# Identification of α-Tocopherol Oxidation Products in Triolein at Elevated Temperatures

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The effect of high-temperature treatment on the stability of α-tocopherol (**1**) in triolein was assessed under a reduced-pressure atmosphere (4−40 mbar) simulating the deodorization step of the refining of vegetable oils. A marked degradation of **1** was observed, which increased with increasing temperature (180−260 °C) and heating time (20−80 min). The degradation of **1** in triolein at 240 °C was inhibited by the addition of the synthetic antioxidant TBHQ or when heating was performed under nitrogen atmosphere, indicating oxidative degradation. The oxidation products were isolated and identified as α-tocopherolquinone (**2**), 4a,5-epoxy-α-tocopherolquinone (**3**), and 7,8-epoxy-α-tocopherolquinone (**4**).

**Keywords:** *α-Tocopherol; α-tocopherolquinone; epoxy-α-tocopherolquinone; thermoxidation; triolein*

## INTRODUCTION

Studies on the tocopherol balance during deodorization showed that upon refining of vegetable oils, tocopherols are not only partially distilled but also oxidized during the deodorization process (*1*). Tocopherols are the most important natural antioxidants present in vegetable oils, protecting lipids from peroxidation. The antioxidant properties of tocopherols have been ascribed to the easy hydrogen transfer from their phenolic hydrogen atom to a peroxyl radical (*2*). The hydrogen transfer produces a tocopheroxyl radical, which combines with another lipid peroxyl radical in a termination reaction yielding nonradical tocopherol oxidation products (*3*, *4*, *31*).

Participation of tocopherols in antioxidation reactions (eqs 1 and 2) leads to their degradation and consumption, presumably by oxidation (*5*). A rapid tocopherol

$$LOO^{\bullet} + TOH \rightarrow LOOH + TO^{\bullet} \quad (1)$$

$$LOO^{\bullet} + TO^{\bullet} \rightarrow TO{-}OOL \quad (2)$$

degradation at frying conditions and during microwave heating has been observed, indicating the heat sensitivity of tocopherols (*6*−*8*). Relative stabilities of the different tocopherol homolgues indicate that α-tocopherol is less stable than *δ*-tocopherol at high temperature (*9*−*11*). Several tocopherol oxidation products have been identified (*12*−*18*). However, little information is available on the stability of tocopherols and on the degradation products formed during oxidation of tocopherols in a lipid matrix at high temperatures (*5*, *19*, *20*).

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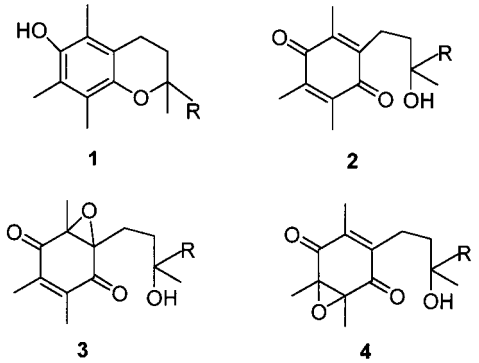


**Figure 1.** Structures of **1**−**4**.

The overall objective of this study was to investigate the influence of high-temperature treatment on the stability of tocopherols dissolved in a triacylglycerol matrix and to identify the most important oxidation products formed. Special emphasis was made to check the thermal stability and to evaluate the susceptibility of α-tocopherol to oxidation reactions at temperatures >200 °C and low pressure during short heating experiments simulating industrial deodorization conditions.

## MATERIALS AND METHODS

**Chemicals.** Pure α-tocopherol and silica gel 60 for chromatography were purchased from Merck (Darmstadt, Germany), and technical grade triolein (OOO) was delivered by Sigma Chemical Co. (St. Louis, MO). HPLC grade solvents (hexane and isopropyl alcohol) were purchased from Merck and were used without further purification. Water was distilled twice and additionally purified with activated char.

