Oat Tocols: Concentration and Stability in Oat Products and Distribution Within the Kernel[1]

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ABSTRACT

To determine the stability of tocols (vitamin E) in oat products under various storage conditions, several oat products were stored in jars at −24°C or in jars or envelopes at room temperature for up to seven months. At approximately monthly intervals, products were ground and tocols were extracted with methanol and analyzed by high-performance liquid chromatography. Tocols were stable for seven months in all products in jars at −24°C. At room temperature, all tocols degraded in all processed products, but were stable in undried groats. Tocols degraded faster in envelopes than in jars at room temperature, indicating that air may be involved in the degradation process. α-Tocopherol and α-tocotrienol decreased faster than the other homologues during room temperature storage in envelopes, indicating differential stabilities. Analysis of hand-dissected fractions indicated that the germ was the location for most of the α- and γ-tocopherol. Tocotrienols were concentrated in the endosperm and absent from the germ.

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Tocols (vitamin E) occur in at least eight naturally occurring forms, α-, β-, γ-, and δ-tocopherol and α-, β-, γ-, and δ-tocotrienol (Barnes 1983a). These tocols are physiologically active in alleviating symptoms of vitamin E deficiency. Vitamin E is an important antioxidant and free radical scavenger, and its presence has been linked to prevention of chronic disease and premature ageing, cancer, cardiovascular disease, and stroke (Packer and Fuchs 1993). Recently, several reports have implicated tocotrienols as cholesterol synthesis inhibitors (Qureshi et al 1986, Pearce et al 1992, Wang et al 1993).

Cereal grains are important sources of tocols. Total tocol concentration in oat ranges from about 20 to 30 mg kg^{-1}, with α-tocotrienol as the predominant homologue (Lásztity et al 1980, Barnes 1983b, Peterson and Qureshi 1993). However, there is little information about the effects of processing and storage on the tocol concentration in oat. The production of rolled oats had little effect on α-tocopherol concentration, but more extensive processing resulted in substantial losses (Herting and Drury 1969). Piironen et al (1986) found 32 mg kg^{-1} total tocols in rolled oats with a distribution of homologues similar to that of oat grain, but in puffed oats, the α-tocotrienol concentration was lower. In wheat flour and rye and barley meals, tocols degraded with time (Piironen et al 1988, Työppönen and Hakkarainen 1985), but they were stable in intact barley grain over 10 months (Hakkarainen et al 1983). A six-year stored oat grain sample was 73% lower in α-tocopherol than one of recent harvest (Herting and Drury 1969).

The objective of this study was to examine the effects of different storage conditions on the stability of tocols in unprocessed oat groats and several oat products. Tocol concentration of hand-dissected oat groats was also measured to explain differences observed among some of the oat products.

MATERIALS AND METHODS

Freshly processed samples of oat groats and products (undried groats, dried groats, flour, bran, rolled oats, quick oats, and instant oats) from one production date were obtained from The Quaker Oats Company. Briefly, the processing of undried groats is as follows. Groats are heated from 82 up to 105–115°C over 90–120 min, driving the moisture down 7–9%. For quick and instant oats, the dried groats are steel cut. Then whole or cut groats are steamed for 8–12 min, bringing the moisture back to 10–11%, and then rolled. Rolled oat flakes, produced from whole groats, are thicker than quick and instant oat flakes. Bran and flour are produced by grinding and sieving quick oats. The coarse outer layers of the endosperm that are held on a 540-μm sieve are defined as bran, and the finer starchy endosperm material that passes through the sieve is defined as flour.

Moisture levels of the samples as received were determined, and the samples were subdivided into jars or paper coin envelopes for storage. Three storage conditions were compared: capped jars at −24°C, capped jars at room temperature, and envelopes at room temperature. Immediately upon receipt of the samples, and at approximately monthly intervals thereafter, a sample of each product from each storage condition was analyzed in duplicate. At seven months (the final sampling), two samples of each product were analyzed in duplicate.

