) / III	0.35±0.02^b	0.52±0.02^b	0.87±0.03^b	1.19±0.04^b	42.2	17.0	25.2	0.73
W (70%) / IV	0.14±0.01^c	0.24±0.02^c	0.38±0.02^c	1.27±0.08^b	23.0	8.5	14.5	0.30
DZ (100%) / I	2.39±0.28^a	1.77±0.12^a	3.16±0.38^a	3.27±0.20^a	49.1	37.2	27.5	0.97
DZ (95%) / II	0.24±0.03^b	0.99±0.02^b	1.24±0.03^b	0.60±0.02^b	60.8	11.8	48.5	2.07
DZ (90%) / III	0.24±0.01^b	0.94±0.04^b	1.28±0.03^b	1.11±0.06^b	53.6	10.0	39.3	1.15
DZ (70%) / IV	0.04±0.01^b	0.37±0.05^c	0.42±0.06^c	0.71±0.07^b	37.2	3.5	32.7	0.59

A (100%) / I – rye variety (flour extraction rate) / type of bread. Data expressed as mean ± standard deviation (n=3). Within each column, means with the same letter are not significantly different (p 0.05).

tion and 6.5 times in protecting cytochrome P-450 from oxidative damage [Serbinova *et al.,* 1991]. Also, γ-T3 and α-T3 were able to protect Cu-induced LDL lipoprotein oxidation [Pearce *et al.,* 1992]. Recently, Qureshi *et al.* [2002] confirmed a dose-dependent (25–200 mg/day) suppression of serum cholesterol by a tocotrienol-rich fraction of rice bran in hypercholesterolemic humans following the American Heart Association Step-1 diet.

CONCLUSIONS

The tocotrienols found in whole grains of three rye cultivars were α-T3 and β-T3, while the pool of tocopherol was formed by α-T, β-T and small quantity of γ-T. Tocotrienols found in whole grains or in endosperm with embryo fraction contributed more than 50% to total tocols, however those noted in pericarb with testa fraction were about of 90% of total tocols. The milling process decreased contents of tocotrienols, however milling into flours with extraction rate from 100 to 90% kept the T3/T ratio above one whereas for flour with extraction rate of 70% this ratio was less than one. The baking process (230°C, 35 min) decreased significantly the content of tocotrienols and tocopherols, and the main rye bread tocotrienol's fraction was formed by α-T3 and β-T3.

In the light of the above evidences and results of this study, it can be suggested that consumption of tocotrienols originated from natural sources or tocotrienols supplemented products will probably be in the nearest future an important factor for both prevention and treatment of various human diseases.

ACKNOWLEDGEMENTS

We gratefully acknowledge research grant No. PBZ-KBN-094/P06/2003/13 from the Polish State Committee for Scientific Research. This article is a part of a Ph.D. thesis of A. Michalska.