**Synthesis of α-Tocopherol Oxidation Products.** Several oxidation products of α-tocopherol (**1**) (structure shown in Figure 1) have been synthesized and isolated according to literature reports. Alkaline ferricyanide is the most used reagent for the preparation of α-tocopherol spirodimers and α-tocopherol spirotrimers (*12*, *15*, *21*−*23*). Oxidation of α-tocopherol with ferric chloride preferentially forms α-tocopherol quinone (**2**) (*24*, *25*). α-Tocopherol−α-tocopheroxyl dimer and

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α-tocopherol−α-tocopherol quinone spirodimer were isolated from the oxidation of α-tocopherol with *tert*-butylhydroperoxide (*13*, *14*). Epoxy-α-tocopherols [4a,5-epoxy-α-tocopherol quinone (**3**) and 7,8-epoxy-α-tocopherol quinone (**4**)] were prepared according to a modified method of Csallany (*26*) and Ha (*27*). Briefly described, α-tocopherol was epoxidized in an oxygen-saturated acetonitrile/water mixture by addition of the radical initiator azoisobutyronitrile (AIBN). Tocopherol oxidation products **(2**−**4)** were separated from the crude oxidation mixture by preparative HPLC using a Kontron chromatograph (Serlabo, Brussels, Belgium) equipped with a UV detector (275 nm), a sample loop of 250 $\mu$L, and a normal phase silica column (Lichrosorb, 250 × 20 mm internal diameter and particle size 5 $\mu$m, Optilab, Brussels). The flow rate of the mobile phase (hexane/isopropyl alcohol, 95:5, v/v) was 15 mL/min, corresponding to a column pressure of 25 bar. Collection of the different fractions was performed manually.

$^1$H NMR and $^{13}$C NMR spectra were recorded with a JEOL JNM-EX270 spectrophotometer at 270 and 68 MHz, respectively. The samples were dissolved in deuterated solvents with tetramethylsilane as internal standard. All spectral data were in accordance to literature reports.

**Heat Treatment of Oil Samples.** The α-tocopherol standard was dissolved in triolein, and samples (15 g) were transferred into a 50 mL flask and immersed in a preheated oil bath. The flask was attached to a vacuum pump, and the vacuum was regulated by use of a valve connected to a manometer. After the heat treatment, the samples were transferred into small bottles, purged with nitrogen, and stored in the freezer until analysis. All results listed are the mean values of two experiments, which showed a good reproducibility.

**HPLC Analysis of Residual Tocopherol.** Analysis of tocopherols by normal phase HPLC was carried out on an HP series 1050 chromatograph (Hewlett-Packard, Avondale, PA). A normal phase silica column (Alltima Silica 5U, 250 mm × 4.6 mm i.d., particle size 5 $\mu$m, Alltech, Deerfield, IL) was selected. The mobile phase, hexane/isopropyl alcohol (99.5:0.5), was delivered at a flow rate of 1.5 mL/min corresponding to a column pressure of 50 bar. A HP-1100 fluorescence detector was used with the excitation and emission wavelengths set at 230 and 292 nm, respectively. Identification and quantification of the different tocopherols were accomplished with pure standards as reference compounds.

**Isolation of Tocopherol Oxidation Products from Heated Triolein.** Triolein (28 g) containing 3500 ppm of **1** was heated during 90 min at a temperature of 240 °C and a reduced pressure of 6−7 mbar, which is similar to a treatment of bleached oil in a deodorization plant. After the heat treatment, the triolein was methylated under nitrogen flow. After 30 min, the solution was poured into water and extracted twice with hexane. Methyl esters of oleic acid were distilled (0.5 mbar, 135 °C), yielding a dark brown residue. The concentrated residue was separated by preparative HPLC, as above, to give six fractions (see Results). During a time course of 15 min the column was eluted isocratically with hexane/isopropyl alcohol 99.5:0.5, v/v; afterward, the polarity was gradually increased in 5 min to a ratio of 99:1, v/v. The eluent was monitored at different wavelengths between 290 and 240 nm.

