carried out with the hydroxide ion concentration more than 50 times the substrate concentration.

Pseudo-first-order rate constants were obtained from linear regression analysis of  $\ln (A_{\infty} - A_t)$  vs. time data. The plots were linear for over three half-lives for compound 1 (Z = Cl and Z = H) but the NO<sub>2</sub> derivative gave a downward curvature after about two half-lives. Then the infinite value was calculated on the basis of the initial concentration of the substrate and the extinction coefficient of 2 (Z = NO<sub>2</sub>).

Thermodynamic activation parameters were obtained by standard procedures. (Bunnett, 1974).

**Registry No.** 1 (Z = NO<sub>2</sub>), 97073-93-3; 1 (Z = Cl), 97073-94-4; 1 (Z = H), 97073-95-5; dimethylthiocarbamoyl chloride, 16420-13-6.

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# Tocopherols and Tocotrienols in Finnish Foods: Meat and Meat Products

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This study is part of a comprehensive survey carried out to determine the tocopherol and tocotrienol contents of Finnish foods. Tocopherols and tocotrienols from 40 commodities of meat, animal fats, edible offals, and meat products were analyzed by a high-performance liquid chromatographic method.  $\alpha$ -Tocopherol was the predominant compound, but small amounts of  $\alpha$ -tocotrienol and  $\gamma$ -tocopherol were also found in almost every sample. Some samples also showed small peaks with retention values identical with those of  $\beta$ -tocopherol and  $\beta$ -tocotrienol. The  $\alpha$ -tocopherol content of meat samples ranged from 0.16 to 0.84 mg/100 g of fresh weight, of fat samples from 0.52 to 2.68 mg, of offal samples from 0.23 to 1.37 mg, and of meat product samples from 0.14 to 0.74 mg. There was a clear seasonal variation in the  $\alpha$ -tocopherol contents of the meat, fat, and liver of both cows and steers. The  $\alpha$ -tocopherol content of meat and edible offals is about 0.8 mg per capita.

The vitamin E content of meat and edible offals is reported to be low or moderate. The  $\alpha$ -tocopherol content of raw meat is usually below 0.5 mg/100 g and that of edible offals no more than 1.0 mg/100 g (Paul and Southgate, 1978; McLaughlin and Weihrauch, 1979; Bauernfeind, 1980; Souci et al., 1981). Animals do not synthesize tocopherols or tocotrienols, and the vitamin E content of animal products is therefore influenced by diet.

Only  $\alpha$ -tocopherol and small amounts of other tocopherols, but no tocotrienols, have been found in meat and offals (McLaughlin and Weihrauch, 1979; Bauernfeind, 1980).  $\gamma$ -Tocopherol has been shown to be absorbed about as efficiently as  $\alpha$ -tocopherol, but it disappears faster from tissues than  $\alpha$ -tocopherol (Bieri and Poukka Evarts, 1974). Behrens and Madere (1983), on the other hand, have suggested that the absorption, transport, and tissue-uptake mechanisms of tocopherols are specific for  $\alpha$ -tocopherol and that small amounts of  $\alpha$ -tocopherol are sufficient to displace  $\gamma$ -tocopherol.

In this study the most important meats, edible offals, animal fats, and meat products commonly consumed in Finland were analyzed for tocopherols and tocotrienols. The study is part of a comprehensive survey carried out to determine the tocopherol and tocotrienol contents of Finnish foods (Piironen et al., 1985; Syväoja et al., 1985a; Syväoja et al., 1985b; Syväoja et al., 1985c; Syväoja et al., 1985d).

## EXPERIMENTAL SECTION

**Sampling.** Samples were taken at the end of the indoor feeding season in the spring of 1982 (late April-early May) and again at the end of the grazing season in fall 1982 (late Sept-early Oct). Some commodities were collected only once.

