

- 1980, Springer, Berlin, 1981, pp. 221-228.
44. Grice, H.C., D.J. Clegg, D.E. Coffin, M.T. Lo, E.J. Middleton, E. Sandi, P.M. Scott, N.P. Sen, B.L. Smith and J.R. Withey, in *Carcinogens in Industry and the Environment*, edited by J.M. Sontag, Marcel Dekker, New York, 1981, pp. 439-492.
45. Symon, D.N.K., E.R. Hennessy and P.J. Small, *Lancet*, Sept. 1, 514 (1984).
46. Kromhout, D., E.B. Bosschieter and C. Coulander, *N. Eng. J. Med.* 312:1205.

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## ❁ Tocopherols and Tocotrienols in Finnish Foods: Oils and Fats

E.-L. Syväoja<sup>a</sup>, V. Piironen<sup>b</sup>, P. Varo<sup>b</sup>, P. Koivistoinen<sup>b</sup> and K. Salminen<sup>a</sup>

<sup>a</sup>Valio Finnish Cooperative Dairies' Association, Helsinki, Finland, and <sup>b</sup>Department of Food Chemistry and Technology, University of Helsinki, Helsinki, Finland

The tocopherols and tocotrienols of vegetable oils, cod liver oil, margarines, butter and Voimariini dairy spread were analyzed by HPLC. The total tocopherol content varied from 4 (coconut oil) to 242 mg/100 g (wheat germ oil).  $\alpha$ -tocopherol equivalents varied from 2 (coconut oil) to 225 mg/100 g (wheat germ oil). Semisoft and soft margarines had an average total tocopherol of 53 and 61 mg, and an average  $\alpha$ -tocopherol equivalent of 17 and 27 mg/100 g, respectively. Hard margarines averaged 29 mg total tocopherol and 9 mg  $\alpha$ -tocopherol equivalent/100 g. The average tocopherol content of butter and Voimariini was 2 and 15 mg/100 g, respectively, and the average  $\alpha$ -tocopherol equivalent 2 and 6 mg/100 g.

lated from fatty acid compositions determined in this laboratory by gas chromatographic methods (9).

### RESULTS AND DISCUSSION

The proportions of the individual tocopherols ( $\alpha$ -T,  $\beta$ -T,  $\gamma$ -T and  $\delta$ -T) and tocotrienols ( $\alpha$ -T3,  $\beta$ -T3,  $\gamma$ -T3 and  $\delta$ -T3) and the total tocopherol contents of the oils are given in Table 1. The results are the mean values (6-10 determinations) of each oil purchased from 3 to 5 different manufacturers. All tocopherols and tocotrienols were found, although tocotrienols were not detected in every oil. Tocotrienols might have been present, but the determination of tocopherols and tocotrienols together was difficult because of very large differences in concentration. Differences between crude and refined rapeseed, soybean, sunflower and palm oils were determined. The refining losses were about 10-33% of the  $\alpha$ -tocopherol, 20-33% of the other tocopherols and 43-48% of the tocotrienols.

The study reported here is part of a research project to survey in detail the vitamin E content of Finnish foods, including complete diets (1,2), human milk and baby foods (3), milk products and egg (4), fish and fish products (5), meat (6) and cereals (7). In this study the tocopherol levels in vegetable oils, cod liver oil, margarines and butter available in Finland were measured and the  $\alpha$ -tocopherol/polyunsaturated fatty acid ratios derived.

### EXPERIMENTAL

The tocopherols and tocotrienols were determined by high-performance liquid chromatography (Hewlett Packard 1084B), a LiChrosorb Si60 column (5  $\mu$ m, 25  $\times$  0.4 cm, Merck) and a di-isopropyl ether gradient of 8 to 17% in hexane. The oil (0.2, 1 and 5 g) or fat (1 and 5 g) was dissolved in 100 ml n-hexane; a clear solution was obtained after a small amount of insoluble material had settled. The solution was filtered through a Millipore 0.45  $\mu$ m FH membrane and injected directly into the column. The column temperature was 30 C (45 C for the separation of  $\gamma$ -tocopherol and  $\beta$ -tocotrienol). A Perkin-Elmer M3000 fluorescence spectrometer was the detector. The excitation and emission wavelengths were 290 and 325 nm. Calibration was made with purified tocopherols as described before (5). The recovery of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols added to oils was essentially quantitative (mean values 98%, 96%, 98% and 98%). The individual tocopherol and tocotrienol values were converted to  $\alpha$ -tocopherol equivalents (mg/100 g) (8).