## RESULTS

The influence of different heating conditions on the α-tocopherol degradation is listed in Table 1. After 60 min of heating, the loss of **1** at 180 and 200 °C was ∼5%, but it increased to 8.1 and 13.7% at 240 and 260 °C, respectively (experiments 1, 4, 5, and 7). The operating pressure (40 or 4 mbar) had little influence on the tocopherol loss (experiments 5−8) with slightly higher tocopherol retention at lower pressure. Tocopherol loss gradually increased with increase in heating time (experiments 2−4).

**Table 1. Influence of Heating Conditions on Tocopherol Loss**

| expt | temp (°C) | time (min) | pressure (mbar) | α-tocopherol[a] (ppm) | α-tocopherol loss (%) |
|---|---|---|---|---|---|
| 1 | 180 | 60 | 40 | 2070 | 5.7 |
| 2 | 200 | 20 | 40 | 2157 | 1.7 |
| 3 | 200 | 40 | 40 | 2118 | 3.5 |
| 4 | 200 | 60 | 40 | 2086 | 5.0 |
| 5 | 240 | 60 | 40 | 1996 | 9.1 |
| 6 | 240 | 60 | 4−5 | 2017 | 8.1 |
| 7 | 260 | 80 | 40 | 1895 | 13.7 |
| 8 | 260 | 60 | 4−5 | 1957 | 10.8 |

[a] The initial level of α-tocopherol in all samples was 2195 ppm.

**Table 2. Influence of Heating Experiments on Tocopherol Loss**

| | α-tocopherol (ppm) | α-tocopherol loss (%) |
|---|---|---|
| initial α-tocopherol | 2566 | |
| reference conditions[a] | 2326 | 9.3 |
| TBHQ (initial 4000 ppm) | 2488[b] | 3.0 |
| $N_2$ flush during whole expt | 2560 | 0.3 |
| initial α-tocopherol | 3421 | |
| reference conditions[a] | 3042 | 11.1 |
| $N_2$ flush until 240 °C is reached | 3086 | 9.8 |
| $N_2$ flush during whole expt | 3411 | 0.3 |

[a] Heating conditions: 240 °C/5 mbar/80 min. [b] TBHQ 1100 ppm after heat treatment.

The impact of additional factors influencing the tocopherol loss is shown in Table 2. Two sets of experiments with different initial **1** contents (2566 and 3421 ppm) were studied. Heating of **1** under the reported reference conditions resulted in remarkable losses of **1** of 9.3 and 11.1%, respectively, in accordance with the results listed in Table 1. Addition of a high concentration (4000 ppm) of the synthetic antioxidant *tert*-butylhydroquinone (TBHQ) to the sample during the same heating procedure reduced the tocopherol loss to only 3%. This protection was accompanied by a remarkable decrease in TBHQ concentration to 1100 ppm.

In a third set of experiments, nitrogen was gently blown through a capillary into the oil during the complete heating experiment. Only a small amount of nitrogen was blown into the oil in order to make sure no distillation of **1** took place. Heating of the oil under the gentle agitation of a nitrogen flow did not result in any tocopherol loss (Table 2). The experiment under nitrogen indicated that under specialized conditions, where the atmosphere is constantly renewed, **1** is thermally stable in a triacylglycerol matrix up to temperatures of 240 °C. To check that the observed tocopherol loss was not due to the oxygen initially dissolved in the oil, it was nitrogen flushed, and after 3 min the nitrogen valve was closed. This heat treatment resulted in a loss of **1** of 9.8%, which is similar to the reference heating experiment.