Meat, offal, and fat samples were collected from two slaughterhouse chains that together represent 80–90% of

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Table I. Tocopherol and Tocotrienol Contents of Meat and Animal Fats (Number of S	amples: Generally One Pooled Sample
for Each Item and Season, See Text) <sup>a</sup>	- · ·

				toco	pherols ar	;/100 g			
item		moisture, %	fat, %	$\alpha$ -T	α-T3	$\beta$ -T <sup>b</sup>	<i>β-</i> T3	$\gamma$ -T	mg $lpha$ -T/g fa
cow beef brisket, boneless	F	66.9	13.4	0.79	0.05	tr	tr	0.01	0.06
cow beef chuck, boneless	F	68.0	11.5	0.79	0.06	tr	tr	0.02	0.07
cow beef top round	$\mathbf{F}$	73.7	1.7	0.47	0.01			0.01	0.28
ground cow beef	s	67.9	13.1	0.34	0.05			0.01	0.03
0	F	70.1	9.0	0.60	0.04	tr	tr	0.01	0.07
	x	69.0	11.1	0.5	0.1			< 0.1	
steer beef brisket, boneless	S	63.5	18.4	0.23	0.07		tr	0.01	0.02
	F	62.8	18.6	0.47	0.05		tr	0.01	0.03
	x	63.2	18.5	0.4	0.1			<0.1	
steer beef chuck, boneless	S	71.7	7.2	0.20	0.04	•••	tr	0.01	0.03
	F	71.6	7.3	0.45	0.02		tr	0.01	0.06
	ź	71.7	7.3	0.3	<0.1	•••	01	<0.1	0.00
steer beef top round	ŝ	74.3	2.1	0.16	0.02			0.01	0.08
ster beer top reality	$\tilde{\mathbf{F}}$	74.7	1.1	0.34	0.01			0.01	0.31
	Ī	74.5	1.6	0.3	<0.01			< 0.1	0.01
ground steer beef	ŝ	69.8	10.0	0.19	0.04		tr	0.01	0.02
ground steer beer	F	70.6	9.0	0.43	0.04	•••		0.01	0.02
	x	70.2	9.5	0.45	<0.01		•••	<0.01	0.05
pork short plate, boneless and skinless	ŝ	45.8	44.8	0.58	0.14		<b>+-</b>	0.01	0.01
pork short plate, boneless and skinless	F	46.9	44.8 39.9	0.38	0.14	•••	tr	0.01	
	Ī	46.4	42.4	0.45 0.5	0.11		tr	<0.03	0.01
pork shoulder picnic, boneless and skinless	ŝ	66.9		$0.3 \\ 0.47$	0.1		<b>*</b>		0.00
pork shoulder pictic, boneless and skinless	F	65.7	$15.7 \\ 15.2$	0.47			tr	0.01	0.03
	г x			-	0.06	•••	tr	0.02	0.03
mark have namelar accord and	x S	66.3 66.2	15.5	0.4	0.1		4	<0.1	0.00
pork ham, regular round cut	S F		14.7	0.44	0.05	•••	tr	< 0.01	0.03
		68.7	11.9	0.33	0.04	•••	tr	0.01	0.03
	x	67.5	13.3	0.4	0.1			< 0.1	0.04
pork chop	S	69.7	7.8	0.32	0.03	•••	tr	0.01	0.04
	F	67.8	10.6	0.32	0.05	•••	tr	0.02	0.03
	x	68.8	9.2	0.3	<0.1			< 0.1	0.00
mutton forequarter, boneless	S	60.4	23.8	0.47	0.06	tr	tr	0.01	0.02
	F	66.9	14.6	0.70	0.03	tr	•••	0.01	0.05
<b>,</b>	x	63.7	19.2	0.6	<0.1			<0.1	
mutton round	s	68.8	10.6	0.32	0.03	•••	•••	0.01	0.03
reindeer meat forequarter, boneless	F	71.5	6.0	0.84			•••	0.01	0.14
venison, boneless	F	73.2	3.5	0.76		•••		0.01	0.22
chicken flesh	S	73.3	6.4	0.70	0.03	tr <sub>.</sub>	tr	0.06	0.11
$cow tallow^c$	s	9.5	87.3	1.22	0.24	nd	nd	nd	0.02
	F	14.9	86.8	2.68	0.29	nd	nd	nd	0.03
	x	12.2	87.1	2.0	0.3			_	
steer tallow <sup>c</sup>	s	14.8	81.0	0.52	0.26	nd	nd	nd	0.01
	F	17.1	80.0	0.69	0.09	nd	nd	nd	0.01
	x	16.0	80.5	0.6	0.2			_	
lard <sup>c</sup>	s	8.7	90.1	0.79	0.22	nd	nd	nd	0.01
	F	11.6	88.5	0.67	0.22	nd	nd	nd	0.01
	x	10.2	89.3	0.7	0.2				
pork kidney fat <sup>c</sup>	$\mathbf{S}$	10.1	88.2	1.27	0.25	nd	nd	nd	0.01
	$\mathbf{F}$	8.4	91.1	0.75	0.16	nd	nd	nd	0.01
	x	9.3	89.7	1.0	0.2				