The polyunsaturated fatty acid contents were calcu-

The contents of the tocopherols and tocotrienols in margarines (representing the most popular brands from all five manufacturers in Finland) are given in Table 2. The tocopherol content and composition of the margarines varied greatly, in accordance with the oils and fats used in their manufacture. On the basis of their tocopherol content the margarines can be divided into three groups. The first group comprises the hard margarines containing  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -tocopherols at about 7, 0, 17 and 3 mg/100 g, respectively. The second and third groups contain the semisoft and soft margarines with corresponding tocopherol figures of 13, 0, 32 and 8 mg and 24, 1, 27 and 9 mg/100 g. With the exception of  $\beta$ -tocotrienol, small amounts of tocotrienols were found; none were detected at those sample concentrations used for the measurement of the tocopherols.

The butter samples contained  $\alpha$ -tocopherol (2 mg/100 g in summer and 1 mg/100 g in winter) and small amounts of  $\alpha$ -tocotrienol (4). In Voimariini, a butterfat-vegetable oil mixture, the tocopherol level reflected the proportion of the oil ingredient used, being higher in winter than in summer (Table 2).

The  $\alpha$ -tocopherol (and  $\alpha$ -tocopherol equivalent)/PUFA ratio (Table 1) was low in linseed, peanut and soybean oil: 0 (0.1), 0.3 (0.3) and 0.2 (0.3) mg/g, respectively. All the margarines whose PUFA content had been determined were found to have, with one exception,  $\alpha$ -tocopherol equivalent/PUFA ratios higher than the value of 0.6 mg/g (11). The  $\alpha$ -tocopherol/PUFA ratio was less than 0.6 mg/g in three brands only. For butter and Voimariini average ratios of 0.8 and 0.6 mg/g, respectively, were found.

\*To whom correspondence should be addressed at Valio Finnish Cooperative Dairies' Association, Research and Development Department, Kalevankatu 56 B, SF-00180 Helsinki 18, Finland.

TOCOPHEROLS OF OILS AND FATS

**TABLE 1**  
The Tocopherol ( $\alpha$ -T,  $\beta$ -T,  $\gamma$ -T and  $\delta$ -T) and Tocotrienol ( $\alpha$ -T3,  $\beta$ -T3,  $\gamma$ -T3 and  $\delta$ -T3) Content of Oils

	mg/100 g								mg/g			
	$\alpha$ -T	$\alpha$ -T3	$\beta$ -T	$\beta$ -T3	$\gamma$ -T	$\gamma$ -T3	$\delta$ -T	$\delta$ -T3	Total tocopherol	$\alpha$ -Teq <sup>a</sup>	$\alpha$ -Teq/ PUFA <sup>b</sup>	$\alpha$ -T/ PUFA <sup>b</sup>
Castor oil	0.90	— <sup>d</sup>	0.92	—	45.87	—	34.30	—	81.99	6.20	2.2	0.3
Coconut oil (hardened)	1.82	1.09	0.25	—	tr <sup>c</sup>	0.33	0.39	—	3.88	2.25	6.3	5.1
Corn oil	25.69	1.50	0.95	—	75.23	2.03	3.25	—	108.65	34.09	0.6	0.5
Linseed oil	0.54	—	—	—	57.33	—	0.75	—	58.62	6.28	0.1	0
Olive oil	11.91	—	—	—	1.34	—	—	—	13.25	12.04	1.9	1.9
Palm oil	6.05	5.70	—	0.82	tr	11.34	—	3.33	27.24	7.91	0.7	0.6
Peanut oil	8.86	—	0.38	—	3.50	—	0.85	—	13.59	9.37	0.3	0.3
Rapeseed oil	18.88	—	—	—	48.59	—	1.20	—	68.67	23.75	0.7	0.6
Safflower oil	44.92	—	1.20	—	2.56	—	0.65	—	49.33	45.54	0.6	0.6
Soybean oil	9.53	—	1.31	—	69.86	—	23.87	—	104.57	17.28	0.3	0.2
Sunflower oil	62.20	—	2.26	—	2.67	—	—	—	67.13	63.37	1.0	1.0
Wheat germ oil	150.75	3.62	31.19	—	52.73	1.85	—	—	240.14	169.60	2.7	2.5
Wheat germ oil (capsules)	217.00	—	18.00	3.21	3.95	—	—	—	242.16	224.75	nd <sup>e</sup>	nd
Cod liver oil	20.26	—	—	—	—	—	—	—	20.26	20.26	0.8	0.8

<sup>a</sup> $\alpha$ -Teq,  $\alpha$ -tocopherol equivalent.