Extraction and analysis of the groat and product samples for tocols was previously described (Peterson and Qureshi 1993). Briefly, duplicate 0.5-g samples were ground and extracted with methanol. Supernatants were dried under vacuum, and the residues were redissolved in hexane. Tocols were separated by

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high-performance liquid chromatography (HPLC) on a silica column using a mobile phase of 0.5% isopropanol in hexane and detected fluorimetrically. Ogle oat kernels were hand-dehulled with a small wringer; the groats were tempered in a petri dish; and germs excised with a small spatula. Samples (0.5 g for endosperm and hull, 0.1 g for germ) were extracted and analyzed as described above. Results are reported on an as is weight basis.

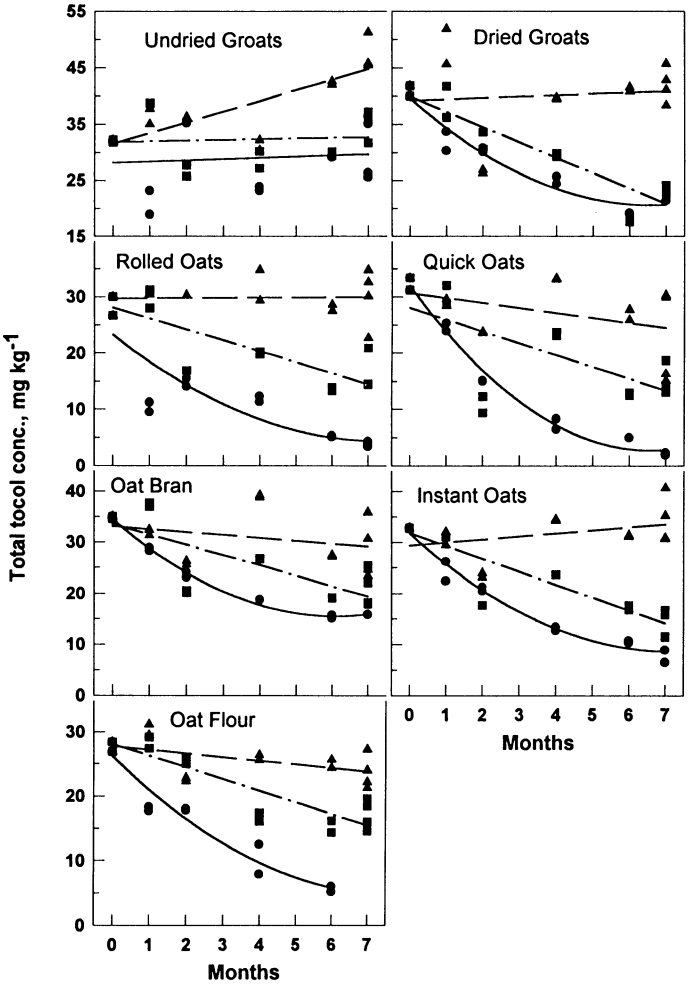

Fig. 1. Effects of storage condition on total tocol concentration of several oat products over seven months of storage. ▲ = Jars at −24°C; ■ = jars at room temperature; ● = envelopes at room temperature. The significance of the linear and quadratic fit to the data is shown in Table III.

RESULTS AND DISCUSSION

Analysis of the fresh products revealed that total tocol concentration was highest in the dried groats, about 41 mg kg^{-1}, significantly lower in undried groats, bran, and quick oats (32–35 mg kg^{-1}), and lowest in flour and rolled oats (28 mg kg^{-1}) (Table I). The higher total tocol concentration in dried groats may, in part, be a result of lower moisture (6 vs. 8% in undried groats). Groats were steamed before flaking, increasing the moisture percentage to 10%, which partly accounts for the lower tocol concentration in the flaked products. The difference in tocol concentration between regular rolled oats and quick oats is unexplained, because the only processing differences between them are that for quick oats, the groats are steel cut before flaking and the flakes are thinner. The higher tocol concentration of bran than flour indicates an uneven distribution of tocols between the inner and outer layers of the endosperm.