<sup>a</sup>Abbreviations: T, tocopherol; T3, tocotrienol; S, spring; F, fall. <sup>b</sup>Key: ..., not detected; tr, trace; nd, not determined. <sup>c</sup>Only  $\alpha$ -T and  $\alpha$ -T3 determined.

Finland's total slaughterhouse capacity. The number of slaughterhouses was five (two from one chain and three from the other), and they were located in southern and central Finland. At each slaughterhouse the cuts and offals were taken from two each of cow, steer, and pig carcasses of the most common quality class (Tables I and II). The quality class was chosen on the basis of the Finnish consumption figures. For each cut and offal, 10 subsamples were obtained. The number of subsamples was smaller for reindeer meat (3), venison (3), mutton in fall sampling (7), and frozen chicken (6).

The carcasses were cut and sorted normally 3 days after the slaughter, and the next day cut samples were sent refrigerated to Helsinki. Edible offals were sent to Helsinki the day after the slaughter. These periods represent the average time lag between slaughter and retail. In Helsinki the cuts were trimmed according to common household practice, and each cut was deboned and reduced to  $2 \times$  2 cm cubes. Offals were reduced to cubes in the same way. Top round samples (pieces of 1 kg) were kept in polyethylene bags at 5 °C for 2 weeks before being reduced to cubes. The cubes from the 10 subsamples were pooled. Subsamples of reindeer meat, venison, and cow beef top round were not pooled but analyzed individually.

Meat products were collected from two factories from each slaughterhouse chain. Two subsamples, about 0.5–1.0 kg, each from two different batches of production were sent refrigerated to Helsinki. Sausages and cured meat had been prepared about 10 days before sampling and canned meat about 3 months before. The aim was to imitate the average time lag between preparation and retail. The eight subsamples were cut into  $2 \times 2$  cm cubes and pooled.

**Pretreatment.** About 1.0–1.5 kg of each pooled sample was homogenized under reduced light in a blender (Braun Multiquick, West Germany, for other samples but Kenwood, UK, for liver samples) and vacuum packed in ca.

Table II. Tocopherol and Tocotrienol Contents of Edible Offals (Number of Samples: One Pooled Sample for Each Item and Season)<sup>a</sup>

