

Dependence of Tocopherol Stability on Different Cooking Procedures of Food

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Abstract: The influence of the kind of treatment during the preparation of hot meals (roasting, baking, stewing) on the stability of the tocopherols, which were added to the food through the margarines used, were examined in different food matrices. All preparation methods resulted in a loss of tocopherols. They could be divided into a group of only small loss of tocopherols (lower than 20%) and into a second group with nearly 70% loss of tocopherols (roasting of meat, steaming of peas). In the first group losses of tocopherols were directly associated with the fatty acid patterns of the used margarines, especially with the share of polyunsaturated fatty acids. On the other hand, during the roasting of meat nearly 70% of the tocopherols were destroyed by direct oxidation without a prohibitive effect on the lipid oxidation. The extreme high loss of tocopherols during the steaming of peas may be caused by the catalytic effect of the metal surface of the used pot. There were no losses of tocopherols observed when the experiments were repeated under identical conditions in an inert glass pot. Only tocopherol losses during baking may have a nutritional importance because of the great fat amount which are taken in with cookies.

Key words: Tocopherols, meat, peas, potatoes, pastry, margarines, steaming, baking, roasting, steel pot, glass pot

Introduction

Tocopherols with their strong vitamin activity form the most important part of vitamin E which has antioxidative and detoxifying properties.

Figure 1 presents the structure of the tocopherols. Regarding the possible stereoisomers, the tocopherol complex comprises 32 isomers. Together with the tocotrienols the whole complex of tocopherols includes 64 isomers. The exact composition of vitamin E as used in nutrition studies is scarcely known.

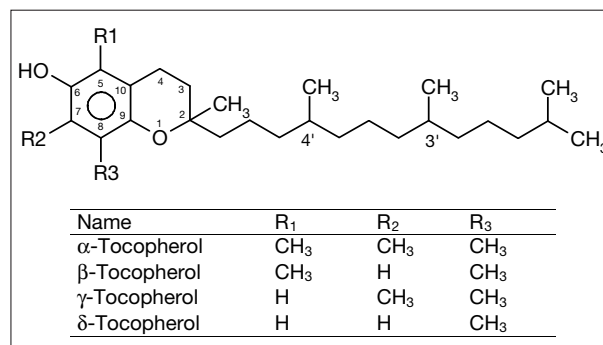


Figure 1: Structure of Tocopherols.

Table I: Losses of Vitamin E during Preparation of Food [2]

Preparation	Losses (%)	Food
Cooking	0	Eggs, Beef
	51	Poultry
Stewing	0	Fish, Potatoes, Rhubarb
	0–22	Fruits
	38	Sweet Corn
Baking	4	Fruits
	15	Potatoes
Roasting	0	Fish, Beef
	32	Potatoes
Grilling	0	Fish, Beef, Pork
	35	Lamb

It is well known that the diet of the population does not meet the recommended amounts as concerns vitamin E. A vitamin E deficiency results in manifold health problems. Vitamin E is sensitive to daylight and ultraviolet light. In presence of heavy metals and rancid fat, vitamin E is quickly oxidized by atmospheric oxygen. Losses appear also with the preparation of food. According to literature, the loss in vitamin E on a normal household diet and preparation of food amounts to about 10% but increases significantly on stronger heating conditions [1]. Table I shows the losses during the preparation of food dependent of the kind of preparation and food [2]. The highest losses are caused by roasting and stewing.

Materials and Methods

Food and Preparation

In this study, the stability of tocopherols during a normal household preparation of foods was analysed. We analysed the behaviour of tocopherols during three different heating procedures: stewing, roasting and baking. For each heating procedure, three different kinds of margarine (two standard margarines (SM 1, SM 2) and one diet margarine (DM)) were used. For the stewing procedure, frozen peas were stewed either in a stainless steel pot or a glass pot for 3 min at 70°C and the vitamin E losses were determined in the food. For the roasting procedure, steaks were roasted for 6 min at 180°C and potato slices were roasted for 15 min at 120°C. In each case, the food was analysed.

For the baking procedure, a dough was prepared and baked in a form for 60 min at 175°C. Additionally, cookies made of short pastry were prepared and baked for 12 min at 200°C. In these cases, the dough was analysed before and after the baking process. Each analysis was performed in sixfold.