Milled oat products and dried groats had lower percentages of α-tocopherol and α-tocotrienol than did the undried groats (Table I). β-Tocopherol and δ-tocotrienol were almost absent in undried groats as compared to substantial levels in all other products. We have found a significant loss of the α-homologues and increased amounts of β-tocopherol when ground oat groats are heated at 130°C for 2 hr (unpublished data). Heat-induced demethylation of α-homologues to di- and mono-methyl homologues is unlikely. Possibly, bound unextractable forms of β-tocopherol and δ-tocotrienol are released by heating, concomitantly with the destruction of the α-homologues. α-Tocopherol is located almost exclusively in the germ (Table II). Yiu (1986) showed by fluorescence microscopy that lipid bodies were destroyed in flaked oats and replaced by pools of aggregated lipid-staining material. The higher percentage of α-tocopherol in flour than in the other products may have resulted from adhesion of the leaked oil to the starch granules.

Analysis of hand-dissected oat fractions revealed that the hulls were almost devoid of tocols (Table II). This contrasts with barley, where hulls had considerable quantities of all eight homologues (Peterson 1994). The germ was the location of most of the α- and γ-tocopherol, whereas almost all tocotrienols were in the endosperm. The differential distribution of tocopherols and tocotrienols between germ and endosperm is similar to that observed for other cereal grains (Barnes 1983a).

Figure 1 and Table III show the effects of time and storage conditions on the concentration of total tocols in the oat products.

TABLE I
Tocol Composition of Fresh Oat Products

Product	Total Tocol (mg kg^{-1})	Percentage of Total Tocol							
		α-T[a]	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	δ-T3
Undried groats	32.0 b[b]	22.3 a	66.5 a	0.7 e	6.8 a	3.6 a	0.0 c	0.0 a	0.0 c
Dried groats	40.9 a	20.0 b	55.7 d	10.9 b	5.0 c	3.4 ab	0.6 b	0.0 a	4.4 a
Flour	27.7 c	23.0 a	53.8 e	9.7 cd	5.3 bc	3.9 a	0.0 c	1.1 a	3.3 b
Bran	34.8 b	15.1 e	63.8 b	10.0 c	5.6 b	2.3 c	0.0 c	0.0 a	3.1 b
Rolled oats	28.3 c	17.1 d	60.1 c	9.5 d	6.9 a	3.5 a	0.0 c	0.0 a	2.9 b
Quick oats	32.3 b	18.9 c	52.8 e	12.5 a	6.4 a	3.8 a	1.7 a	0.0 a	3.6 ab
Instant oats	32.7 b	18.8 c	58.8 c	9.7 cd	5.6 b	2.8 bc	0.0 c	0.0 a	4.3 a

[a]T = tocopherol, T3 = tocotrienol.
[b]Within a column, means followed by the same letter are not significant at $P = 0.05$.

TABLE II
Tocol Concentration (mg kg^{-1}) of Hand-Dissected Oat (cv. Ogle) Fractions[a]

Fraction	α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	δ-T3	Total-T
Hulls	0.95	1.69	0.00	0.00	0.00	0.27	0.00	0.14	3.05
Hulls	0.50	1.05	0.25	0.00	0.00	0.37	0.00	0.14	2.31
Germ	107.94	0.00	0.00	1.43	20.18	1.51	0.00	0.18	131.23
Endosperm	3.37	32.14	0.15	2.24	0.61	0.24	0.00	0.18	38.92
Endosperm	3.58	37.52	0.00	2.48	0.68	0.32	0.00	0.28	44.85

[a]Duplicate fractions for hull and endosperm. T = tocopherol, T3 = tocotrienol.

