Nutrient Composition of Selected Wheats and Wheat Products. III. Tocopherols

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ABSTRACT

A variety of wheats and wheat products have been analyzed for the various forms of vitamin E. Data in micrograms per g. are given for the amounts of alpha-tocopherol, beta-tocopherol, gamma-tocopherol, delta-tocopherol, alpha-tocotrienol, and beta-tocotrienol, as determined by gas-liquid chromatography of their trimethylsilyl ethers. Eleven wheats, the flours from them, and products made from the flours were analyzed in duplicate. In addition, ten pooled consumer product samples from each of ten representative U.S. cities have been analyzed. The data from the wheat→flour→product series permit an assessment of the fate of the tocopherols present in wheat and their relative contributions to the tocopherols in the products. Although all the wheats had similar amounts of the same tocopherols, durum wheats were slightly lower in alpha- and beta-tocopherol and higher in alpha- and beta-tocotrienol. Processing into white flour removed the major part of all forms. The variation in the identity and quantity of tocopherols in the consumer products reflected, in most instances, differences in the nonwheat ingredients. Most baked products contained gamma- and delta-tocopherols, characteristic of vegetable fats, along with variable amounts of the tocopherols from wheat.

Wheat has been known as a source of tocopherols, or vitamin E, for almost half a century. During this time more than 60 papers have appeared on the vitamin E content of wheats, wheat fractions, and wheat products (1). Most of this work gives information only on total tocopherol content and not on the amounts of specific forms. Only in recent years have methods been devised for determining individual tocopherols. While total tocopherol data may be adequate for evaluating the vitamin E content of some foods, most contain a variety of forms that differ widely in both biological potency (2) and antioxidant activity (3). Estimates of either of these characteristics based on total tocopherols or total reducing substances can be misleading.

Since the requirement for vitamin E is related to the amount of polyunsaturated fat in the diet (4), an increased consumption of this type of fat has created a greater need for accurate estimates of available dietary vitamin E. Published data for baked wheat products indicate that their contribution to dietary vitamin E is small. However, recent changes in both the techniques and materials used in the baking industry, notably an increased use of vegetable shortening, suggest that a new assessment be made of wheat products in terms of variations in the content of individual tocopherol forms.

This report concerns the tocopherol content of samples of wheats and wheat products submitted to an intensive multinutrient analytical study (5). The first group of samples was derived from a study of the effect of processing on the nutrients in wheat as the grain is transformed into flour and then into wheat products. The second group of samples evaluates the regional variability of the nutrient content of ten wheat products available to the consumer. No study as extensive as this has been reported; some of the products included have not

TABLE I. FORMS OF VITAMIN E

Trivial Names I	Trivial Names II	Abbreviation
Alpha-tocopherol	5,7,8-trimethyltocol	α-T
Beta-tocopherol	5,8-dimethyltocol	β-T
Gamma-tocopherol	7,8-dimethyltocol	γ-T
Delta-tocopherol	8-methyltocol	δ-T
Alpha-tocotrienol[a]	5,7,8-trimethyltocotrienol	α-T-3
Beta-tocotrienol[b]	5,8-dimethyltocotrienol	β-T-3
Gamma-tocotrienol[c]	7,8-dimethyltocotrienol	γ-T-3
Delta-tocotrienol	8-methyltocotrienol	δ-T-3

[a]Also known as zeta-1 tocopherol.

[b]Also known as epsilon-tocopherol.

[c]This may be the form known as eta-tocopherol, and identified as 7-methyltocol.

previously been analyzed by the newer methods capable of distinguishing and estimating the different tocopherols.

The tocopherol nomenclature used conforms to the Tentative Rules of the IUPAC-IUB Commission on Biochemical Nomenclature (6). Its relation to the older nomenclature is given in Table I. The abbreviations given in Table I and used throughout this paper are also in accordance with that commission's tentative rules (7).

