Tocopherols and Tocotrienols in Cereal Products from Finland

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ABSTRACT

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This study is part of a comprehensive survey carried out to determine the tocopherol and tocotrienol contents of Finnish foods. They were analyzed from 39 milling, flour-based, and bakery products using a high-performance liquid chromatographic method. Their compositions were highly variable. Among the milling and flour-based products α-tocopherol was predominant in wheat germ only. Wheat flour of ash content 1.2–1.4% and rye flour of ash content 0.9–1.0% contained about equal amounts of α-tocopherol and β-tocotrienol. In most other milling products α-tocotrienol or β-tocotrienol predominated. The richest sources of vitamin E were wheat germ, bran, meal and flour of ash content 1.2–1.4%, rye meal, and oat products (vitamin E content ≥1.3 mg of α-tocopherol equivalents/100 g), and the poorest sources were white wheat flour, macaroni, semolina, polished rice, rice crispies, whole grain millet, and corn flakes (≤0.3 mg). The composition and content of vitamin E in bakery products were greatly dependent on the type and amount of added fat. For most bakery products the vitamin E content ranged from 0.8 to 1.5 mg of α-tocopherol equivalents/100 g. Cereal products make a substantial contribution to the vitamin E intake of Finns.

Cereal grains are relatively good sources of vitamin E (McLaughlin and Weihrauch 1979, Bauernfeind 1980). Their vitamin E composition is fairly complex; in barley, all four tocopherols and four tocotrienols have been found (Morrison 1977). The vitamin E content of cereal grains is influenced by plant genetics, weather conditions during the growing and harvest seasons, the state of maturity at harvest, and handling after harvesting (Herting and Drury 1969, Slover and Lehmann 1972, Bauernfeind 1980, Davis et al 1980, Karaiwanow et al 1982, Hakkarainen et al 1983).

The tocopherol and tocotrienol contents of different fractions of the kernel differ from each other (Hall and Laidman 1968, Grams et al 1970, Morrison et al 1982). The variation between different milling products of the same cereal can be great (Herting and Drury 1969, Slover et al 1969, Lorenz and Limjaroenrat 1974, Morrison et al 1982). Furthermore, vitamin E losses may vary as a result of differing processing techniques. The variation between the products of different processors has been shown to be great (Herting and Drury 1969).

Vitamin E in bakery products usually is derived from flour, fat, and eggs. The vitamin E content may vary greatly in relation to the fat content. Fat may be the major source of vitamin E in some bakery products (Slover et al 1969).

In this study the most important Finnish flours, other milling products, special products, and bakery products were analyzed for tocopherols and tocotrienols. The study is a part of a comprehensive survey carried out to determine the tocopherol and tocotrienol content of Finnish foods (Piironen et al 1986, Syväoja et al 1985a–c, 1986).

MATERIALS AND METHODS

Sampling

The sampling system was designed to produce composite samples of various commercial food items sold by the four major food chain stores in Finland. Each food item listed in the tables (Tables I and II) represents a composite of four commercial food products from the leading brand of each chain. The food products were sampled in 1981 and 1982. Five items (rye meal sampled in 1983, popcorn, doughnuts and sponge cakes with fruit and cream fillings sampled in 1984) represent a composite of ten commercial products bought according to the above principle from ten different stores of the four chains. Food products for each composite item were purchased on the same day.

Pretreatment

Flours required no pretreatment. Macaroni, rice, whole grain buckwheat, and whole grain millet were homogenized in a mill usually used for falling number determinations (Koneteollisuus Oy, Finland). A blender was used for homogenization of breakfast cereals (Bamix, Switzerland) and bakery products (Kenwood, England or Braun Multiquick, West Germany).

Homogenized subsamples (4 or 10) were pooled (subsamples of rye meal, puffed oats, and wheat flour of ash content 1.2–1.4% were analyzed separately in 1983), and vacuum-packed portions, each of approximately 100 g in aluminum laminate bags, were stored at −18° C for generally no more than two weeks until analyzed.

