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Effects of α-, γ-, and δ-Tocopherols on the Autoxidation of Purified Rapeseed Oil Triacylglycerols in a System Containing Low Oxygen

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Controversial data on the antioxidant effects of tocopherols have already been shown in different test systems, yet δ-tocopherol was hardly considered. This study was designed to assess the effects and degradation of α-, γ-, and δ-tocopherol in four concentrations from between 0.01 and 0.25% on the oxidation of purified rapeseed oil trigacylglycerols (RO-TAG) at 40 °C in the dark in a low oxygen containing system for 11 weeks. Oxidation experiments were performed weekly by assessing primary (peroxide value, PV; conjugated dienes, CD) and secondary (*p*-anisidine reactive products, *p*-AV; hexanal) oxidation products, the degree of unsaturation with the iodine value (IV), and the stability of tocopherols. Test approaches were performed with and without the addition of 0.01% α,α′-azoisobutyronitrile (AIBN), which is a known radical initiator. α- and γ-Tocopherols increased the rate of lipid oxidation, which was more pronounced in the presence of AIBN. Only the lowest amount of 0.01% γ-tocopherol was comparable to the control sample in the test without AIBN. The most effective was shown to be δ-tocopherol, which did not elevate lipid oxidation except the PV in the AIBN test, but they did not delay it either. δ-Tocopherol was the most stable followed by γ- and α-tocopherol. For α- and γ-tocopherol, but not for δ-tocopherol, strong correlations were found between the tocopherol degradation and the extent of oxidation. Results suggest that (i) at concentrations higher than 0.05%, tocopherols are less efficient and turn their mode of action or participate in side reactions in RO-TAG and (ii) δ-tocopherol was shown to be the most stable and effective under these low oxygen conditions.

KEYWORDS: α-, γ-, δ-Initiator; lipid oil; oxidation; primary products; radical; rapeseed

INTRODUCTION

Lipid peroxidation, a general term for a multifactorial process that results in the generation of oxidation products, reduces the lifetime of foods and is responsible for the loss of nutritional and organoleptic quality. To delay this autoxidation process, several natural and synthetic substances have been tested for their effectiveness as antioxidants. As the major group of primary antioxidants occurring in plant oils and fats, tocopherols were the main subject of numerous investigations (*1*−*6*). Generally, tocopherols exhibit high stability and good "carry through properties". Their mode of action is mainly due to the ability to inhibit free radical propagation by donating hydrogens from their phenolic group to peroxy radicals in order to stabilize them. However, this general conclusion must be verified with respect to the tocopherol form and concentration (α-, γ-, or δ-tocopherol), test conditions and systems, and substrates and oxidation temperatures (*7*). Recently, controversial results on the effectiveness of different tocopherols on the oxidation of lipids have been published (*7*−*9*). Several investigators demonstrated that α-tocopherol acts as a prooxidant when present in high concentrations in autoxidizing lipids (*1*, *2*, *11*, *12*), whereas γ-tocopherol seems to have more antioxidative potential than α-tocopherol (*1*−*6*, *7*, *9*). However, less focus in this concern is directed toward δ-tocopherol, especially when testing purified triaclyglycerols (*5*, *6*). Kulas and Ackman (*6*) reported at one of the first on the high potential of δ-tocopherol in purified fish oil. Recently, we found that especially at higher temperatures of more than 100 °C δ-tocopherol was antioxidatively the most active (*12*).

The aim of this current work was to compare the stability and the effects of α, γ-, and δ-tocopherol on the autoxidation of purified rapeseed oil triacylglycerols (RO-TAG) at a moderate temperature of 40 °C in the dark with and without the added catalyst α,α′-azoisobutyronitrile (AIBN). Emphasis was put on the large range and higher concentrations between 0.01 and 0.25%. In contrast to most studies in this field, we used storage systems with a low amount of oxygen, which makes it more comparable to the storage conditions in technology and households.