Analysis of Tocopherols and Fatty Acids in Margarine Samples

Because the composition of the samples changes during the household treatment as a function of temperature and duration the fat content was determined in all samples. The tocopherol contents were related to 100 g fat. The analysis of tocopherols followed the procedure described by Pfalzgraf *et al* [3]. Figure 2 shows the flow scheme of the analytical procedure.

The sample was saponified at 80°C after addition of ascorbic acid and a methanolic solution of potassium hydroxide. Ethanol was added to the saponified sample, extraction was performed with n-hexane/ethyl acetate in a shaking machine. After centrifugation, the organic layer was separated and analysed by HPLC. Figure 3 shows chromatograms of a tocopherol standard mixture and tocopherols in margarine.

The tocopherol contents of the margarines used are listed in Table II. The diet margarine has a high content of α -tocopherol acetate (determined as α -tocopherol) of 72.9 mg/100 g fat. The content of γ -tocopherol in standard margarine 2 was as high as 49.1 mg/100 g fat. δ -Tocopherol was measured only in small amounts in the stan-

Table II: Tocopherol Content of the Margarines

	SM 1 (mg/ 100 g fat)	SM 2 (mg/ 100 g fat)	DM (mg/ 100 g fat)
α -Tocopherol	14.4	16.7	72.9
γ -Tocopherol	16.4	49.1	23.3
δ -Tocopherol	1.9	8.0	n.d.
$\Sigma \alpha, \gamma, \delta$ -Tocopherol	32.7	73.8	96.2

SM 1: standard margarine 1, SM 2: standard margarine 2, DM: diet margarine

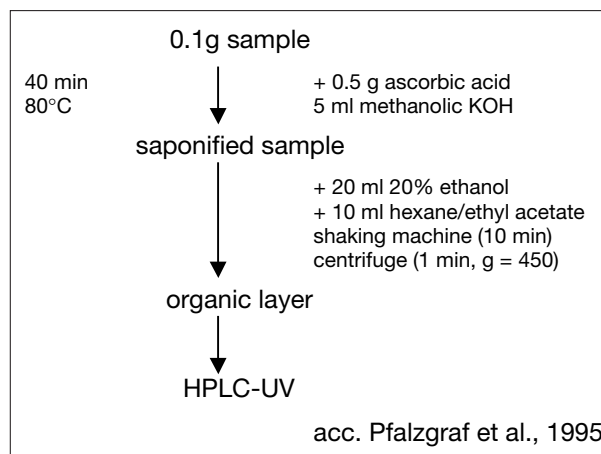


Figure 2: Flow-scheme of the Analysis of Tocopherols.