Analytical Method

Tocopherols and tocotrienols were analyzed by the high-performance liquid chromatographic method previously described in detail for diet samples (Piironen et al 1984). A room temperature saponification was used for sample preparation. The samples were allowed to rest in alcoholic solution with ascorbic acid for about 20 min before the addition of potassium hydroxide. After saponification, tocopherols and tocotrienols were extracted with *n*-hexane, and the washed and evaporated extracts were usually redissolved in 25 ml of *n*-hexane. The saponification conditions were tested as for diet samples. Separation of tocopherols and tocotrienols was carried out in a 5 μm LiChrosorb Si 60 column, 25 cm × 4 mm id (Merck, Darmstadt) maintained at 32 or 38° C. The column was developed with *n*-hexane-diisopropylether (93:7) at a flow rate of 1.9 or 2.1 ml/min. Determinations were made in duplicate.

The consistency of the results was tested by analyzing the same wheat flour sample seven times during a three-week period. The coefficients of variation for α-tocopherol, α-tocotrienol, β-tocopherol, and β-tocotrienol were 5.3, 3.4, 2.5, and 5.0%, respectively. Recoveries of α-, β-, γ-, and δ-tocopherols were determined by adding known amounts to rye bread and rye flour samples and by carrying them through the whole procedure. The recoveries of the added α-, β-, γ-, and δ-tocopherols (n = 8) were 94.3, 95.2, 96.5, and 95.7%, respectively. Because of a lack of pure tocotrienol standards, recoveries of tocotrienols could not be determined. They were, however, found to behave very similarly to the corresponding tocopherols.

The moisture content of the samples was determined using the ICC (1976) approved method no. 110/1.

RESULTS AND DISCUSSION

The vitamin E composition of flours, other milling products and special products is given in Table I. δ-Tocotrienol was not quantified. A peak eluated in the place of δ-tocotrienol was, however, detected in barley meal and rice products. α-Tocopherol was the predominant tocopherol in wheat germ only. Wheat flour

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of ash content 1.2–1.4% and rye flour of ash content 0.9–1.0% contained about equal amounts of α-tocopherol and β-tocotrienol. β-Tocotrienol predominated in other wheat milling products; α-tocotrienol in rye meal, barley meal, and oat products; γ-tocopherol in whole-meal buckwheat, whole-meal millet, and popcorn; and γ-tocotrienol in rice products and corn flakes.

The rate of extraction in wheat milling had a great effect on the contents of α-tocopherol and total biologically active tocopherols

TABLE I
Tocopherol and Tocotrienol Content of Flours, Other Milling Products, and Special Products