MATERIALS AND METHODS

Materials and Reagents. Rapeseed oil that was purified of tocopherols was obtained as a gift from Unilever, Germany; its

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Table 1. Chemical and Stability Characteristics of the RO-TAG Used in This Study[a]

	RO-TAG
main fatty acids (% of total fatty acids)	
palmitic acid (C16:0)	6.7
palmitoleic acid acid (C16:1n9)	0.3
stearic acid (C18:0)	2.2
oleic acid (C18:1n9)	58.2
linoleic acid (C18:2n6)	21.6
γ-linolenic acid (C18:3n6)	0.6
α-linolenic acid (C18:3n3)	8.9
saturated fatty acids	9
monounsaturated fatty acids	60
polyunsaturated fatty acids	31
p/s ratio	3.4
α-tocopherol (mg/100 g)	<0.5
γ-tocopherol (mg/100 g)	<0.5
δ-tocopherol (mg/100 g)	<0.5
IV	66.2
PV	0.59
hexanal (mg/100 g)	ND
p-AV value	0.99

[a] ND, not detectable.

Table 2. Correlations between Remaining Tocopherols (T) and Formation of Primary and Secondary Oxidation Products with the Addition of the Radical Initiator AIBN (Same Trends for the Formation of CDs; Data Not Shown in the Table)[a]

	PV+[a]	*p*-AV+	hexanal+	PV–[a]	*p*-AV–	hexanal–
			α-T			
0.01%	–0.765**	–0.779**	–0.592	–0.619*	–0.630	–0.354
0.05%	–0.882**	–0.749**	–0.794*	–0.799**	–0.772**	–0.618*
0.1%	–0.948**	–0.942**	–0.969**	–0.911**	–0.925**	–0.817**
0.25%	–0.983**	–0.977**	–0.922**	–0.980**	–0.960**	–0.779*
			γ-T			
0.01%	–0.001	0.073	0.462	–0.136	0.419	0.487
0.05%	–0.980**	–0.975**	–0.864**	–0.429	–0.176	–0.047
0.1%	–0.959**	–0.949**	–0.863**	–0.954**	–0.931**	–0.425
0.25%	–0.975**	–0.963**	0.937**	0.979**	–0.982**	–0.650*
			δ-T			
0.01%	–0.047	0.417	0.539	0.300	0.523	–0.115
0.05%	–0.214	–0.321	–0.159	–0.034	0.102	–0.444
0.1%	–0.328	–0.39	–0.426	–0.263	–0.430	–0.448
0.25%	–0.901**	–0.922**	–0.885**	–0.932**	–0.824**	–0.575

[a] +, with AIBN; –, without AIBN. *$p < 0.05$; **$p < 0.01$.

specification and chemical composition are given in **Table 1**. α- and δ-Tocopherol were purchased from Merck (Vienna, Austria) and Sigma (Vienna, Austria), and γ-tocopherol was kindly donated as a gift by Roche (Basel, Switzerland). All solvents and reagents were either HPLC or proanalysis grade and obtained from Sigma unless otherwise stated. AIBN was obtained from Fluka (Vienna, Austria).

Oil Enrichment and Preparation. α-, γ-, or δ-tocopherols dissolved in hexane were each added to a round-bottomed flask, the hexane was evaporated thereafter under a stream of nitrogen, and an appropriate amount of the RO-TAG was added to the tocopherols and rotated for 10 min for a good tocopherol distribution to obtain the final concentrations of 0.01, 0.05, 0.1, and 0.25%. In a second test approach, 0.01% AIBN, a known radical initiator, was added to the RO-TAG samples, which were afterward enriched with the same concentrations of tocopherols. AIBN was given to induce oxidative stress in the sample and therefore to intensify the use of the tocopherols.

Oxidation Experiments. The enriched samples (100 g each) were oxidized in screw-capped 100 mL Schott-flask flasks at 40 °C for 11 weeks in the dark. The flasks were filled until the neck of the bottle so that there was only a little headspace left and therefore can be defined as a low oxygen containing system. Samples for oxidation and tocopherol analyses were obtained weekly, and values are based on double determinations.