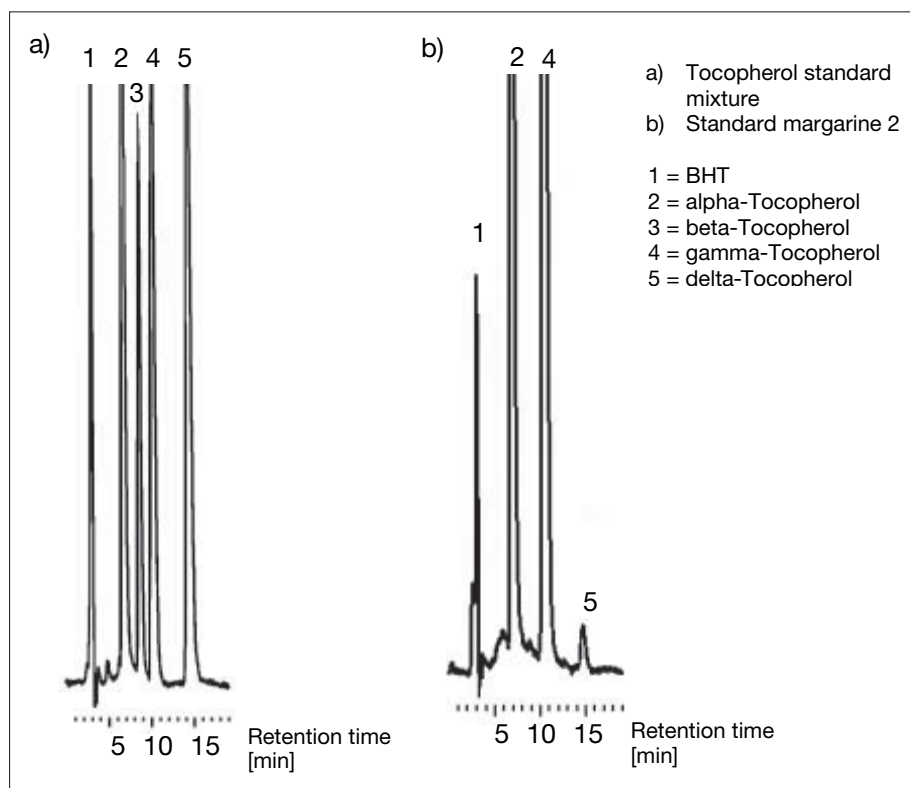


Figure 3: HPLC Chromatogram of a Tocopherol Standard Mixture (a) and Tocopherols in Standard Margarine 2 (b). Fluorescence detection Ex/Em $\lambda = 295/345$ nm.

dard margarines 1 (1.9 mg/100 g fat) and 2 (8 mg/100 g fat). β -Tocopherol was absent in all margarines.

In the fatty acid pattern of the margarines their intended purpose is reflected. SM 1 and 2 have high contents in saturated fatty acids (SFA) of more than 40% and 36%, resp. The contents of monounsaturated fatty acids (MUFA) is about equally high in all margarines (approx. 24%), while the DM shows the highest content of polyunsaturated fatty acids (PUFA) of over 50% and a lower content of SFA of 22% (see Fig. 4).

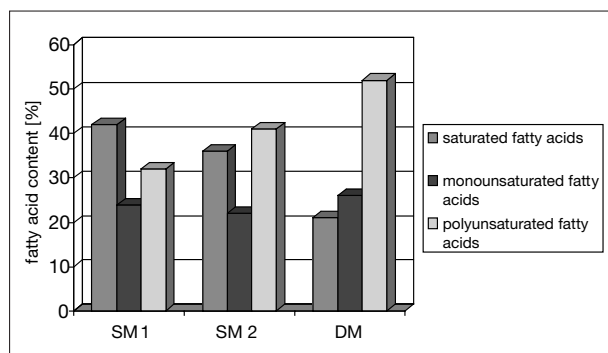


Figure 4: Fatty Acids of the Margarines. SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

Results

Tocopherol Losses with Different Foods and Preparation Techniques

Baking of Pastry and Cake

The tocopherol losses during the baking of short pastry with different margarines are presented in Figure 5. The total loss of tocopherols is dependent on the kind of margarine. SM 2 (9.9 mg/100 g fat) and DM (11.3 mg/100 g fat) lost even more tocopherols than SM 1 (1.6 mg/100 g fat). Different losses were observed for the tocopherols. While SM 1 suffered only very low losses of all three tocopherols, SM 2 showed a decomposition of α -tocopherol of 2.1 mg/100 g fat and of γ -tocopherol of 6.2 mg/100 g fat. In the DM α -tocopherol was decomposed by 7.1 mg/100 g fat and γ -tocopherol by 4.2 mg/100 g fat.

The distribution of the total tocopherol losses after the baking of cake corresponded to the short pastry (see Fig. 6). However, the losses were much higher with all margarines. The highest loss was suffered by α -tocopherol in the DM with 18.1 mg/100 g fat. Both other margarines showed only a slight decomposition of this tocopherol.

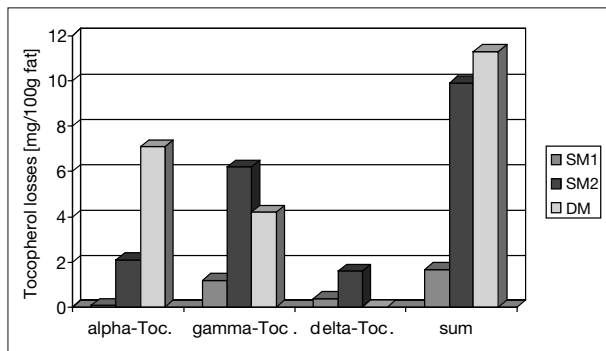


Figure 5: Tocopherol Losses during Baking of Short Pastry. SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

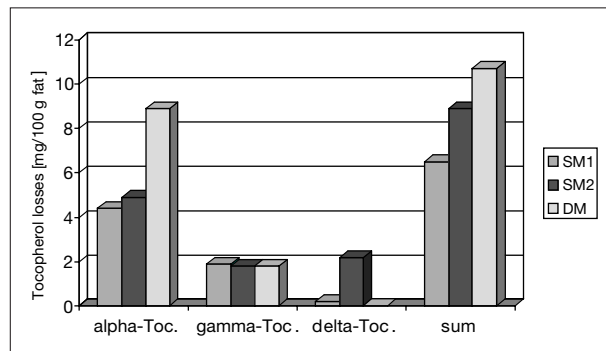


Figure 7: Tocopherol Losses during Roasting of Potatoes. SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