<sup>b</sup>PUFA, polyunsaturated fatty acid.

<sup>c</sup>tr, traces.

<sup>d</sup>—, not detected.

<sup>e</sup>nd, not determined.

**TABLE 2**  
The Tocopherol ( $\alpha$ -T,  $\beta$ -T,  $\gamma$ -T and  $\delta$ -T) and Tocotrienol ( $\alpha$ -T3,  $\gamma$ -T3 and  $\delta$ -T3) Content of Margarines, Butter and Voimariini Dairy Spread Samples

	mg/100 g							Total tocopherol	$\alpha$ -Teq (mg/g)
	$\alpha$ -T	$\alpha$ -T3	$\beta$ -T	$\gamma$ -T	$\gamma$ -T3	$\delta$ -T	$\delta$ -T3		
Margarine (hard) (range)	7.56 (4.00-8.96)	0.44 (0-1.75)	—	16.80 (6.21-28.00)	0.65 (0-2.34)	3.13 (1.37-11.07)	0.40 (0-0.78)	28.98 (14.14-51.86)	9.47 (4.88-11.39)
Margarine (semisoft) (range)	13.26 (10.21-16.30)	—	—	31.74 (20.72-42.76)	0.10 (0-0.20)	8.22 (5.98-10.45)	0.14 (0-0.28)	53.46 (43.48-63.42)	16.51 (14.59-18.43)
Margarine (soft) (range)	23.96 (17.57-44.62)	0.04 (0-0.18)	0.79 (0-1.44)	26.84 (2.69-43.74)	0.31 (0-1.01)	9.07 (0.67-16.56)	0.31 (0-0.62)	61.32 (49.42-81.27)	27.07 (20.88-45.47)
Butter (summer)	2.00	tr	—	—	—	—	—	2.00	2.00
Butter (winter)	1.01	0.11	—	—	—	—	—	1.12	1.04
Voimariini (summer)	4.90	tr	—	7.25	—	0.40	—	12.55	5.67
Voimariini (winter)	5.56	tr	—	11.97	—	0.33	—	17.86	6.79

Symbols as in Table 1.

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**REFERENCES**

- Piironen, V., P. Varo, E.-L. Syväoja, K. Salminen and P. Koivistoinen, *Int. J. Vit. Nutr. Res.* 54:35 (1984).
- Piironen, V., P. Varo, E.-L. Syväoja, K. Salminen, P. Koivistoinen and H. Arvilommi, *Ibid.* 54:41 (1984).
- Syväoja, E.-L., V. Piironen, P. Varo, P. Koivistoinen and K. Salminen, *Ibid.* 55:159 (1985).
- Syväoja, E.-L., V. Piironen, P. Varo, P. Koivistoinen and K. Salminen, *Milchwissenschaft* 40:467 (1985).
- Syväoja, E.-L., V. Piironen, P. Varo, O. Kerojoki, P. Koivistoinen and K. Salminen, *J. Am. Oil Chem. Soc.* 62:1245 (1985).
- Piironen, V., E.-L. Syväoja, P. Varo, K. Salminen and P. Koivistoinen, *J. Agric. Food Chem.* 33:1215 (1985).
- Piironen, V., E.-L. Syväoja, P. Varo, K. Salminen and P. Koivistoinen, *Cereal Chem.*, in press.
- McLaughlin, P.J., and J.L. Weihrauch, *J. Am. Diet. Assoc.* 75:647 (1979).
- Homer, D., *Proc. 12th Scand. Symp. Lipids* 213 (1983).
- Harris, P.L., and N.D. Embree, *Am. J. Clin. Nutr.* 13:385 (1963).

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