				tocop					
item		moisture, %	fat, %	$\alpha$ -T	α-T3	$\beta$ -T <sup>b</sup>	β-T3	γ <b>-</b> Τ	mg $\alpha$ -T/g fat
liver, cow	S	71.0	7.8°	0.25	0.01		tr	0.01	0.03
	$\mathbf{F}$	74.5	$7.8^{c}$	1.37	tr			0.01	0.18
	x	72.8	7.8	0.8	<0.1			<0.1	
liver, steer	S	72.1	7.8°	0.26	0.01	•••	tr	0.01	0.03
	$\mathbf{F}$	70.9	7.8°	1.15	tr	•••		0.01	0.15
	x	71.5	7.8	0.7	<0.01			< 0.1	
liver, pig	S	69.7	6.8 <sup>c</sup>	0.49	0.01		tr	0.01	0.07
	F	71.3	6.8°	0.62	tr	•••		0.01	0.09
	x	70.5	6.8	0.6	< 0.1			<0.1	
kidney, steer	S	75.4	7.9	0.30	0.03	•••	tr	0.01	0.04
kidney, pig	S	78.6	5.4	0.45	0.01	•••	tr	0.01	0.08
heart, steer	$\mathbf{S}$	73.5	8.5	0.34	0.04		tr	0.01	0.04
heart, pig	$\mathbf{S}$	77.3	3.7	0.64	0.02		tr	0.01	0.17
tongue, steer	S	70.8	10.3	0.23	0.11		tr	0.01	0.02
tongue, pig	$\mathbf{S}$	69.9	11.5	0.53	0.07	•••	tr	0.02	0.05

<sup>a</sup>Abbreviations: T, tocopherol; T3, tocotrienol; S, spring; F, fall. <sup>b</sup>Key: ..., not detected; tr, trace. <sup>c</sup>After Paul and Southgate (1978).

Table III. Tocopherol and Tocotrienol Contents of Meat Products (Number of Samples: One Pooled Sample for Each Item and Season)<sup>a</sup>

				toco	/100 g				
item		moisture, %	fat, %	$\alpha$ -T	α-T3	β-T <sup>b</sup>	β <b>-</b> Τ3	$\gamma$ -T	mg $\alpha$ -T/g fa
hot dog	S	59.9	23.6	0.29	0.06		tr	0.02	0.01
cooked meat sausage, "lenkkimakkara"	$\mathbf{S}$	61.1	17.6	0.27	0.04		tr	0.01	0.02
	F	61.8	16.0	0.27	0.05		tr	0.01	0.02
	x	61.5	16.8	0.3	0.1			< 0.1	
cooked meat sausage, "lauantai"	$\mathbf{S}$	65.1	15.6	0.29	0.04		tr	0.01	0.02
cooked meat sausage, "balkan"	$\mathbf{S}$	56.2	24.4	0.44	0.10		tr	0.01	0.02
	$\mathbf{F}$	56.8	22.7	0.40	0.08		tr	0.01	0.02
	x	56.5	23.6	0.4	0.1			< 0.1	
dry sausage, salami type, quality A	$\mathbf{S}$	30.4	44.0	0.74	0.12		tr	0.01	0.02
cooked liver sausage	$\mathbf{S}$	59.8	19.0	0.39	0.10		tr	0.02	0.02
Ū.	$\mathbf{F}$	59.9	19.8	0.42	0.06		tr	0.01	0.02
	x	59.9	19.4	0.4	0.1			< 0.1	
ham, cooked, smoked	$\mathbf{S}$	71.8	7.3	0.27	0.03		•••	0.01	0.04
	$\mathbf{F}$	72.5	3.5	0.24	0.02	•••	•••	0.01	0.07
	x	72.1	5.4	0.3	0.1			< 0.1	
cured meat	$\mathbf{S}$	75.8	1.4	0.14	0.01			0.01	0.10
	$\mathbf{F}$	75.1	1.8	0.22	0.01			< 0.01	0.12
	x	75.5	1.6	0.2	<0.1			< 0.1	
canned beef	S	61.2	14.4	0.44	0.04		tr	0.02	0.03
	$\mathbf{F}$	61.0	61.1	0.46	0.05		tr	0.01	0.03
	x	61.1	15.3	0.5	0.1			< 0.1	
canned pork	$\mathbf{S}$	48.3	35.1	0.47	0.09		tr	0.01	0.01
-	$\mathbf{F}$	48.4	35.2	0.46	0.07		tr	0.02	0.01
	x	48.4	35.2	0.5	0.1			<0.1	

<sup>a</sup>Abbreviations: T, tocopherol; T3, tocotrienol; S, spring; F, fall. <sup>b</sup>Key: ..., not detected; tr, trace.