The primary oxidation status of the triacylglycerol samples was determined by measuring the peroxide value (PV) (*13*) and the formation of conjugated dienes (CD) (*14*); secondary oxidation products were characterized via *p*-anisidine (*p*-AV) reactive products (*15*), and the formation of hexanal was measured by headspace capillary gas chromatography as described by Medina and co-workers (*16*). The unsaturation of the samples was evaluated by the iodine value (IV) (*17*). Tocopherol degradation was measured by RP-HPLC and UV detection at 295 nm as was described earlier (*18*).

Quality criterion of the analytical methods was the coefficient of variation (CV); CV%: α-tocopherol, 3.5; γ-tocopherol, 4.1; δ-tocopherol, 3.9; PV, 2.1; CD, 2.5; IV, 3.6; *p*-AV, 3.1; and hexanal, 5.2.

Statistical Analysis. All tests were performed in single glasses, and the results are based on double determinations. Pearson correlation coefficients were conducted using SPSS 10.0 for Windows and considered to be significant at a value of $p < 0.05$.

RESULTS AND DISCUSSION

The antioxidative potential of α-, γ-, or δ-tocopherols in a concentration range from between 0.01 and 0.25% was tested in RO-TAG at a moderate oxidation temperature of 40 °C. Purified triacylglycerols are the most valid model to study the oxidation of plant oils because they contain the natural complexity of the fatty acid pattern and exhibit a viscosity near to the oil of origin. Rapeseed oil was chosen because it is a commonly used dietary oil in the northern hemisphere and a good source of oleic and linoleic acid. Moreover, it contains less saturated fatty acids than most of the other habitually consumed plant oils. The state of oxidation was observed by assessing primary and secondary oxidation products, as well as the degradation of tocopherols. In contrast to some other studies, we stored the RO-TAG in nearly full and closed glasses, with a low amount of oxygen exposed to the samples. Our chosen conditions are closer to the conditions in real life considering storage and frequent use in households.

Generally, no effects of the tocopherols were found on the degree of unsaturation of the RO-TAG, and the IV remained stable between 60 and 65 g/100 g, which is based on the high content of monounsaturated fatty acids of 60% of the total fatty acids.

Effects of the Tocopherols on the Formation of Primary Oxidation Products (Figure 1; Table 2). Neither in low nor in high concentrations was α-tocopherol able to show antioxidative behavior. Both PV and CD formation were induced by α-tocopherol with increasing amounts. γ-Tocopherol showed the same effects, only the RO-TAG enriched with the lowest concentration of 0.01% developed similarly to the control sample. With higher amounts, an increase in PV and the CD was also observed. This means that both α- and γ-tocopherol lose their activity to inhibit hydroperoxide formation at higher concentrations. Only δ-tocopherol did not show any oxidation accelerating effects; however, it was also not antioxidative.

The same forced oxidation, which was even more pronounced, was found in the second test with AIBN. The higher the concentration, the higher the PV was. Especially α-tocopherol induced hydroperoxide formation from the second week onward, whereas γ- and δ-tocopherol showed the same effects only after weeks four and six, respectively. The same trends were observed for CD. These results are partly in contrast to some published papers on this topic (*2*, *3*, *6*) and our results obtained before with other test systems (*1*, *12*); however, the concentrations added were deliberately set rather high. Antioxidative effects were mainly observed at low concentrations, and prooxidant effects were noted mainly in higher doses (*4*, *8*, *19*, *20*). These results might also be discussed in respect of