**Isolation and Identification of α-Tocopherol Degradation Products.** During the normal-phase HPLC analysis of tocopherols with UV detection, the appearance of unknown peaks in the chromatogram could not be observed. It was supposed that the concentration of tocopherol oxidation products was too low for their detection due to the abundance of the triolein. Methylation of the triolein and subsequent distillation of the methyl oleate were used to obtain a residue highly concentrated in tocopherol and tocopherol oxidation products. This residue was separated by use of preparative HPLC to give six fractions. The first three fractions

had NMR spectra containing the typical ester function and two unsaturated carbons: $^1$H NMR ($CDCl_3$) $\delta$ 2.3 (t, 2H, $OCCH_2-$, $J$ = 7.6 Hz), 3.7 (s, 3H, $-COOCH_3$), 5.3 ppm (m, $CH_2CH{=}CH-$); $^{13}$C NMR ($CDCl_3$) $\delta$ 173 (C=O), 130.1, 129.9 ($-CH{=}CH-$), 50.6 ($-OCH_3$). These components were identified as residual methyl oleate and oxidation products of methyl oleate according to their spectral data. No other functional groups indicating tocopherol or tocopherol oxidation products could be detected in the NMR spectra of these fractions.

Fraction 4 eluted as a sharp peak at 21 min and was identified as residual α-tocopherol by comparison with reference standard **1**: UV $\lambda_{max}$ 292 nm; IR (KBr) 2930, 2874, 1600, 1461, 1420, 1382, 1151, 1110 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 1.79 (t, 2H, $Ar-CH_2CH_2C$, $J$ = 7.26 Hz), 1.96 (s, 3H, $Ar-CH_3$), 2.01 (s, 3H, $Ar-CH_3$), 2.08 (s, 3H, $Ar-CH_3$), 2.58 (t, 3H, $CH_2CH_2-Ar$, $J$ = 7.26 Hz), 4.1 (s, 1H, $-OH$); $^{13}$C NMR $\delta$ 149.36 (C6), 140.55 (C8b), 126.7, 124.9, 123.0, 117.3 (C4a, C5, C7, C8), 75.0 (C2).

The fifth fraction eluted at 25.4 min, had a deep red color, and was identified as **2** from its spectral data: UV $\lambda_{max}$ 276 nm; IR (NaCl) 3495 (OH), 2925, 2845, 1642 ($-C{=}O$), 1460, 1374, 1309 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 2.0 (s, 6H, 2 × $Ar-CH_3$), 2.04 (s, 3H, $Ar-CH_3$) 2.54 (t, 2H, $-CH_2-Ar$, $J$ = 4.95 Hz); $^{13}$C NMR ($CDCl_3$) $\delta$ 187.7 (C8b), 187.3 (C6), 144.5 (C4a), 140.4, 140.2, 140.1 (C7, C5, C8), 72.6 (C2)

Fraction 6 eluted at 33.2 min and had no spectral data that corresponded to any of the previous reported tocopherol oxidation products. The $^{13}$C NMR spectral data revealed two conjugated keto functions (194.3 and 193.9 ppm), one unsaturation in conjugation with the keto (141.2 and 140.9 ppm), methoxy and hydroxy function. Combining these data, the component was expected originally to contain an epoxy group, which was opened during the methylation reaction. Formation of the quinone could occur during the methylation or due to an easy hydrolysis in the oil. To confirm this component originated from epoxy-α-tocopherol quinone and the sample cleanup hydrolyzed the epoxy function, authentication of this fraction was checked by use of standard epoxytocopherol quinone. A mixture of **3** and **4** was synthesized and treated with the same sample cleanup as the triolein. Spectral data of the hydrolyzed epoxy-α-tocopherol quinone fraction completely matched the spectral data of the isolated fraction 6: UV $\lambda_{max}$ 273 nm; IR (NaCl) 1682, 1461, 1377 cm$^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 3.66 (s, 1H, OH), 2.96 (s, 3H, $-OCH_3$), 1.96 (s, 6H, 2 × $-CH_3$), 1.63 (s, 3H, $-CH_3$), 1.26 (m); $^{13}$C NMR ($CDCl_3$) $\delta$ 194.3, 193.9, 141.2, 140.9, 65.8, 63.5. The identity of this degradation product of epoxytocopherone has not been established.