Item	Year	Moisture (%)	Tocopherols (T) and Tocotrienols (T3), mg/100 g Fresh Product							Vitamin E, mg of α-T eq[a]
			α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	
Wheat meal	1981	12.3	1.04	0.42	0.57	2.06	...	...	<0.01	1.50
	1982	10.7	0.95	0.40	0.50	2.16	...	...	...	1.38
	$\bar{x}$	11.5	1.0	0.4	0.54	2.1	...	...	<0.1	1.4
Wheat flour,[b] 1.2–1.4% ash	1981	12.2	1.62	0.28	0.87	1.73	...	...	...	2.14
	1982	11.6	1.59	0.31	0.85	1.93	...	...	...	2.12
	1983	11.5	1.51	0.35	0.77	1.54	...	...	...	2.00
	$\bar{x}$	11.8	1.6	0.3	0.8	1.7	...	...	...	2.1
Wheat flour,[c] approximately 0.7% ash	1981	12.9	0.41	0.15	0.25	1.50	...	...	...	0.63
	1982	12.3	0.36	0.16	0.19	1.51	...	...	...	0.56
	$\bar{x}$	12.6	0.4	0.2	0.2	1.5	...	...	...	0.6
Wheat flour,[d] approximately 0.5% ash	1981	12.6	0.19	0.14	0.11	1.35	...	...	...	0.34
	1982	12.2	0.16	0.12	0.09	1.43	...	...	...	0.30
	$\bar{x}$	12.4	0.2	0.1	0.1	1.4	...	...	...	0.3
Wheat bran	1981	11.0	1.63	1.39	0.82	4.92	...	...	...	2.62
	1982	10.2	1.63	1.53	0.75	6.23	...	...	...	2.70
	$\bar{x}$	10.6	1.6	1.5	0.8	5.6	...	...	...	2.7
Wheat germ	1981	10.1	23.88	0.20	9.54	0.86	...	...	<0.01	27.80
	1982	9.9	20.28	0.32	7.65	1.05	...	...	<0.01	23.49
	$\bar{x}$	10.0	22.1	0.3	8.6	1.0	...	...	<0.1	25.7
Rye meal	1981	12.0	1.06	1.53	0.33	1.26	...	...	...	1.71
	1982	10.9	0.99	1.38	0.31	1.13	...	...	...	1.59
	1983	10.8	1.00	1.42	0.30	1.00	...	...	...	1.60
	$\bar{x}$	11.2	1.0	1.4	0.3	1.1	...	...	...	1.6
Rye flour,[e] 0.9–1.0% ash	1981	11.8	0.54	0.44	0.28	0.69	...	...	...	0.82
	1982	11.8	0.56	0.42	0.24	0.58	...	...	...	0.81
	$\bar{x}$	11.8	0.6	0.4	0.3	0.6	...	...	...	0.8
Rye, rolled	1983	11.0	0.39	1.46	0.11	0.94	...	...	...	0.92
Barley meal	1981	11.0	0.29	1.48	0.03	0.59	0.11	0.52	<0.01	0.79
	1982	10.6	0.30	1.77	0.02	0.51	0.13	0.57	<0.01	0.88
	$\bar{x}$	10.8	0.3	1.6	<0.1	0.6	0.1	0.6	<0.1	0.8
Oats, rolled	1981	11.1	0.77	1.88	0.07	0.22	...	<0.01	...	1.37
	1982	10.0	0.94	2.16	0.07	0.26	...	<0.01	...	1.63
	1983	8.9	0.83	2.01	0.06	0.27	...	<0.01	...	1.47
	$\bar{x}$	10.0	0.8	2.0	0.1	0.3	...	<0.1	...	1.5
Four-grain cereals, rolled[f]	1983	11.3	0.42	1.36	0.12	0.97	...	0.08	...	0.93
Rice, brown	1981	14.1	0.69	0.34	0.06	<0.01	0.10	0.84	<0.01	0.84
	1982	14.0	0.57	0.35	0.03	<0.01	0.07	0.51	<0.01	0.70
	$\bar{x}$	14.1	0.6	0.4	0.1	<0.01	0.1	0.7	<0.1	0.8
Rice, polished	1981	14.4	0.02	0.06	<0.01	<0.01	0.01	<0.29	...	0.04
	1982	13.9	0.06	0.08	<0.01	<0.01	0.02	0.33	<0.01	0.09
	$\bar{x}$	14.2	<0.1	0.1	<0.1	<0.1	<0.1	0.3	<0.1	0.1
Buckwheat, whole grain	1981	11.4	0.19	<0.01	...	...	5.49	<0.01	0.26	0.74
	1982	11.7	0.24	<0.01	<0.01	...	6.05	0.01	0.27	0.85
	$\bar{x}$	11.6	0.2	<0.1	<0.1	...	5.7	<0.1	0.3	0.8
Millet, whole grain	1981	13.0	0.04	...	0.05	...	1.65	<0.01	0.53	0.23
	1982	10.9	0.08	<0.01	0.05	...	1.76	<0.01	0.58	0.28
	$\bar{x}$	11.1	0.1	<0.1	0.1	...	1.7	<0.1	0.6	0.3
Semolina	1982	11.5	0.15	0.11	0.08	1.33	...	...	...	0.28
Macaroni	1981	11.4	0.14	0.08	0.12	0.91	...	...	...	0.26
	1982	11.2	0.09	0.05	0.08	0.74	...	...	...	0.18
	$\bar{x}$	11.3	0.1	0.1	0.1	0.8	...	...	...	0.2
Corn flakes	1981	3.8	0.02	0.22	...	...	0.09	0.38	0.04	0.10
	1982	4.9	0.02	0.18	...	...	0.05	0.33	<0.01	0.08
	$\bar{x}$	4.4	<0.1	0.20	...	...	0.1	0.4	<0.1	0.1
Popcorn	1984	4.7	0.35	0.27	0.03	...	2.61	0.23	0.15	0.71
Rice crispies	1981	3.7	0.26	0.33	0.02	0.01	0.03	0.59	<0.01	0.38
	1982	4.4	0.14	0.17	0.02	0.01	0.02	0.35	<0.01	0.21
	$\bar{x}$	4.1	0.2	0.3	<0.1	<0.1	<0.1	0.5	<0.1	0.3
Oats, puffed	1981	6.8	0.90	1.45	0.09	0.31	...	0.02	<0.01	1.39
	1982	4.6	0.66	1.34	0.08	0.27	...	0.04	...	1.11
	$\bar{x}$	5.7	0.8	1.4	0.1	0.3	...	<0.1	<0.1	1.3