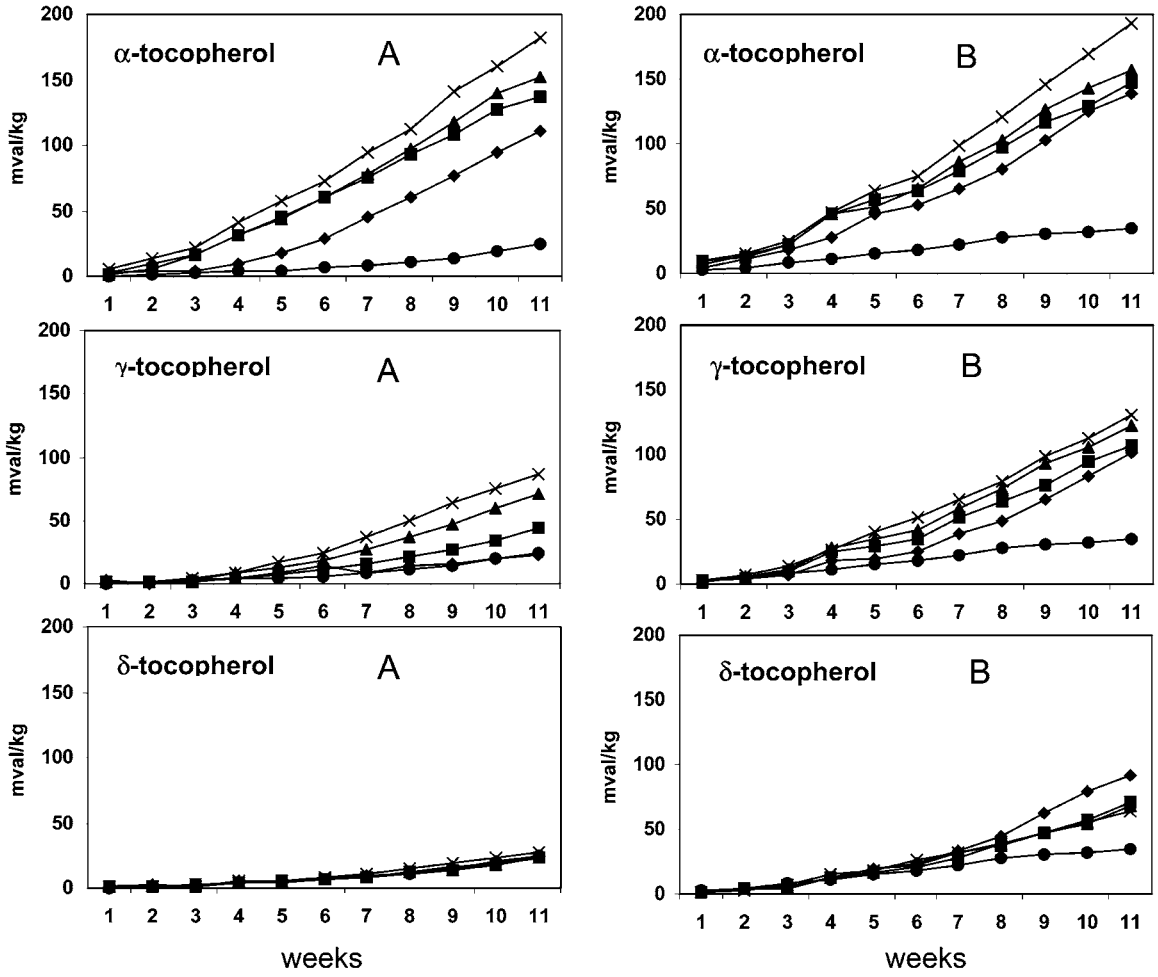

Figure 1. Effects of added α-, γ-, and δ-tocopherols at 0.01–0.25% on the hydroperoxide formation (PV) in RO-TAGs at 40 °C in the dark without (**A**) and with (**B**) AIBN. Symbol key: 0.01 (◆), 0.05 (■), 0.1 (▲), and 0.25% (×) tocopherol addition and control (●).

the hydroperoxides formed by oleates and the participation of tocopherols in side reactions (*3*, *5*, *21*, *22*), which seem to increase with higher enrichments (R2, R3) (*23*):

$$TH + LOO^{\circ} \rightarrow LOOH + T^{\circ} \text{ (antioxidative)} \quad (1)$$

$$TH + LOO^{\circ} \leftarrow LOOH + T^{\circ} \text{ (prooxidative)} \quad (2)$$

$$TH + L^{\circ} \leftarrow LH + T^{\circ} \text{ (prooxidative)} \quad (3)$$

However, tocopherols are not only considered to react as tocopheroxyl radicals but also with generated hydroperoxides to form peroxyl radicals (R4) (*24*):

$$T^{\circ} + LO^{\circ} + H_2O \leftarrow LOOH + TOH \text{ (prooxidative)} \quad (4)$$

The free radicals formed in these side reactions may act as catalysts to reinitiate new oxidation reduction sequences.