100-g portions into aluminum laminate bags. The samples were immediately deep-frozen at -30 °C and stored frozen at -18 °C until analyzed (usually no more than 1 week).

Analytical Method. Tocopherols and tocotrienols were analyzed by the high-performance liquid chromatographic method previously described for diet samples (Piironen et al., 1984). Room-temperature saponification overnight was used for sample preparation. Sample size was 10 g. except for fat samples, which weighed 5 g. Ascorbic acid (1 g), distilled water (40 mL), 99.5% ethanol (100 mL), and 50% potassium hydroxide (10 mL, except for fat samples, 20 mL) were used in the saponification solution. The samples were allowed to stand in alcoholic solution with ascorbic acid for about 20 min before the addition of potassium hydroxide. After the saponification, tocopherols and tocotrienols were extracted with n-hexane, and the washed and evaporated extracts were usually redissolved in 10 mL of *n*-hexane. BHT (1%, w/v) was also added to the hexane extracts. The saponification conditions were tested as for diet samples. Tocopherols and tocotrienols were separated in a 5- $\mu$ m LiChrosorb Si 60 column, 25 cm

× 4 mm i.d. (Merck, Darmstadt) held at 37 °C. The column was eluted with *n*-hexane–diisopropyl ether (93:7) at a flow rate of 2.1 mL/min.

The reproducibility of the determinations was tested by analyzing the same cow beef chuck sample on four successive days (n = 8). The coefficients of variation for  $\alpha$ -tocopherol,  $\alpha$ -tocotrienol, and  $\gamma$ -tocopherol were 3.7%, 6.7%, and 6.7%, respectively. These values include also variation caused by the homogenization procedure of this study. Recoveries of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -tocopherols were determined by adding known amounts of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -tocopherols to steer beef chuck (n = 4), pork butt, (n = 4) 5), cooked meat sausage (n = 3), and liver samples (n = 3)5 for  $\alpha$ -tocopherol, n = 3 for other tocopherols) and by carrying them through the whole procedure. Recoveries of  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -tocopherol added to steer beef chuck samples were 96.9%, 99.6%, 97.4%, and 67.7%, respectively. For the pork butt sample the respective values were 99.0%, 93.8%, 94.5%, and 48.8%, for the cooked sausage sample 96.1%, 93.6%, 99.1%, and 69.0%, and for the liver sample 95.8%, 99.7%, 99.1%, and 91.7%. In meat and

sausage samples some  $\delta$ -tocopherol was probably destroyed. This is, however, insignificant because  $\delta$ -tocopherol was not detected in any sample. Recovery of the  $\alpha$ -tocopherol added to fat samples was 95.2% (n = 5). In fat samples, only  $\alpha$ -tocopherol and  $\alpha$ -tocotrienol were determined. Under these saponification conditions other compounds were not stable enough in fat samples.

The moisture content of the samples was determined from the loss in weight at 135 °C in 1.5 h. Homogenized sample (5 g) was used for the determinations. Total fat content was determined by the Gerber method (Kroll and Meester, 1963).

## **RESULTS AND DISCUSSION**

The tocopherol compositions of meats, fats, edible offals, and meat products are shown in Tables I–III. The most important compound was  $\alpha$ -tocopherol. Small amounts of  $\gamma$ -tocopherol were detected in all samples, and small amounts of  $\alpha$ -tocotrienol were found in all samples except venison and reindeer meat. Some samples also showed small peaks with retention values similar to those of  $\beta$ tocopherol and  $\beta$ -tocotrienol. The specificity and sensitivity of the analytical method made is possible to detect tocotrienols previously not reported.