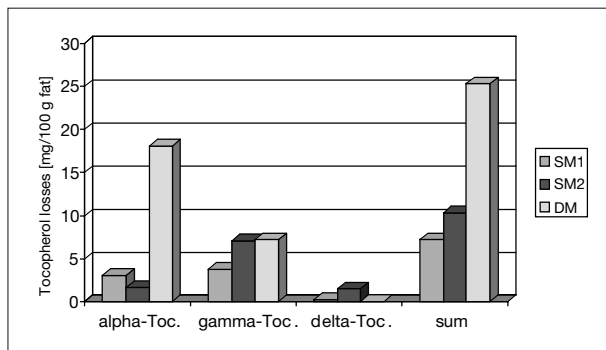


Figure 6: Tocopherol Losses during Baking of Cake Mixture. SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

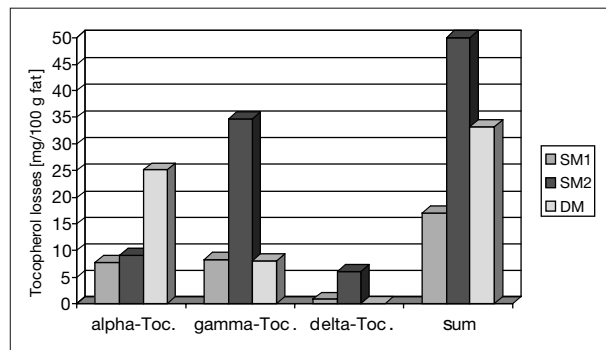


Figure 8: Tocopherol Losses during Roasting of Steaks. SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

Roasting of Potatoes and Steaks

Figure 7 shows that the roasting of potatoes has similarly high total tocopherol losses as the baking of short pastry. In this case, the highest losses were suffered by DM (10.8 mg/100 g fat). α -tocopherol showed the highest degree of decomposition in all margarines, however, the loss in the DM was twice as high as in the other margarines (8.9 mg/100 g fat). The losses in γ -tocopherol with approx. 1.9 mg/100 g fat in all margarines were lower than during the baking of short pastry.

The highest losses of tocopherols in all experiments took place during the roasting of steaks (Fig. 8).

The total tocopherol losses amounted to between 17.2 and 49.9 mg/100 g fat and the highest loss was suffered by SM 2. This corresponds with a loss of the tocopherols originally contained in the margarine of 68%. The high losses with SM 2 are predominantly based on the decomposition of γ -tocopherol and essentially lower amounts of α -toco-

pherol. But δ -tocopherol was also decomposed to over 75%. Both other margarines showed a similar picture as with the baking of short pastry and with the roasting of potatoes.

Stewing of Peas

The distribution of the losses during the stewing of peas in the stainless steel pot (see Fig. 9) was very similar to the roasting of the steaks. However, the total tocopherol losses were lower. The loss of γ -tocopherol (29.1 mg/100 g fat) of SM 2 was also particularly high. SM 1 (5.8 mg/100 g fat) and the DM (10.3 mg/100 g fat) lost essentially lower amounts of γ -tocopherol. The decomposition of δ -tocopherol corresponded to the roasting of potatoes.

Additionally, the stewing of peas was executed with the SM 2 in a glass pot (see Fig. 10). In contrast to the experiments in the stainless steel pot the total tocopherol losses with 0.5 mg/to 100 g fat amounted to only 0.7% instead of 56% with the stewing in the stainless steel pot.

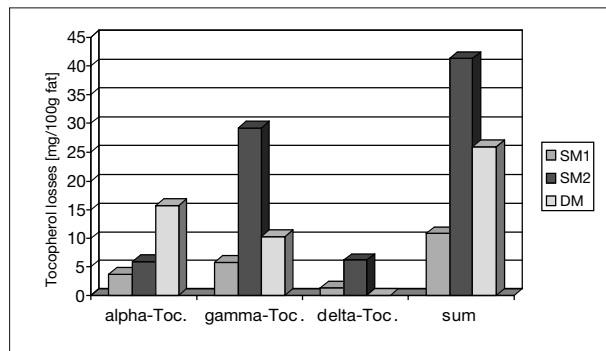


Figure 9: Tocopherol Losses during Stewing of Peas in a Stainless Steel Pot.

SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

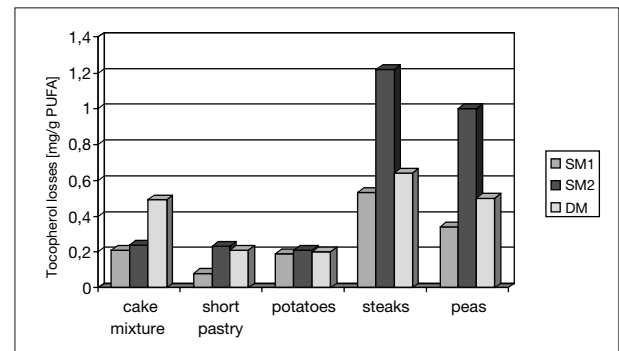


Figure 11: Dependence of Tocopherol Losses on the Content of Polyunsaturated Fatty Acids (PUFA).

SM1: standard margarine 1, SM2: standard margarine 2, DM: diet margarine.

Tocopherol Losses related to the PUFA Content of Margarines

In Figure 11, the dependence of the tocopherol losses on the PUFA content of the margarines is shown. Two groups can be seen: both baking procedures and the roasting of potatoes in one group and the roasting of steaks and stewing of peas in the other one.

This means that in processes causing only lipid oxidation, the PUFA content of the margarines commands the amount of tocopherol losses (high losses when PUFA are high). In processes with strong oxidative conditions, tocopherols are not only used for preventing lipid oxidation but are also oxidized themselves.

Discussion

Wennemark and Jägerstad [4] stated with the baking of bread (250°C, 50 min) losses of the tocopherols contained

in the dough of 20–60%. Ochi *et al* [5] found with the baking of cookies with very different tocopherol additions losses of α - and δ -tocopherol of 20–30%. These higher losses of tocopherols compared to those during the baking of short pastry and cake can be attributed to the different fat contents, fatty acid and tocopherol patterns. Menger [6] as well as Gassmann and Schneeweiß [7] assigned in this connection a high influence to the temperature and they stated a tocopherol gradient of the crust to crumb with the baked bread. Because of the low temperature the tocopherol losses were smaller with the baking of the cake and short pastry than with the bread baking [4]. The comparison of the baking of the cake and the short pastry makes it particularly clear that the duration of the baking process has a high influence on the tocopherol losses apart from the temperature.

The high losses with the roasting of steaks already after a single roasting process are due to the higher temperature of 180°C. The comparison to the roasting of pota-

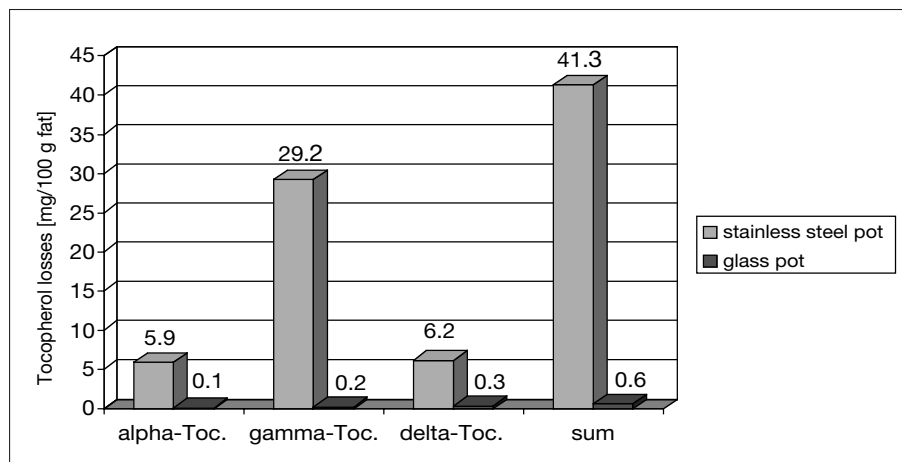


Figure 10: Comparison of the Tocopherol Losses depending on Different Materials.

toes shows the same: despite the longer heating (15 min instead of 6 min) the tocopherol losses were lower because of the lower temperature (120°C). On the other hand the surface-to-layer thickness of the cooking fat has a high influence when comparing roasting and frying. Due to the low layer thickness of the fat during the roasting, the oxygen partial pressure is higher than during frying. Subsequently the tocopherols contained in the cooking fat are also defeated by stronger oxidative conditions which leads to raised losses in tocopherols. Coors and Montag [8] also showed the dependence of the stability of tocopherols on the oxygen partial pressure in storage experiments with different vegetable oils. Already at room temperature a raised oxygen partial pressure led to instability of the tocopherols.