In addition, our study was one of the first that used oxygen deficient conditions. Because it is known that the speed of the lipid oxidation process is highly related to the accessibility of oxygen (*25*, *26*), the different outcome of our study can be related to our conditions. Because of the low amount of headspace, the conditions were not comparable with the majority of studies in this field, which had a higher availability of oxygen for their samples, which might also explain the different results. Under these conditions, as the overall rate of oxygen is low, the participation of tocopherols in the above-mentioned side reactions becomes more significant (R2−4).

Sparse research on the influence of triacylglycerol unsaturation on hydroperoxide formation and tocopherol degradation shows that tocopherols degraded faster in less unsaturated oils (*27*−*29*). The explanation for this is quite different, as either it is the rate of hydroperoxide formation (*29*) or the hydroperoxides formed in highly unsaturated oils that decompose rapidly before they react with tocopherols (*30*). However, this phenomenon would help to explain that some studies with unsaturated triacylglycerols from sunflower or corn oil could especially find a higher antioxidative potential of tocopherols (*1*−*3*, *21*). Furthermore, it is known that the physical states of the lipid system affect the potential of antioxidants especially with respect to the interfaces between air and oil, which can influence the distribution of antioxidants (*31*).

Tocopherol Stability (Figure 2). What was remarkable from this study was that δ-tocopherol was the most stable, with and without AIBN, followed by γ-tocopherol. The least stable in both test approaches was α-tocopherol, which was degraded first. A 0.01% α-tocopherol amount was entirely consumed after 4 (without AIBN) or 5 (with AIBN) weeks, while for the higher concentrations 8−24% residual α-tocopherol without AIBN and less than 5% with AIBN was recovered after 11 weeks of oxidation. From γ-tocopherol, 26−56% without AIBN and 0 (0.01%)−13% with AIBN was left after 11 weeks of oxidation. The most stable being δ-tocopherol was available after 11 weeks within 73−100% without AIBN and 42−73% with AIBN. The difference between the absolute amounts used up during oxidation was considerable. For the AIBN approach at additional