The  $\alpha$ -tocopherol content of meat ranged from 0.16 to 0.84 mg/100 g (Table I). The tocopherol values of cow beef were higher than those of steer beef, and the levels in pork were about as high as those in steer beef in fall sampling. Cow beef and steer beef have not been compared before. In the Finnish practice steers are young animals raised specifically for meat production. Cows are older animals no longer capable of effective milk production. The  $\alpha$ -tocopherol contents of mutton were comparable with those of cow beef. The  $\alpha$ -tocopherol contents of reindeer meat, venison, and chicken were higher than those of other meats with about the same fat content.

There was a clear seasonal variation in the  $\alpha$ -tocopherol contents of cow beef, steer beef, and mutton. The values were about twice as high in the fall as in the spring. No seasonal variation was detected for pork. The differences between pork and beef were probably caused by different feeding practices. Feeding of fresh grass is probably the main reason for the difference in the tocopherol values of the fall and spring samples, and only cows, steers, and sheep get fresh grass in summer. A seasonal variation has previously been demonstrated in milk and milk products (Bauernfiend, 1980; Syväoja et al., 1985c).

During the same season the tocopherol concentration in different cuts of the same animal species followed the fat content: the higher the fat content, the higher the tocopherol values. However, the  $\alpha$ -tocopherol:fat ratio fell as the content of fat rose (Table I).

The  $\alpha$ -tocopherol values of fat samples ranged from 0.52 to 2.68 mg/100 g (Table I) and showed the same difference between animal species as did meats. There was also a clear seasonal variation for cow tallow. For some unknown reason, the  $\alpha$ -tocopherol content of steer tallow was surprisingly low in fall sampling.

There was an extremely great seasonal variation for cow and steer liver but not for pig liver (Table II). In the fall, cow and steer liver were moderately good sources of  $\alpha$ tocopherol. The great differences between  $\alpha$ -tocopherol values of cow and steer liver in spring and fall were in accordance with previous studies. The rate of depletion of vitamin E from tissues upon withdrawal of vitamin E from the diet has been shown to be more rapid in liver than in skeletal muscle and adipose tissue (Bieri, 1972). Samples of other offals were taken only in spring, and their  $\alpha$ -tocopherol contents were in the same range as those of meat from the same animal species in the same season. However, the  $\alpha$ -tocopherol:fat ratio was frequently higher than in meat with a similar fat content.

The  $\alpha$ -tocopherol contents of meat products ranged from 0.14 to 0.74 mg/100 g, and the values followed the fat content. No seasonal variation was detected.

No comprehensive survey of this kind has been carried out before, and only isolated tocopherol values have been reported for meat and meat products. Exact comparison of the present results with those from previous studies is therefore impossible. However, the order of magnitude of the tocopherol levels is about the same (Paul and Southgate, 1978; McLaughlin and Weihrauch, 1979; Bauernfeind, 1980; Souci et al., 1981). Tocopherol levels in meat, edible offals, and meat products are only low or moderate.

The average per capita meat consumption in Finland was 175 g/day in 1982 (Agr. Econ. Res. Inst., 1984). The proportions of beef, pork, edible offals, and poultry were 33%, 45%, 12%, and 5%, respectively. On the basis of the results of this study, the estimated daily intake of  $\alpha$ -tocopherol from meat and edible offals is about 0.8 mg (includes meat and offals used in meat products, losses in processing not taken into account), which is only 8–10% of the 1980 recommended daily allowance for adults (U.S. National Academy of Sciences, 1980). Meat and meat products are probably only minor sources of vitamin E for most Finns.

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**Registry No.**  $\alpha$ -Tocopherol, 59-02-9;  $\alpha$ -tocatrienol, 1721-51-3;  $\gamma$ -tocopherol, 7616-22-0;  $\beta$ -tocopherol, 148-03-8;  $\beta$ -tocotrienol, 490-23-3.

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