PROCEDURE

Details of sample collection and preparation are given elsewhere (5). Samples were received in sealed cans, under nitrogen, and stored at 0° to −10°C. until analyzed. Cans were brought to room temperature before being opened, to minimize moisture absorption.

The individual tocopherols were quantitatively determined by a method based on a gas-liquid chromatographic separation of their trimethylsilyl ether derivatives (8), after a preliminary saponification and thin-layer purification. Extraction techniques requiring hot solvent or prolonged sample exposure gave poor tocopherol recoveries. The best results were obtained by shaking with absolute ethanol for 1 hr.

The efficiency of this technique was tested by re-extracting the residue of one sample of each type analyzed. The second extraction removed further tocopherol from only two samples: wheat grain (1.1% of the β-T-3) and doughnuts (2.1% of δ-T and 0.9% of γ-T). The extracts were filtered and then saponified under nitrogen in the presence of pyrogallol. The unsaponifiable fraction was extracted with purified petroleum ether and washed to remove excess base. A known amount of didecyl pimelate was then added to serve as a gas-chromatographic reference compound and as an internal standard for quantitation. After removal of interfering unsaponifiables by thin-layer chromatography, the tocopherol fraction was converted to trimethylsilyl ethers and analyzed by gas-liquid chromatography. All

TABLE II. TOCOPHEROLS IN WHEATS, FLOURS, AND PRODUCTS
(γ per g., DRY-WEIGHT BASIS)

Sample[a]	N	Alpha-T	Beta-T	Gamma-T	Delta-T	Alpha-T-3	Beta-T-3
H-W	5	13.5 ± 1.64 (11.6 - 15.4)	7.3 ± 0.44 (6.7 - 7.8)	-----	-----	4.7 ± 0.21 (4.5 - 5.0)	32.8 ± 2.03 (30.1 - 34.9)
H-F	5	0.2 ± 0.16 (0 - 0.4)	0.5 ± 0.20 (0.4 - 0.8)	-----	-----	-----	5.7 ± 2.29 (4.1 - 9.7)
H-B-1	5	0.1 ± 0.05 (0 - 0.1)	0.2 ± 0.07 (tr - 0.16)	-----	-----	-----	1.0 ± 0.49 (0.5 - 1.6)
H-B-2	5	0.2 ± 0.05 (tr - 0.3)	0.3 ± 0.05 (0.2 - 0.3)	1.9 ± 1.36 (0.9 - 4.0)	3.6 ± 1.32 (2.5 - 5.7)	-----	0.9 ± 0.26 (0.6 - 1.2)
S-W	4	12.4 ± 0.71 (11.7 - 13.3)	6.5 ± 0.44 (5.9 - 6.9)	-----	-----	5.0 ± 0.45 (4.6 - 5.6)	30.4 ± 3.86 (25.5 - 34.9)
S-F-Ca	6	0.4 ± 0.91 (0 - 2.24)	0.3 ± 0.46 (0.1 - 1.3)	-----	-----	0.7[b]	1.9 ± 3.65 (0.2 - 9.3)
S-Ca	6	11.6 ± 1.39 (10.0 - 13.8)	tr	65.9 ± 6.58 (58.3 - 77.7)	21.2 ± 3.85 (17.5 - 25.5)	-----	1.7[b]
S-F-Cr	7	7.4 ± 4.63 (0.6 - 14.2)	4.3 ± 2.23 (1.0 - 7.8)	-----	-----	1.7 ± 0.86 (0 - 2.8)	18.5 ± 7.31 (3.3 - 24.6)
S-Cr	7	3.9 ± 2.09 (1.0 - 6.9)	2.5 ± 1.16 (0.7 - 4.0)	1.0 ± 0.18 (0.6 - 1.2)	0.3 ± 0.03 (0.2 - 0.3)	0.9 ± 0.33 (0.2 - 1.2)	10.5 ± 3.57 (2.8 - 13.2)
D-W	2	9.9 (9.5, 10.2)	4.8 (4.8, 4.9)	-----	-----	6.7 (6.5, 6.8)	36.7 (36.5, 36.8)
D-F	2	3.0 (2.6, 3.4)	1.5 (1.4, 1.7)	-----	-----	2.5 (2.3, 2.6)	17.8 (17.6, 18.0)
D-M	2	0.2 (0.1, 0.2)	0.2 (0.2, 0.2)	-----	-----	0.2 (0.2, 0.2)	2.4 (2.1, 2.6)