## DISCUSSION

Studying the stability of **1** at high temperature in a real vegetable oil matrix is very difficult due to the abundance of several interfering minor components (e.g. other tocopherols, sterols, and minor phenolic compounds) that might synergize or antagonize the oxidation of this tocopherol and interfere with the purification as well. Therefore, the research was carried out in a model system, in which **1** was dissolved in triolein and the oil was subjected to heat treatments under vacuum while still avoiding distillation of the tocopherols. The origin of the tocopherol loss was investigated by changing the working conditions; temperature, residual pressure, time, additional antioxidants, and nitrogen purging.

The results listed in Tables 1 and 2 indicate a marked loss of **1** upon heating of the model system even if the concentration of oxygen was rather low. Heating of the model system at 240 °C during 80 min resulted in a loss of **1** of 9%. The loss of **1** was strongly related to the heating temperature and the heating time. The headspace pressure (4−40 mbar) and, consequently, the oxygen concentration above the oil hardly influenced the tocopherol loss. Additional experiments, using the synthetic antioxidant TBHQ and flushing with nitrogen, were performed to check if the tocopherol loss is inevitable due to a thermal breakdown or has to be explained by an oxidation of the tocopherols. Addition of TBHQ to the model system significantly reduced the tocopherol loss to only 3%. Probably TBHQ, which also is an effective antioxidant, reduced the tocopherol loss by competing with tocopherols to capture radicals formed in the model system during the heating experiment. Experiments under nitrogen indicated that under specialized conditions, where the atmosphere is constantly renewed, **1** is thermally stable in a triacylglycerol matrix up to temperatures of 240 °C. Tocopherols could only be protected against degradation when nitrogen, as inert gas, was constantly blown through the triolein.

It is very difficult to compare these data with literature reports as previous studies at high temperatures have dealt with tocopherol losses during conditions similar to frying temperatures of 180 °C. In all studies an almost linear decrease of tocopherols in relation to the heating time was observed. Murkovic et al. (*5*) and Barrera-Arellano et al. (*11*) reported a tocopherol decrease of almost 10% per hour at 180 °C, leading to complete tocopherol depletion after 9−10 h.

The level of polymeric triacylglycerols has not been quantified but is expected to be insignificant at these low levels of tocopherol degradation. The total content of polymeric triacylglycerides in deodorized oils rich in polyunsaturated fatty acids (e.g., soybean oil) ranged between 4 and 7% and was found to be independent of the deodorization temperature (*28, 29*). Only in the absence of tocoperols can a higher level of thermal and oxidative triacylglycerol polymers be expected (*30*). Work is in progress in our laboratories to study the effect of fatty acid unsaturation on the rate of tocopherol degradation.

In this research **2**−**4** were identified as the major oxidation products formed during the heating experiments in the model system. This indicates a degradation of α-tocopherol proceeding after formation of adducts with peroxyl radicals (eq 2) at the 5-, 7-, and 8a-positions, respectively. Breakdown of these peroxyl adducts will generate epoxy species with carbon-centered radicals that capture oxygen and form 8a-hydroperoxy derivatives. Further degradation of 8a-hydroperoxy-4a,5-epoxy-α-tocopherol, 8a-hydroperoxy-7,8-epoxy-α-tocopherol, and 8a-hydroperoxy-α-tocopherol will generate **3**, **4**, and **2**, respectively. Murkovic et al. (*5*) studied the kinetics of the epoxytocopherol quinone formation at several temperatures in corn oil triacylglycerides and found its content to reach levels >1000 ppm after 5 h of heating at 180 °C. Even longer heating times resulted in a reduction of the epoxytocopherol quinone yielding other dimeric oxidation products. Only upon working under an inert atmosphere, where all oxygen is excluded, was no degradation of **1** at temperatures up to 240 °C observed. Any trace of oxygen

present will immediately oxidize **1**. These results also support previous observations that tocopherol loss during deodorization is partly due to oxidative degradation.