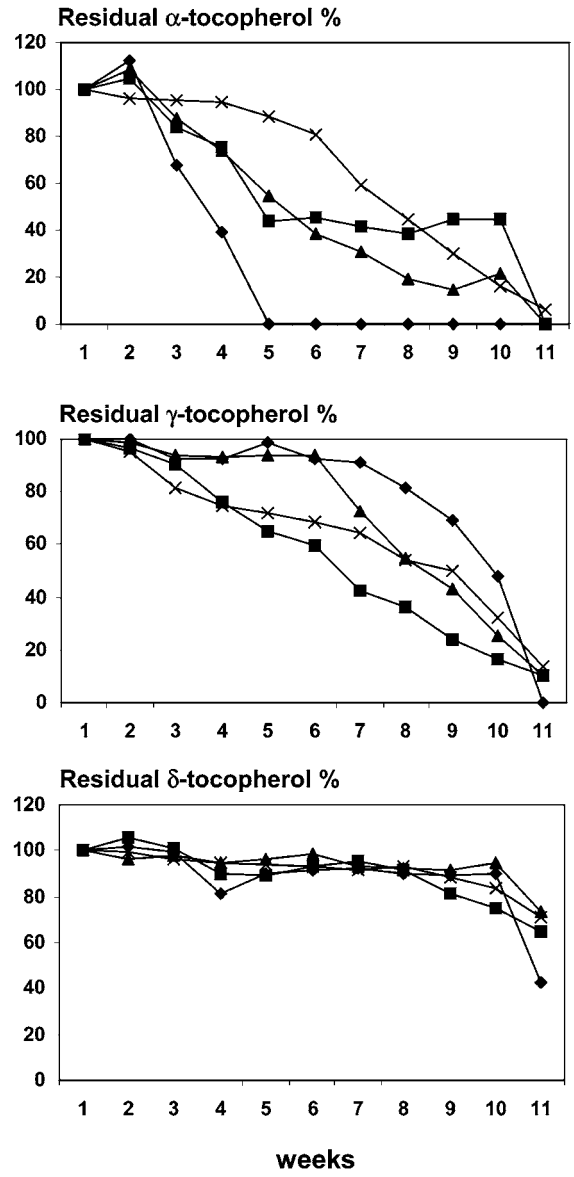

Figure 2. Residual α-, γ-, and δ-tocopherol contents of added 0.01–0.25% levels during oxidation of RO-TAGs at 40 °C in the dark in the presence of 0.01% of the radical initiator AIBN. Symbol key: 0.01 (◆), 0.05 (■), 0.1 (▲), and 0.25% (×) tocopherol addition.

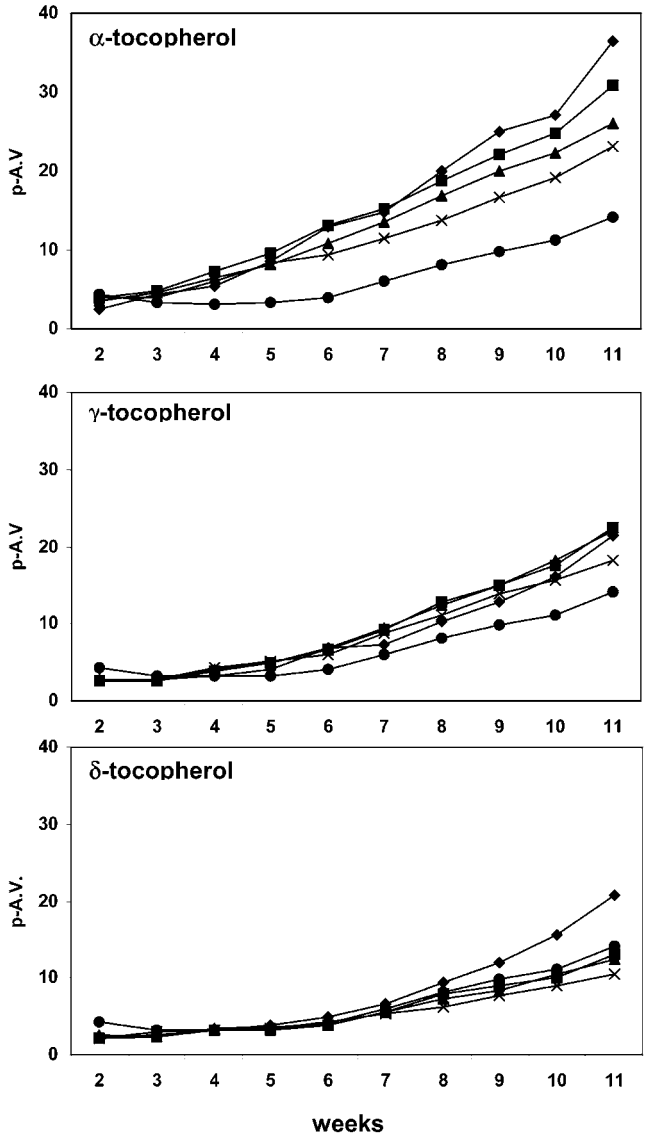

Figure 3. Effects of added α-, γ-, and δ-tocopherols at 0.01–0.25% on the formation of secondary oxidation products in RO-TAGs at 40 °C in the dark in the presence of 0.01% of the radical initiator AIBN. Symbol key: 0.01 (◆), 0.05 (■), 0.1 (▲), and 0.25% (×) tocopherol addition and control (●).

levels of 10, 50, 100, and 250 mg/100 g, the respective amounts of α-tocopherol consumption were 10, 50, 100, and 237 mg/100 g, of γ-tocopherol 10, 46, 94, and 223 mg/100 g, while those of δ-tocopherol were 8, 27, 52, and 117 mg/100 g, respectively.