Tocols were stable for seven months in all products at −24°C; their concentration in undried groats even increased. With the notable exception of undried groats, tocol concentrations of all products decreased at room temperature. This indicates that heating the groats for processing rendered the tocols unstable at room temperature. By seven months, tocol concentrations of all products except groats had declined to 5–10 mg kg^{-1}. The decline was initially more rapid in the envelopes than in sealed jars. This indicates that exposure to air may be a significant factor in the rate of degradation. The equations describing decreases in tocol concentration in envelope-stored samples had significant quadratic terms, whereas for those stored in jars, the decrease was linear (Table III). The tocol concentration of samples stored at −24°C did not change, except for an increase in undried groats.

The degradation rate of tocol homologues was not uniform, and there were differences between storage conditions. Table IV shows linear regression equations for all homologues where the change with time, as a percent of total tocols, was statistically significant. All products stored in envelopes at room temperature, except undried groats, showed a percentage decrease in α-tocopherol and/or α-tocotrienol, the major isomers. By contrast, γ-tocopherol, β-tocopherol, and β-tocotrienol increased as a percentage of the total in many of these samples. This indicated greater stability of the γ- and β- homologues than the α-homologues. All homologues declined in absolute values, except γ-tocopherol, which for some products increased slightly (data not shown). In contrast to envelope storage, samples in jars at room temperature declined only in δ- tocotrienol as a percentage of the total. The slopes of these regression equations, although significantly different from 0, were much lower than those for the α-isomers of the envelope-stored samples. Exposure to air had a greater influence on the degradation of α-tocopherol and α-tocotrienol than on the other homologues.

An explanation for this differential degradation of tocol homologues may lie in differences in their redox potentials and reactivities. Second-order rate constants for the reaction of tocopherol homologues with free radicals (Burton et al 1985, Mukai et al 1989) and singlet oxygen (Grams and Eskins 1972, Mukai et al 1991) were determined, and decreased in the order $\alpha>\beta>\gamma>\delta$. These rate constants were negatively correlated with the redox potentials (Mukai et al 1991). α-Tocopherol, with the highest rate constant and lowest redox potential, is most likely to degrade in the presence of air. Likewise, antioxidant activities of tocotrienol homologues were measured in the order $\alpha>\beta>\gamma>\delta$ (Seher et al 1973), indicating the greater likelihood of degradation of the α- homologue. A comparison of the relative antioxidant activity of α-tocopherol and α-tocotrienol indicated much higher activity by α-tocotrienol (Serbinova et al 1993). The equations (Table IV) showed greater slopes for α-tocotrienol than for α-tocopherol degradation in five of the seven products, correlating with its higher antioxidant activity.

A differential degradation of homologues was also noted by Piironen et al (1988), who reported that in wheat flour and rye whole meal, α-tocopherol and α-tocotrienol were degraded faster than β-tocopherol and β-tocotrienol. In contrast, Työppönen and Hakkarainen (1985) found that the tocol homologue distribution was unchanged when milled barley was stored at room temperature, but at temperatures above 90°C, α-tocotrienol was more stable than other isomers. We found, in contrast to oat, that heating ground barley did not degrade α-tocotrienol (unpublished

TABLE III
Effects of Storage Time and Condition on Total Tocols of Oat Products[a]

Product	Storage Condition		
	Envelopes, room temp.	Jars, freezer	Jars, room temp.
Undried groats	$y = 28 + 0.2x$	$*y = 32 + 1.9x$	$y = 32 + 0.1x$
Dried groats	$*y = 40 - 5.8x + 0.4x^2$	$y = 39 + 0.2x$	$*y = 40 - 2.7x$
Flour	$*y = 26 - 5.6x + 0.4x^2$	$y = 27 - 0.6x$	$*y = 28 - 1.8x$
Bran	$*y = 34 - 6.2x + 0.5x^2$	$y = 33 - 0.6x$	$*y = 33 - 2.0x$
Rolled oats	$*y = 23 - 5.2x + 0.4x^2$	$y = 30$	$*y = 28 - 1.9x$
Quick oats	$*y = 32 - 8.9x + 0.7x^2$	$y = 31 - 0.9x$	$*y = 28 - 2.1x$
Instant oats	$*y = 32 - 6.5x + 0.5x^2$	$y = 29 + 0.6x$	$*y = 32 - 2.5x$

[a]* = Equation significant at $P < 0.05$. y = Total tocol concentration, mg kg^{-1}. x = Months of storage.