## LITERATURE CITED


(1) Verleyen, T.; Verhe, R.; Huyghebaert, A.; Dewettink, K.; De Greyt, W. Tocopherol balance during deoderization. Abstracts: 91st AOCS Annual Meeting & Expo, San Diego, CA, April 25−28. *Int. News Fats, Oils Relat. Mater.* **2000**, *11*, S97.

(2) Kamal-Eldin, A.; Appelqvist, L. The chemistry and antioxidant properties of tocopherols and tocotrienols. *Lipids* **1996**, *31*, 671−701.

(3) Liebler, D.; Baker, P.; Kaysen, K. Oxidation of vitamin E: evidence for competing autoxidation and peroxyl radical trapping reactions of the tocopheroxyl radical. *J. Am. Oil Chem. Soc.* **1990**, *112*, 6995−7000.

(4) Mukai, K.; Sawada, K.; Kohno, Y.; Terao, J. Kinetic study of the prooxidant effect of tocopherol. Hydrogen abstraction from lipid hydroperoxides by tocopheroxyls in solution. *Lipids* **1993**, *28*, 747−752.

(5) Murkovic, M.; Wiltschko, D.; Pfannhauser, W. Formation of α-tocopherolquinone and α-tocopherolquinone epoxides in plant oil. *Fett/Lipid* **1997**, *99*, 165−169.

(6) Yuki, E.; Ishikawa, Y. Tocopherol contents of nine vegetable frying oils, and their changes under simulated deep-fat frying conditions. *J. Am. Oil Chem. Soc.* **1976**, *53*, 673−676.

(7) Pongracz, G. Hitzestabilität der tocopherole. *Fat. Sci. Technol.* **1988**, *90*, 247−251.

(8) Marquez-Ruiz, G.; Polvillo, M.; Jorge, N.; Ruiz-Mendez, M.; Dobarganes, M. Influence of used frying oil quality and natural tocopherol content on oxidative stability of fried potatoes. *J. Am. Oil Chem. Soc.* **1999**, *76*, 421−425.

(9) Yoshida, H.; Tatsumi, M.; Kajimoto, G. Relationship between oxidative stability of vitamin E and production of fatty acids in oils during microwave heating. *J. Am. Oil Chem. Soc.* **1991**, *68*, 566−570.

(10) Yoshida, H.; Kajimoto, G.; Emura, S. Antioxidant effects of tocopherols at different concentrations in oils during microwave heating. *J. Am. Oil Chem. Soc.* **1993**, *70*, 989−995.

(11) Barrera-Arellano, D.; Ruiz-Mendez, V.; Ruiz, G.; Dobarganes, C. Loss of tocopherols and formation of degradation compounds in triacylglycerol model systems heated at high temperature. *J. Sci. Food Agric.* **1999**, *79*, 1923−1928.

(12) Skinner, W.; Parkhurst, R. Oxidation products of vitamin E and its model, 6-hydroxy-2,2,5,7,8-pentamethylchroman. VII. Trimer formed by alkaline ferricyanide oxidation. *J. Org. Chem.* **1964**, *29*, 3601−3603.

(13) Suarna, C.; Craig, D.; Cross, K.; Southwell-Keely, P. Oxidation of vitamin E (α-tocopherol) and its model compound 2,2,5,7,8-pentamethyl-6-hydroxychroman. A new dimer. *J. Org. Chem.* **1988**, *53*, 1281−1284.

(14) Suarna, C.; Southwell-Keely, P. Effect of alcohol on the oxidation of the vitamin E model compound, 2,2,5,7,8-pentamethyl-6-chromanol. *Lipids* **1989**, *24*, 56−60.