[a] The total biologically active tocopherols (mg of α-tocopherol equivalents/100 g fresh product) were calculated according to McLaughlin and Weihrauch (1979).
[b] Milled mainly from the aleurone tissue.
[c] Extraction rate approximately 78%.
[d] Extraction rate approximately 74%.
[e] Extraction rate approximately 70%.
[f] Mixture of wheat, rye, barley, and oats.

(Table I). The total biologically active tocopherols were calculated according to McLaughlin and Weihrauch (1979). The calculated values are sums of the weight in milligrams of each tocopherol and tocotrienol multiplied by the appropriate biological activity factor. The factor is 1 for α-tocopherol, 0.3 for α-tocotrienol, 0.4 for β-tocopherol, 0.05 for β-tocotrienol, 0.1 for γ-tocopherol, 0.01 for γ-tocotrienol, and 0.01 for δ-tocopherol (McLaughlin and Weihrauch 1979). Compared with other wheat flours and wheat meal, the flour milled mainly from the aleurone layer (ash content 1.2–1.4%) had the highest contents of α-tocopherol and total biologically active tocopherols. As expected, tocopherols and tocotrienols in macaroni and semolina were comparable with those of the most refined wheat flours. These results concerning wheat milling products are in accordance with the previous reports dealing with the distribution of tocopherols and tocotrienols in wheat grain. α-Tocopherol is concentrated in the metabolically active parts of the grain, germ, and aleurone tissue (Hall and Laidman 1968, Morrison et al 1982).

Lowering the extraction rate in rye milling also had noticeable effects on the vitamin E content of the flours. Concentrations of α-tocopherol, α-tocotrienol, β-tocopherol, and β-tocotrienol were respectively 40, 71, 0, and 45% lower in refined rye flour than in rye meal. The refining of rice caused extremely high losses of tocopherols and tocotrienols.

The richest sources of vitamin E among the flours, other milling products, and special products analyzed were wheat germ, wheat bran, wheat meal, wheat flour of ash content 1.2–1.4%, rye meal, and oat products (total biologically active tocopherols ≥1.3 mg α-tocopherol equivalents/100 g). The poorest sources were wheat flour of ash content 0.5%, macaroni, semolina, polished rice, rice crispies, whole grain millet and corn flakes (≤0.3 mg of α-tocopherol equivalents/100 g).