The high tocopherol losses during the stewing of peas in the stainless steel pot (up to 56%) under chosen conditions could not only be caused by temperature and duration of the household treatment because these conditions were very mild (70°C). As a comparison pointed out under identical conditions in a glass pot, in this case the material of the cooking vessel had a crucial influence on the stability of the tocopherols. Because the surface of the stainless steel pot could not construct an inert metal oxide layer due to frequent mechanical cleaning, the tocopherols were oxidized catalytically under these conditions by iron and chrome or were oxidized by Fe^{3+} -ions appearing in a redox reaction. This metal-catalysed oxidation of tocopherols to tocopherolchinones in an acidic environment was used for the first chemical determinations of vitamin E [9]. Therefore, for the preservation of the total tocopherols, the choice of an inert cooking vessel is as important as low temperatures.

It was observed that the loss of tocopherols during the heating procedure was dependent on the kind of margarine used as well as on the heating procedure. This was in relation with the total content of each tocopherol in the margarine before a heating procedure. As concerns the dependence on the heating procedure, two groups of losses were observable: in one group (both baking processes, roasting of potatoes) the losses amounted to a maximum of 20%, in the second group (roasting of steaks, stewing) the losses amounted to nearly 70%. Figure 12 shows the heating processes resulting in low losses of tocopherols, Figure 13 those with higher losses.

Similar observations with regard to the amount of the tocopherol losses were performed by Ruiz-Lopez *et al* [10] with the comparison of the heating of olive oil in the microwave oven and in the frying pan. They showed that at a temperature of 175°C and 8 min duration (without fried food) losses of over 60% appeared. The losses while heating up in the microwave oven (8 min with 2450 Hz, $t = 250^\circ\text{C}$) were about 50%. Gordon and Kourimska [11] found essentially lower tocopherol losses in rapeseed oil on frying of potato pieces at temperatures of 162°C and few minutes duration. Only after sixfold repetition the contents decreased under 60% of the initial content.

The dependence on the composition of the margarines used within the framework of this work appeared particularly clear in the case of the consideration of the absolute losses of the single tocopherols after the household treatments. The DM with a very high content of α -tocopherol (or α -tocopherol acetate) has also in all experiments the highest α -tocopherol losses. Correspondingly, the losses of γ -tocopherol during the baking, the roasting of steaks

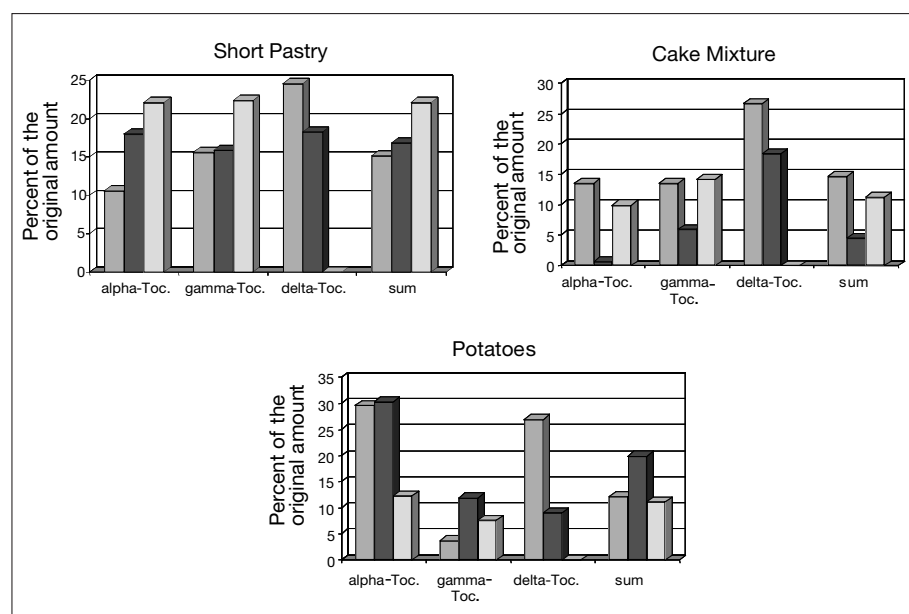


Figure 12: Comparison of the Tocopherol Losses – Low Losses (maximum of 20%). (Sequence of the columns see Fig. 5.)