[a]H = hard; S = soft; D = durum; W = wheat; F = flour; B-1 = conventional type bread; B-2 = continuous-mix bread; Ca = cake; Cr = crackers; M = macaroni.
[b]In only one sample.

work was performed in subdued light. The lower limit of detectability of the method, as used here, was about 0.05 microgram per g.

RESULTS AND DISCUSSION

Wheat→Flour→Product Study

To determine the effect of processing on tocopherols in wheat, five hard, four soft, and two durum wheats, their flours, and bread, cake, crackers, and macaroni prepared from the flours were analyzed for tocopherol content (Table II). The four tocopherols characteristic of wheat, α-T, β-T, α-T-3, and β-T-3, were present in approximately the same amounts in both hard and soft wheats (*Triticum aestivum*). Durum wheats (*T. durum*) were slightly lower in the saturated forms, α-T and β-T, and slightly higher in their unsaturated analogs. All flours were lower in tocopherol content than their parent wheats. The magnitude of this milling loss was related to the quality of the flour: more refined flours contained less tocopherol. This is not surprising, since flour milling is a process designed to selectively remove the germ and the bran in which the vitamin is concentrated. Subsequent chemical treatment causes further loss. Cracker flours (S-F-Cr) and durum flours (D-F) did not receive any special treatment and were relatively high in tocopherol content. Cake flours (S-F-Ca) were exceptionally low, probably because of the severity of cake flour treatment with benzoyl peroxide and chlorine. One cake flour was of a type not generally used for cake. This same flour was higher in tocopherol content than the other cake flours; from the physical and chemical evidence it probably did not receive the normal cake treatment. Bread flours from hard wheats were intermediate between these two extremes in tocopherol content.

Breads made by both conventional (H-B-1) and continuous-mix (H-B-2) processes contained negligible amounts of wheat tocopherols. However, H-B-2 had small amounts of two nonwheat tocopherols, δ-T and γ-T, either or both of which may have come from flakes and emulsifier used in the formula for H-B-2 but not in that for H-B-1.

Cakes were relatively high in α-T, γ-T, and δ-T, all three of which must have come from a nonwheat source, since the cake flours had little or none. Crackers contained slightly more than half the tocopherol content of the original cracker flours, as well as very small amounts of γ-T and δ-T from a nonwheat source. Macaroni was low in all four wheat tocopherols, even though the semolina from which it was made was relatively high. This loss was perhaps due to the prolonged heating used to dry paste products.

Consumer Products

To evaluate the variability of the tocopherol content of wheat products available to the consumer, a representative sampling of each of ten products was taken from two cities in each of five different geographic locations. Four of the ten

TABLE III. TOCOPHEROLS IN CONSUMER WHEAT PRODUCTS (γ per g., DRY-WEIGHT BASIS)

	Alpha-T	Beta-T	Gamma-T	Beta-T-3
All-purpose flour[a]	0.3 ± 0.33 (0.1 - 1.0)	0.3 ± 0.16 (0.2 - 0.7)	0.45[b]	2.9 ± 1.96 (0.7 - 7.9)
Whole-wheat cereal	11.7 ± 3.58 (4.6 - 16.0)	5.7 ± 2.33 (5.1 - 11.1)	3.3 ± 1.12 (0.8 - 4.6)	24.0 ± 6.14 (11.6 - 33.3)
Shredded-wheat cereal[c]	3.9 ± 0.96 (1.8 - 5.4)	3.1 ± 0.42 (2.6 - 4.1)	2.8 ± 0.54 (1.7 - 3.6)	13.6 ± 0.98 (11.7 - 15.7)
Wheat-flakes cereal[d]	4.2 ± 1.19 (1.9 - 5.6)	2.5 ± 0.36 (1.9 - 2.9)	3.2 ± 0.75 (1.6 - 3.9)	12.8 ± 1.68 (10.7 - 14.9)

[a]All brands bleached and enriched.