This high consumption of antioxidants and the formation of primary oxidation products are fairly well-correlated (**Table 2**). For α-tocopherol and for γ-tocopherol (except 0.01%), a highly significant negative correlation between their stability and the PV was observed. For δ-tocopherol, only the 0.25% addition correlated $r = -0.901$ ($p < 0.01$) but not the lower concentrations. The correlation increases with the amounts given.

The findings that α-tocopherol was consumed more quickly can be explained by its lowest redox potential (*32*), which implies that it is a stronger hydrogen donator and more vulnerable to oxidation. The strong correlation of remaining tocopherols and generated oxidation products supports the assumption that the tocopherols are not only consumed in antioxidant reactions but also in the above-mentioned first-order side reactions. Their rates in participation are in the following order: α- > γ- > δ-tocopherol. Data show an accelerated oxidation by α-tocopherol.

Effects of the Tocopherols on the Formation of Secondary Oxidation Products (Figures 3 and 4). Formation of both the *p*-AV and the volatile aldehyde hexanal was slower without AIBN than with its addition and modest as compared to the primary oxidation products. This in particular can be explained by the hydroperoxide breakdown to volatiles, which was not expected to happen within the first weeks from the onset.

After 11 weeks of oxidation, the *p*-AV and the level of hexanal of the RO-TAG control without tocopherol additions reached 5.2 and 0.308 mg/100 g without AIBN and 14.1 and 8.1 mg/100 g with AIBN, respectively.

Similar to the results of the primary oxidation products, independent of whether AIBN was used or not, α-tocopherol affected the oxidation and sped it up in all concentrations when considering the *p*-AV. The same was observed for hexanal without AIBN. With the radical induction, the hexanal content