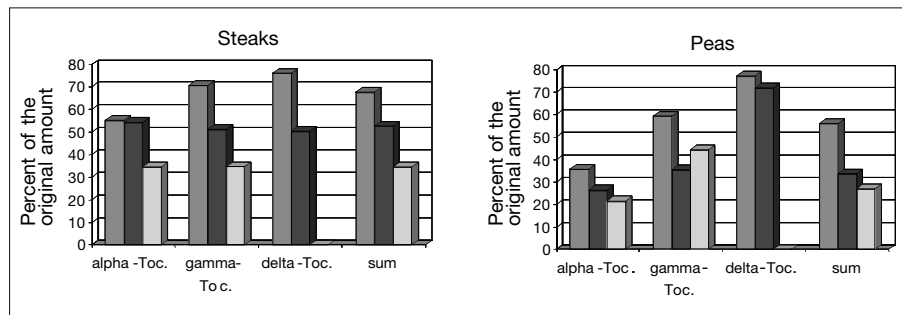


Figure 13: Comparison of the Tocopherol Losses – High Losses (nearly 70%). (Sequence of the columns see Fig. 5.)

and the stewing of peas in the stainless steel pot were highest in SM 2, the margarine with the highest γ -tocopherol content. The SM 1 with only low tocopherol contents shows the lowest absolute tocopherol losses and no tocopherol showed a special stability. The dependence of the tocopherol losses on the sort of oil and therefore on the fatty acid pattern is easily seen when the total tocopherol losses are confronted with the PUFA content which are particularly sensitive to oxidation. As Figure 11 points out, the tocopherol loss-PUFA relation is similar with the baking of cake and short pastry and the roasting of potatoes. The tocopherol losses are therefore essentially affected by the content of PUFA in the margarines (high tocopherol losses go with high PUFA content and vice versa). However, this dependence is only valid if only lipid oxidation is caused by the thermal treatment and not under strongly oxidative conditions like the roasting of steaks or the catalytic-affected decomposition (stewing of peas). In this case the tocopherols are not only needed for preventing lipid oxidation, but are also directly oxidized by the strongly oxidative conditions. In this case the tocopherol losses do not correlate with the PUFA content.

With the relative losses of the single tocopherols during a household treatment, no uniform picture arose. α - and γ -tocopherol showed a similar stability, only during the roasting of potatoes α -tocopherol was more unstable than γ -tocopherol. In almost all cases δ -tocopherol showed the lowest stability. Yoschida *et al* [12] as well as Gottstein and Grosch [13] showed in pilot experiments that for the stability of the tocopherols the following order is to be considered: $\delta > \beta > \gamma > \alpha$. Miyagawa *et al* [14] stated a changed order in the stability of the single tocopherol homologous: $\alpha \geq \delta > \gamma$ with the frying of potatoes (180°C). Besides, they found that this stability order is dependent on the oil used and on the experimental conditions chosen (duration and temperature). Ochi *et al* [5, 15] stated no different stabilities of δ - and α -tocopherol with the baking of biscuits. But during storage of these biscuits, δ -tocopherol was significantly more stable than α -tocopherol.

The tocopherol losses in baking can be of nutritional importance because here also a relatively high fat intake

with the food takes place and therefore the unsaturated fatty acids after the *in vivo* absorption are to be protected by antioxidants. The study shows that the tocopherols are well suited for the protection of oxidation of the unsaturated fatty acids even in spite of the long baking process of cakes at high temperatures. There are still sufficient amounts of tocopherols for the absorption. However, with the roasting of steaks the amount of used and therefore consumed fat is very low. Moreover, the oxidation of the unsaturated fatty acids might progress to higher oxidation products (polymers). Then the remaining tocopherols should be sufficient, particularly as they are partly overdosed in the used margarines in comparison to the PUFA. Noteworthy are the tocopherol losses during the stewing of peas in the stainless steel pot, because these cooking vessels are frequently used. Here inert vessels should be used.

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