[b]Found in only one sample.

[c]One brand contained malt.

[d]All brands contained some additives; e.g., malt and sugars.

TABLE IV. TOCOPHEROLS IN CONSUMER PRODUCTS CONTAINING WHEAT
(γ per g., DRY-WEIGHT BASIS)

Location	Alpha-T	Beta-T	Gamma-T	Delta-T	Beta-T-3
			BISCUIT MIX		
New York	0.3	0.2	0.3	0.2	0.9
Boston	0.3	0.2	0.2	0.1	1.1
Atlanta	3.3	tr	17.8	5.4	1.7
Charlotte	3.2	tr	21.5	10.0	0.6
Chicago	0.2	0.2	0.3	0.2	0.9
Minneapolis	1.9	tr	9.7	2.5	1.7
Seattle	6.6	tr	35.0	11.1	1.0
San Francisco	2.0	tr	4.9	1.6	1.1
Los Angeles	4.8	tr	31.9	8.9	1.5
Dallas	7.8	tr	55.6	14.8	1.5
Av.	3.0	tr	17.7	5.5	1.2
Std. dev.	2.7		18.5	4.6	0.4
			WHITE BREAD – CONVENTIONAL		
New York	2.1	tr	12.8	5.2	3.4
Boston	0.6	0.6	4.5	2.0	3.3
Atlanta	0.1	0.2	0.6	0.2	1.5
Charlotte	0.2	0.2	1.3	0.4	1.0
Chicago	0.2	0.3	1.3	0.8	1.5
Minneapolis	0.1	0.2	1.2	1.0	1.5
Seattle	-	0.2	0.4	0.2	0.9
San Francisco	0.1	0.2	0.2	0.1	2.4
Los Angeles	0.1	0.2	0.5	0.3	1.6
Dallas	0.2	0.1	1.4	0.5	0.7
Av.	0.4	0.2	2.4	1.1	1.8
Std. dev.	0.7	0.1	3.8	1.6	1.0
			WHITE BREAD – CONTINUOUS-MIX		
New York	tr	0.1	0.2	0.2	0.5
Boston	0.2	0.2	1.0	0.3	1.9
Atlanta	-	0.1	0.3	0.4	0.7
Charlotte	tr	0.1	0.1	0.2	0.7
Chicago	-	tr	3.3	1.2	2.7
Minneapolis	-	0.1	0.1	0.1	0.5
Seattle	-	tr	0.1	0.1	0.5
San Francisco	-	0.2	0.2	0.3	2.0
Los Angeles	-	0.1	0.1	0.1	0.5
Dallas	0.1	0.2	0.6	0.8	1.4
Av.	tr	0.1	0.6	0.4	1.1
Std. dev.		0.07	1.0	0.4	0.8
			WHOLE-WHEAT BREAD		
New York	1.3	1.8	4.0	3.5	5.8
Boston	3.5	2.5	12.6	4.6	8.4
Atlanta	0.9	0.3	0.4	0.7	2.0
Charlotte	0.8	0.8	1.3	2.4	4.2
Chicago	2.2	1.9	0.7	0.4	8.0
Minneapolis	0.8	0.7	0.8	2.4	2.9
Seattle	0.2	0.2	tr	0.1	1.2
San Francisco	0.5	0.4	0.2	0.1	2.0
Los Angeles	1.4	2.6	3.7	2.2	10.8
Dallas	4.6	4.2	14.0	4.9	13.1
Av.	1.6	1.5	3.8	2.1	5.8
Std. dev.	1.4	1.3	5.2	1.8	4.1

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TABLE IV. (Continued)