TABLE II
Tocopherol and Tocotrienol Content of Bakery Products

Item	Year	Moisture (%)	Tocopherols (T) and Tocotrienols (T3), mg/100 g Fresh Product α-T	α-T3	β-T	β-T3	γ-T	γ-T3	δ-T	Vitamin E, mg of α-T eq[a]
Rye bread, sour	1981	33.0	0.76	0.93	0.23	0.78	···	···	<0.01	1.17
	1982	33.6	0.61	0.81	0.19	0.69	<0.01	<0.01	<0.01	0.96
	1983	33.2	0.73	0.99	0.20	0.69	<0.01	<0.01	<0.01	1.15
	x̄	33.3	0.7	0.9	0.2	0.7	<0.1	<0.1	<0.1	1.1
Rye bread, brown	1981	31.2	0.97	0.96	0.28	0.92	···	···	<0.01	1.42
	1982	32.4	0.64	0.79	0.21	0.75	<0.01	<0.01	<0.01	1.00
	1983	32.4	0.70	0.85	0.22	0.65	<0.01	<0.01	<0.01	1.12
	x̄	32.0	0.8	0.9	0.2	0.8	<0.1	<0.1	<0.1	1.2
Wheat bread	1981	34.7	0.36	0.12	0.20	0.95	0.31	···	0.09	0.56
	1982	35.8	0.37	0.11	0.16	0.92	0.21	···	0.05	0.54
	x̄	35.3	0.4	0.1	0.2	0.9	0.3	···	0.1	0.6
Wheat bread, dark	1981	37.8	0.60	0.10	0.37	1.04	0.20	···	0.08	0.85
	1982	38.4	0.54	0.13	0.28	0.94	0.17	···	0.04	0.76
	x̄	38.1	0.6	0.1	0.3	1.0	0.2	···	0.1	0.8
Brown bread, seasoned	1981	34.0	0.77	0.20	0.40	1.00	0.35	0.16	0.07	1.08
	1982	34.3	0.66	0.20	0.32	0.97	0.25	0.16	0.05	0.92
	x̄	34.2	0.7	0.2	0.4	1.0	0.3	0.2	0.1	1.0
Hard tack	1981	8.6	0.50	0.77	0.20	0.79	···	···	···	0.85
	1982	9.2	0.44	0.62	0.17	0.63	···	···	···	0.73
	x̄	8.9	0.5	0.7	0.2	0.7	···	···	···	0.8
Rye crisp	1981	4.8	0.64	1.28	0.21	0.93	···	···	···	1.16
	1982	5.1	0.74	1.23	0.23	0.92	···	···	···	1.25
	x̄	5.0	0.7	1.3	0.2	0.9	···	···	···	1.2
Whole wheat rusk	1981	9.7	0.42	0.16	0.32	1.34	0.65	···	0.33	0.73
	1982	8.6	0.38	0.15	0.26	1.38	0.77	···	0.37	0.68
	x̄	9.1	0.4	0.2	0.3	1.4	0.7	···	0.4	0.7
Sweet wheat bread, approximately 7% fat	1981	28.3	0.29	0.05	0.13	0.74	0.39	···	0.10	0.43
	1982	28.4	0.42	0.09	0.12	0.76	0.33	<0.01	0.07	0.57
	x̄	28.4	0.4	0.1	0.1	0.8	0.4	<0.1	0.1	0.5
Sweet wheat bread, approximately 10% fat	1981	27.1	0.99	0.08	0.16	0.82	1.17	<0.01	0.14	1.24
	1982	26.6	0.66	0.11	0.13	0.75	0.83	<0.01	0.17	0.87
	x̄	26.9	0.8	0.1	0.2	0.8	1.0	<0.1	0.2	1.1
Doughnut	1981	28.1	1.31	0.10	0.18	0.71	2.16	···	0.28	1.67
	1984	29.0	0.67	0.11	0.15	0.68	0.85	<0.01	0.17	0.88
	x̄	28.6	1.0	0.1	0.2	0.7	1.5	<0.1	0.2	1.3
Danish pastry	1981	26.6	0.92	0.12	0.13	0.59	1.49	<0.01	0.09	1.19
	1982	25.0	0.79	0.11	0.11	0.62	0.75	<0.01	0.05	0.98
	x̄	25.6	0.9	0.1	0.1	0.6	1.1	<0.1	0.1	1.1
Sponge cake	1981	21.0	1.50	0.19	0.13	0.43	1.64	<0.01	0.16	1.80
	1982	20.6	1.40	0.13	0.08	0.40	1.28	<0.01	0.10	1.62
	x̄	20.8	1.5	0.2	0.1	0.4	1.5	<0.1	0.1	1.7
Sponge cake with fruit filling	1984	49.0	0.99	0.06	0.05	0.11	0.62	<0.01	0.21	1.10
Sponge cake with cream filling	1984	47.5	0.74	0.06	0.03	0.10	0.08	···	<0.01	0.78
Jelly roll	1981	27.3	1.02	0.18	0.10	0.31	1.94	<0.01	0.31	1.33
	1982	26.1	0.98	0.11	0.08	0.20	1.83	<0.01	0.45	1.24
	x̄	26.7	1.0	0.2	0.1	0.3	1.9	<0.1	0.4	1.3
Biscuit	1981	3.2	0.57	0.10	0.24	0.97	1.55	<0.01	0.34	0.90
	1982	3.2	0.50	0.10	0.18	0.86	1.16	<0.01	0.27	0.76
	x̄	3.2	0.5	0.1	0.2	0.9	1.4	<0.1	0.3	0.8