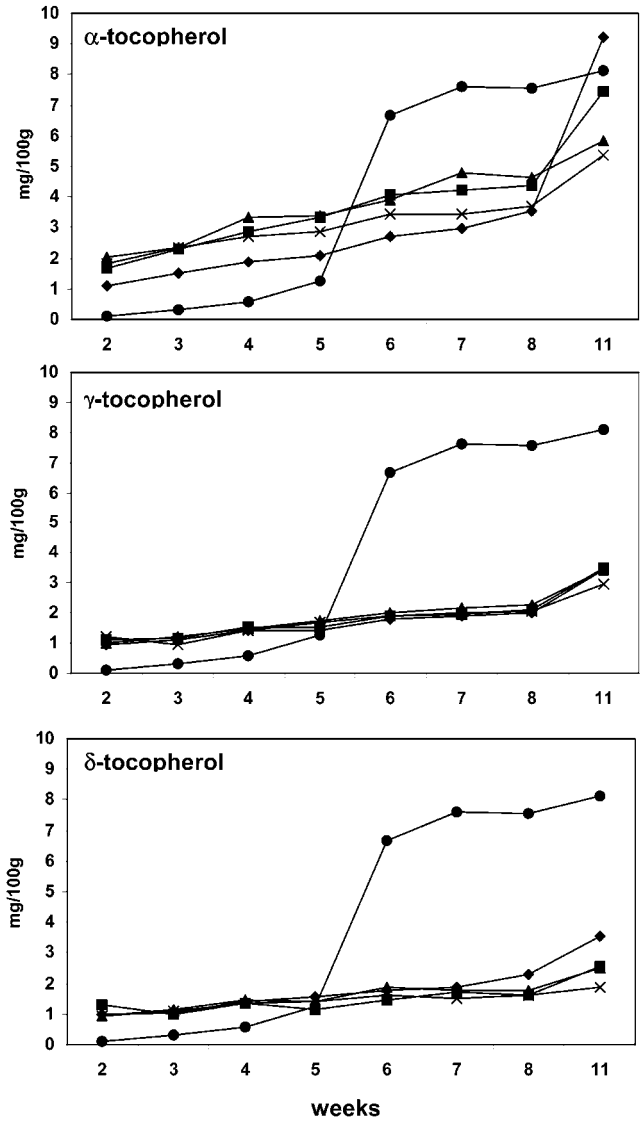

Figure 4. Effect of added α-, γ-, and δ-tocopherols at 0.01–0.25% on the formation of hexanal in RO-TAGs at 40 °C in the dark in the presence of 0.01% of the radical initiator AIBN. Symbol key: 0.01 (◆), 0.05 (■), 0.1 (▲), and 0.25% (×) tocopherol addition and control (●).

in the control increased sharply between weeks five and six, whereas the RO-TAG enriched with α-tocopherol increased in hexanal more moderately. However, it was higher after 11 weeks than it was with the RO-TAG enriched with γ- and δ-tocopherols. The smallest amount of γ-tocopherol suppressed formation of hexanal after 11 weeks of oxidation without AIBN, as the higher enrichments were comparable with the control oil. With AIBN, all γ-tocopherol additions reached hexanal values between 2.9 and 3.5 mg/100 g after 11 weeks of oxidation. Again, δ-tocopherol was most effective and reached hexanal values after 11 weeks between 0.25 and 0.40 mg/100 g without AIBN and 1.9−3.5 mg/100 g with AIBN. This was far lower than the control and the other tocopherols. The development of *p*-AV was similar to the control for all enrichments of δ-tocopherol with or without AIBN, except the 0.01% addition, which slightly increased the volatile formation in the AIBN test.

Again, the formation of volatiles and the stability of α- and γ-tocopherol are negatively correlated (**Table 2**). For α-tocopherol, the strongest correlations were found, followed by γ-tocopherol. For δ-tocopherol, only the 0.25% addition correlated $r = -0.922$ ($p < 0.01$; *p*-AV) and $r = -0.885$ ($p < 0.01$; hexanal) but not the lower concentrations. The higher the concentration tested, the higher the correlation with the secondary oxidation products.

The correlations between the stability of tocopherols and the formation of primary and secondary oxidation products generally show that as long as there are α- and γ-tocopherols available in the system, the oxidation products remained lower. With increasing tocopherol consumption, the oxidations speed up. For δ-tocopherol, this is only true for the 0.25% enrichment due to the high stability of the lower concentrations. The faster decomposition of α-tocopherol could also be responsible for the increase in α-tocopheroxyl radicals, which participate in radical-forming side reactions (R2, R3) and thus reducing stability.

Generally, the system with AIBN responded faster due to the increased oxidative stress. Very interesting in this context is the stronger correlation between the stability of tocopherols and the formation of oxidation products.

On the basis of the results available in the literature, it is not possible to generally define the optimal concentrations for tocopherols. In purified soybean oil, δ-tocopherol was reported to have optimum antioxidant activity at 0.05% and prooxidant activity at 0.1%, based on hydroperoxide and hexanal formation (*11*). In contrast, Huang and co-worker (*2*) found for δ-tocopherol, considering the same analytical parameters, in corn oil inhibitions at higher concentrations up to 0.2%. Several studies, also from our working group, could show antioxidative effects for α- and especially γ-tocopherol (*1*, *3*, *4*, *12*); however, most of the studies used unsaturated oils and lower tocopherol concentrations.

The presented study could show that high tocopherol fortification in an oleate rich TAG oxidized with moderate conditions and with a low amount of available oxygen generally do not protect the system on the formation of neither primary nor secondary oxidation products. The most stable and efficient was δ-tocopherol, but the already considered knowledge that the antioxidative effects of the different tocopherols in TAG and in bulk oils mainly depend on the details of the systems is too complex to allow us to draw any general conclusions.

However, results of the few available studies showing antioxidative potential for δ-tocopherol can be supported by the results of this paper, even though the power was not strong in this system.

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