			HAMBURGER ROLLS		
New York	2.8	tr	17.4	7.8	2.8
Boston	0.5	tr	3.6	1.5	2.1
Atlanta	tr	0.2	0.7	0.4	1.3
Charlotte	-	0.2	0.1	0.1	1.0
Chicago	1.4	tr	11.8	4.4	2.6
Minneapolis	-	0.1	0.1	0.1	1.0
Seattle	-	0.1	0.1	0.1	0.9
San Francisco	-	0.2	0.1	-	1.7
Los Angeles	0.8	tr	5.1	1.6	2.1
Dallas	0.2	0.2	0.7	0.6	1.3
Av.	0.6	0.1	4.0	1.7	1.7
Std. dev.	0.9	0.09	6.0	2.5	0.7
			DOUGHNUTS		
New York	13.8	a	57.5	20.1	5.3
Boston	6.3	a	31.6	11.7	4.4
Atlanta	5.1	a	16.6	3.9	4.0
Charlotte	6.4	a	24.7	6.5	4.8
Chicago	4.9	a	18.4	4.7	5.1
Minneapolis	4.8	a	15.1	3.6	5.7
Seattle	5.1	a	17.8	5.5	4.4
San Francisco	12.8	a	51.7	20.5	4.6
Los Angeles	29.9	a	41.4	10.9	5.4
Dallas	5.5	a	19.6	9.3	4.2
Av.	9.5		29.4	9.7	4.8
Std. dev.	7.9		15.6	6.3	0.6

[a]Not measurable due to large γ-T peak. Small amount usually present, appearing as a small shoulder on the γ-T peak.

consumer products were simple foods made only from wheat or a wheat fraction. These included all-purpose flour and three wheat cereals. Tocopherol data for these products are summarized in Table III.

All-purpose flours were low in all wheat tocopherol forms. The amounts found in the cereals were higher: the values for whole-wheat cereal approached those for the whole grains, shown in Table II.

The remaining six consumer products contained wheat as a major components. Data for these six products, by geographical location, are given in Table IV. In addition to the characteristic wheat tocopherols, all of these foods contained γ-T and δ-T. These two forms are found in vegetable oils commonly used for shortening and for frying. Table V gives the tocopherol content of samples of the major vegetable oils, a processed vegetable shortening, and lard. Lard is very low in tocopherols and was apparently the shortening used in many of the products. White breads of both types appear to have been made with lard in all parts of the country. Doughnuts contained larger amounts of γ-T and δ-T, indicating that vegetable oils were probably used for frying. The shortening used in the biscuit mixes, whole-wheat breads, and hamburger rolls varied in different localities, on the evidence of their tocopherol contents. If the two samples of soybean oil are representative, the ratio of γ-T to δ-T ranges from about 2.7 to 5. In most of the samples containing appreciable quantities of these two tocopherols their ratio is in

TABLE V. TOCOPHEROLS IN MAJOR SHORTENING FATS AND OILS (γ per g.)

Sample	Alpha-T	Gamma-T	Delta-T	Alpha-T-3
Cottonseed oil	320	313	---	---
Soybean oil – sample 1	42	252	53	---
Soybean oil – sample 2	94	630	232	---
Vegetable shortening (processed)	99	662	230	---
Lard	11.5	0.7	---	0.7

that range, indicating that a soybean-based shortening is widely used in preparing these products.

Since none of the fats in Table V contained β-T-3, all of this form in the consumer products probably came from wheat. It should, therefore, serve as a rough index of the contribution of wheat to the tocopherols in the product. On this basis, wheat contributed more to the tocopherol content of whole-wheat bread and doughnuts than to that of the other baked products.

The contribution of wheat to the tocopherols in the diet is variable, depending on the milling fraction used and its subsequent treatment. Greater variations in both quantity and number of tocopherols are found among wheat products made with added fats. Shortenings may in fact be the major source of tocopherol in some products and must be taken into consideration in an assessment of the tocopherol contribution of any one wheat product to a diet.

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