TABLE IV
Differential Degradation of Tocols at Room Temperature as Affected by Storage Container[a]

Storage Container	Product	Decreasing Percentage		Increasing Percentage	
		Regression	R^2	Regression	R^2
Envelopes	Dried groats	$\%\alpha\text{-T} = 19.9 - 0.6x$[b]	0.68	$\%\gamma\text{-T} = 3.1 + 0.5x$	0.63
	Flour	$\%\alpha\text{-T} = 23.0 - 2.3x$	0.97	$\%\beta\text{-T} = 10.7 + 4.7x$	0.90
		$\%\alpha\text{-T3} = 53.9 - 4.3x$	0.94	$\%\gamma\text{-T} = 4.1 + 0.8x$	0.89
				$\%\beta\text{-T3} = 5.7 + 0.9x$	0.82
	Bran	$\%\alpha\text{-T3} = 60.5 - 1.4x$	0.60		
	Rolled oats	$\%\alpha\text{-T} = 16.2 - 1.7x$	0.71	$\%\gamma\text{-T} = -0.7 + 4.4x$	0.50
		$\%\alpha\text{-T3} = 56.3 - 6.3x$	0.89	$\%\beta\text{-T3} = 7.6 + 1.5x$	0.69
	Quick oats	$\%\alpha\text{-T} = 19.2 - 2.5x$	0.57	$\%\beta\text{-T} = 10.3 + 9.6x$	0.94
		$\%\alpha\text{-T3} = 52.7 - 8.0x$	0.92		
	Instant oats	$\%\alpha\text{-T} = 18.8 - 1.2x$	0.76	$\%\beta\text{-T} = 14.2 + 2.7x$	0.67
		$\%\alpha\text{-T3} = 54.5 - 4.0x$	0.81	$\%\gamma\text{-T} = 1.9 + 1.7x$	0.77
Jars	Dried groats	$\%\delta\text{-T3} = 4.3 - 0.6x$	0.80		
	Flour	$\%\delta\text{-T3} = 3.4 - 0.5x$	0.72	$\%\gamma\text{-T} = 3.2 + 0.6x$	0.65
				$\%\beta\text{-T3} = 5.3 + 0.2x$	0.59
	Bran	$\%\delta\text{-T3} = 2.7 - 0.4x$	0.49		
	Rolled oats	$\%\delta\text{-T3} = 2.7 - 0.3x$	0.46[c]		
	Quick oats	$\%\delta\text{-T3} = 3.1 - 0.4x$	0.46		
	Instant oats	$\%\delta\text{-T3} = 4.2 - 0.6x$	0.67		

[a]Significant ($P < 0.01$) linear regression equations for individual tocols (as percent of total tocols) of products that degraded under the indicated storage conditions. T = tocopherol, T3 = tocotrienol.
[b]x = Months of storage.
[c]$P = 0.011$.

data). Total tocols of 20% moisture barley in airtight containers increased slightly during seven months of storage, and then decreased slowly (Hakkarainen et al 1983). The percentage distribution of isomers was stable. At 28% moisture, however, tocol degradation began immediately, and tocotrienol concentration decreased faster than tocopherol concentration. These moisture levels were considerably higher than those in the present study or of normal grain storage conditions.

Heating of oat groats before further processing is essential to inactivate lipase and prevent the development of rancidity. Given this requirement, manufacturers of oat products may wish to investigate the tocol content of their products stored in their packaging for the expected shelf life to determine the stability of vitamin E levels.

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