(15) Yamauchi, R.; Kato, K.; Ueno, Y. Formation of trimers of α-tocopherol and its model compound, 2,2,5,7,8-pentamethylchroman-6-ol, in autoxidizing methyl linoleate. *Lipids* **1988**, *23*, 779−783.

(16) Yamauchi, R.; Kato, K.; Ueno, Y. Free-radical scavenging reactions of α-tocopherol during the autoxidation of methyl linoleate in bulk phase. *J. Agric. Food Chem.* **1995**, *43*, 1455−1461.

(17) Yamauchi, R.; Matsui, T.; Kato, K.; Ueno, Y. Reaction product of α-tocopherol with methyl linoleate−peroxyl radicals. *Lipids* **1990**, *25*, 152−158.

(18) Yamauchi, R.; Miyake, N.; Kato, K.; Ueno, Y. Reaction of α-tocopherol with alkyl and alkylperoxyl radicals of methyl linoleate. *Lipids* **1993**, *28*, 201−206.

(19) Chu, Y.; Lin, W. Effect of soybean pretreatment on the colour quality of soybean oil. *J. Am. Oil Chem. Soc.* **1990**, *67*, 368−372.

(20) Lai, M.; Lin, W.; Chu, Y.; Chen, S.; Kong, K.; Chen, C. The mechanism of color reversion in soybean salad oil. *J. Am. Oil Chem. Soc.* **1989**, *66*, 565−571.

(21) Nelan, D.; Robeson, C. The oxidation product from α-tocopherol and potassium ferricyanide and its reaction with ascorbic and hydrocloric acids. *J. Am. Chem. Soc.* **1962**, *84*, 2963−2965.

(22) Skinner, W.; Alaupovic, P. Oxidation products of vitamin E and its model, 6-hydroxy-2,2,5,7,8-pentamethylchroman. V. Studies of the products of alkaline ferricyanide oxidation. *J. Org. Chem.* **1963**, *28*, 2854−2858.

(23) Bolon, D. Generation of o-quinone methides in solution trimerization. *J. Org. Chem.* **1970**, *35*, 715−719.

(24) Frampton, V.; Skinner, W.; Bailey, P. The production of tocored upon the oxidation of α-tocopherol with ferric chloride. *J. Am. Chem. Soc.* **1954**, *76*, 282−284.

(25) Frampton, V.; Skinner, W.; Cambour, P.; Bailey, P. α-Tocopurple, an oxidation product of α-tocopherol. *J. Am. Chem. Soc.* **1960**, *82*, 4632−4634.

(26) Csallany, A.; Ha, Y. α-Tocopherol oxidation mediated by superoxide anion ($O_2^-$). I. Reactions in aprotic and protic conditions. *Lipids* **1992**, *27*, 195−200.

(27) Ha, Y.; Csallany, A. α-Tocopherol oxidation mediated by superoxide anion ($O_2^-$). I. Identification of the stable α-tocopherol oxidation products. *Lipids* **1992**, *27*, 201−205.

(28) De Greyt, W. Effect of physical refining on selected minor components in vegetable oils. Doctoral thesis, University of Ghent, 1998.

(29) Dobarganes, M.; Perez-Camino, M.; Marquez-Ruiz, G. High performance size exclusion chromatography of polar compounds in heated and non heated fats. *Fat Sci. Technol.* **1988**, *90*, 308−310.

(30) Lampi, A.-M.; Kamal-Eldin, A. Effects of α- and γ-tocopherols on thermal polymerization of purified high oleic sunflower triacylglycerols. *J. Am. Oil Chem. Soc.* **1998**, *75*, 1699−1703.

(31) Lucarini, M.; Pedrielli, P.; Pedulli, G. Bond dissociation energies of O−H Bonds on substituted phenols from equilibration studies. *J. Org. Chem.* **1996**, *61*, 9259−9263.


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