REFERENCES

1. Andlauer W., Furst P., Does cereals reduce the risk of cancer? Cereal Foods World, 1999, 44, 76–78.
2. Birrringer M., Pfuger P., Kluth D., Landes N., Brigelius-Flohe R., Identities and differences in the metabolism of tocotrienols and tocopherols in HepG2 cells. J. Nutr., 2002, 132, 3113–3118.
3. Burton G.W., Traber M.G., Vitamin E: antioxidant activity, biokinetics and bioavailability. Annu. Rev. Nutr., 1990, 10, 357–382.
4. Bushuk W., Rye production and uses worldwide. Cereal Chem., 2001, 46, 70–73.
5. Chao J.T., Gapor A., Theriault A., Inhibitory effect of delta-tocotrienol, a HMG CoA reductase inhibitor, on monocyte-endothelial cell adhesion. J. Nutr. Sci. Vitamol., 2002, 48, 332–337.
6. Faostat data, 2006, [http://faostat.fao.org].
7. Fratianni A., Caboni M.F., Irano M., Panfili G., A critical comparison between traditional methods and supercritical carbon oxide extraction for the determination of tocochromanols in cereals. Eur. Food Res. Technol., 2002, 215, 353–358.
8. Gąsiorowski H., Żyto – chemia i technologia. Poznań, 1994, PWRiL, p. 106–107 (in Polish).
9. Holasova M., Distribution of tocopherols and tocotrienols in the main products of wheat and rye milling. Potrav. Vedy, 1997, 15, 343–350.
10. Holasova M., Velisek J., Davidek J., Tocopherol and tocotrienol contents in cereal grains. Potrav. Vedy, 1995, 13, 409–417.
11. Horvath G., Wessjohann L., Bigirimana J., Jansen M., Guisez Y., Caubergs R., Horemans N., Differential distribution of tocopherols and tocotrienols in photosynthetic and non-photosynthetic tissues. Phytochemistry, 2006, 67, 1185–1195.
12. Kamal-Eldin A., Appelqvist L.A., The chemistry and antioxidant properties of tocopherols and tocotrienols. Lipids, 1996, 31, 671–701.
13. Kamat J., Devasagayam T.P.A., Tocotrienols from palm oil as potent inhibitors of lipid peroxidation and protein oxidation in rat brain mitochondria. Neurosci. Lett., 1995, 195, 179–182.
14. Khanna S., Roy S., Ryu H., Bahadduri P., Swaan P.W., Ratan R.R., Sen C.K., Molecular basis of vitamin E action: tocotrienol modulates 12-lipoxygenase, a key mediator of glutamate-induced neurodegeneration. J. Biol. Chem., 2003, 278, 43508–43515.
15. Mutalib M.S.A., Khazaai H., Wahle K.W.J., Palm-tocotrienol rich fraction (TRF) is more effective inhibitor of LDL oxidation and endothelial cell lipid peroxidation than alpha-tocopherol *in vitro*. Food Res. Int., 2003, 36, 405–413.
16. Nesaretnam K., Devasagayam T.P.A., Singh B.B., Basiron Y., Influence of palm oil or its tocotrienol-rich fraction on lipid peroxidation potential on rat liver mitochondria and microsomes. Biochem. Mol. Biol. Int., 1993, 30, 159–167.
17. Nilsson M., Aman P., Harkonen H., Bach Knudse K.E., Mazur W., Adlercreutz H., Content of nutrients and lignans in roller milled fractions of rye. J. Sci. Food Agric., 1997, 73, 143–148.
18. Panfili G., Fratianni A., Irano M., Normal phase high-performance liquid chromatography method for the determination of tocopherols and tocotrienols in cereals. J. Agric. Food Chem., 2003, 51, 3940–3944.
19. Peterson D.M., Qureshi A.A., Genotype and environmental effects on barley and oats. Cereal Chem., 1993, 70, 157–162.
20. Pearce B.C., Parker R.A., Deason M.E., Qureshi A.A., Wright J.J., Hypercholesterolemic activity of synthetic and natural tocotrienols. J. Med. Chem., 1992, 35, 3595–3606.
21. Piironen V., Syvaoja E-L., Varo P., Salminen K., Koivistoinen P., Tocopherols and tocotrienols in cereal products from Finland. Cereal Chem., 1986, 63, 78–81.
22. Qureshi A.A., Sami S.A., Salser W.A., Khan F.A., Dose-dependent suppression of serum cholesterol by tocotrienol-rich fraction (TRF25) of rice bran in hypercholesterolemic humans. Atherosclersis, 2002, 161, 199–207.
23. Ryynanen M., Lampi A.-M., Salo-Vaananen P., Ollilainen V., Piironen V., A small-scale sample preparation method with HPLC analysis for determination of tocopherols and tocotrienols in cereals. J. Food Comp. Anal., 2004, 17, 749–765.
24. Schaffer S., Muller W.E., Eckert G.P., Tocotrienols: constitutional effects in aging and disease. J. Nutr., 2005, 135, 151–154.
25. Sen C.K., Khanna S., Roy S., Tocotrienols: Vitamin E beyond tocopherols. Life Sci., 2006, 78, 2088–2098.
26. Serbinova E., Kagan V., Han D., Packer L., Free radical recycling and intramembrane mobility in the antioxidant properties of α-tocopherol and α-tocotrienol. Free Radic. Biol. Med., 1991, 10, 263–275.
27. Serbinova E.A., Tsuchiya M., Goth S., Kagan V.E., Packer L., Antioxidant action of α-tocopherol and α-tocotrienol in membranes. 1993, *in*: Vitamin E in Health and Disease (eds. L. Packer, J. Fuchs). Marcel Dekker Inc., New York, pp. 235–243.
28. Slavin J.L., Mechanisms for the impact of whole grain foods on cancer risk. J. Am. Coll. Nutr. 2000, 19, 300–307.
29. Suzuki Y.J., Tsuchiya M., Wasall S.R., Structural and dynamic membrane properties of α-tocopherol and α-tocotrienol: Implication to the molecular mechanism of their antioxidant potency. Biochemistry, 1993, 32, 10692–10699.
30. Theriault A., Chao JT., Wang Q., Gapor A., Adeli K., Tocotrienols: a review of its therapeutic potential. Clin. Biochem., 1999, 32, 309–319.
31. Wilson T.A., Idreis H.M., Taylor Ch.M., Nicolosi R.J., Whole fat

rice bran reduces the development of early aortic atherosclerosis in hypercholesterolemic hamsters compared with wheat bran. Nutr. Res., 2002, 22, 1319–1332.
32. Zieliński H., Ciska E., Kozłowska H., The cereal grains: focus on vitamin E. Czech J. Food Sci., 2001, 19, 182–188.
33. Zieliński H., Kozłowska H., Lewczuk B., Bioactive compounds in the cereal grains before and after hydrothermal processing. Inn. Food Sci. Emerg. Technol., 2001, 2/3, 159–169.

Received February 2002. Revision received May and accepted June 2007.

TOKOTRIENOLE TRZECH ODMIAN ŻYTA: OD ZIARNIAKA DO CHLEBA

Henryk Zieliński, Anna Michalska, Dorota Szawara-Nowak, Wiesław Wiczkowski, Mariusz K. Piskuła

Instytut Rozrodu Zwierząt i Badań Żywności Polskiej Akademii Nauk w Olsztynie

W pracy przedstawiono udział tokotrienoli w ogólnej puli tokoli składających się na aktywność witaminy E w trzech krajowych odmianach żyta, produktach przemiału oraz chlebach wypieczonych metodą tradycyjną bez dodatku drożdży. Poziom tokotrienoli (T3) (α-T3, β-T3, γ-T3) i tokoferoli (T) (α-T, β-T, γ-T, δ-T) analizowano metodą HPLC. W ziarniakach i jego frakcjach morfologicznych spośród analizowanych tokotrienoli dominującym był α-T3 i β-T3. W ziarniakach zawartość tokotrienoli była wyższa niż tokoferoli a proces przemiału ziarna żyta w kierunku mąk jasnych powodował obniżenie ich zawartości. Dalszy spadek zawartości tych związków następował w wyniku wypieku chleba. Stwierdzono, że chleb wypieczony z mąki pochodzącej z pełnego przemiału (wyciąg maki 100%) charakteryzował się ich najwyższą zawartością tokotrienoli.