[a]The total biologically active tocopherols (mg of α-tocopherol equivalents/100 g fresh product) were calculated according to McLaughlin and Weihrauch (1979).

The vitamin E composition of bakery products is shown in Table II. The α-tocopherol content ranged from 0.4 mg/100 g for sweet, low-fat wheat bread to 1.5 mg/100 g for sponge cake. For most products the α-tocopherol concentration was between 0.5 and 1.0 mg/100 g, and the total biologically active tocopherols between 0.8 and 1.5 mg of α-tocopherol equivalents/100 g. Bakery products made from refined wheat flours contained added fat. The tocopherols and tocotrienols from fat compensated for the low tocopherol and tocotrienol content of the flours. These products also contained γ- and δ-tocopherols absent from wheat and rye flours.

The most important factor influencing the vitamin E content of bakery products was found to be the type and amount of added fat. The vitamin E content of flours was usually less significant (Table II). However, the richest sources of vitamin E were rye breads, as well as high-fat products baked from wheat flours. The poorest sources were low-fat products made from white wheat flours.

Variation between the sampling years in vitamin E content was usually small. It was greatest in highly processed milling products, in special products, and in bakery products containing added fat. The variation between subsamples bought at the same time can be calculated only for the samples of wheat flour (ash content 1.2–1.4%), rye meal, and puffed oats bought in 1983. For rye meal and puffed oats the variation was marked: the concentration of total biologically active tocopherols in rye meal ($n = 10$) ranged from 1.03 to 2.20 mg of α-tocopherol equivalents (mean 1.61 ± SD 0.38 mg) and in puffed oats ($n = 4$) from 1.09 to 1.95 mg of α-tocopherol equivalents (1.47 ± 0.36 mg), respectively. For wheat flour ($n = 4$) the respective values were: range 1.70–2.13 mg, mean 2.01 ± SD 0.26 mg. The differences were probably caused by different periods of storage in retail stores.

The tocopherol and tocotrienol compositions and levels found in this study for Finnish milling products were generally in agreement with the tabulations collected by McLaughlin and Weihrauch (1979) and Bauernfeind (1980). Some of the trace components have not been previously reported. Variations in the milling procedures make exact comparisons difficult, however. A comparison of the tocopherol and tocotrienol levels in bakery products with the values previously reported is also difficult. The effects of fat and processing techniques are highly variable.

The estimated per capita consumption of cereal products in Finland has been calculated by Salovaara (*unpublished*). Based on the consumption figures and on the tocopherol and tocotrienol values in Tables I and II, the estimated average daily amount of vitamin E received from cereal products is about 2.8 mg of α-tocopherol equivalents, which is about 30% of the 1980 recommended dietary allowance (National Academy of Sciences 1980). Cereal products can be assumed to make a substantial contribution to the vitamin E intake in Finland.

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