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Effect of fatty acids and tocopherols on the oxidative stability of vegetable oils

The oxidative stability of vegetable oils is determined by their fatty acid composition and antioxidants, mainly tocopherols but also other non-saponifiable constituents. The effect of fatty acids on stability depends mainly on their degree of unsaturation and, to a lesser degree, on the position of the unsaturated functions within the triacylglycerol molecule. Vegetable oils contain tocopherols and tocotrienols, especially α- and γ-tocopherols, as their main antioxidants. The antioxidant behavior of tocopherols represents a complex phenomenon as they are efficient antioxidants at low concentrations but they gradually lose efficacy as their concentrations in the vegetable oils increase. The "loss of efficacy" of tocopherols, sometimes referred to as a "pro-oxidant effect", is witnessed by an increase in the rate of oxidation during the induction period, despite elongation of this phase. The phenomenon is much obvious for α-tocopherol, but is also evident for other tocopherols. In agreement with nature's wisdom, the tocopherol levels in vegetable oils seem to be close to the optimal levels needed for the stabilization of these oils. The presence of other antioxidants in the oils, *e.g.* carotenoids, phenolic compounds, and Maillard reaction products, may synergize with tocopherols and minimize this loss of efficacy.

Keywords: Vegetable oils, fatty acids, tocopherols, oxidative stability.

1 Introduction

Vegetable oils are currently used mainly for food applications such as salad and cooking oils, frying fats, liquid and solid shortenings, spreads, and ingredients in bakery products. They are used to a lesser extent in other products such as soaps, cosmetics, and skin care products. With a wider range of utilization of vegetable oils, appropriate knowledge about their composition and quality parameters is necessary. One important quality aspect relates to their stability during processing and storage.

Oxidative stability of edible vegetable oils is important for their sensory and nutritional quality [1]. The degradation of the hydroperoxides, the primary oxidation products, to secondary oxidation products with aldehydic and ketonic functions negatively affects their flavor. Fortunately, the resultant rancidity is offensive enough to stop consumers from using these oils in foods. The susceptibility of certain oils to oxidation, *e.g.* flaxseed oils, limits their utilization as nutritious oils and adds to significant economical losses [2]. Indeed, the instability of vegetable oils also limits their utilization in other products like cosmetics and skin care products. Moreover, stable vegetable oils might find great future applications as diesel oils which can also utilize non-conventional oils.

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Vegetable oils are diverse with respect to source and composition. They are produced from seeds, nuts, grain germs, fruit mesocarps, *etc.* Vegetable oils consist mainly of triacylglycerols (ca. 95%) which act as a solvent for sterols, fat-soluble vitamins (mainly tocopherols/tocotrienols), pigments including chlorophylls and carotenoids, phenolic compounds including lignans, phospholipids, free fatty acids, and mono- and diacylglycerols [3]. The oils differ in the degree of unsaturation, of the fatty acids constituting their triacylglycerols, as well as in the quantity and quality of the compounds in their non-saponifiable constituents. Differences in composition are translated into differences in the stability, sensory and technical qualities of the oils. This review paper addresses the influence of fatty acid unsaturation and tocopherol/tocotrienol composition of vegetable oils on their oxidative stability under ambient and frying conditions. The involvement of other minor components in the oxidation and antioxidation reactions is also discussed.

2 Fatty acid composition and tocopherol content of vegetable oils

There is a great variation between vegetable oils with regard to their triacylglycerol and fatty acid composition. The triacylglycerol composition [4, 5] and calculated fatty acid percentages and iodine values of the major edible vegetable oils are given in Tab. 1, and tocochromanol

Review Article

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Tab. 1. Triacylglycerols and calculated fatty acid composition and iodine values of common edible vegetable oils.

Oil[§]	PO	OO	GNO	CSO	RSO	CO	SFO	SBO	FSO
Triacylglycerol composition [relative%][$, #]									
PPP	7.8	–	–	–	–	–	–	–	–
POS	4.9	1.1	1.4	0.8	0.5	0.7	0.8	0.5	–
PLP	9.0	1.2	1.9	11.9	0.7	2.9	1.8	1.6	–
PLS	2.6	–	1.3	1.7	–	2.8	1.3	–	–
POP	35.5	3.1	2.6	3.9	0.9	2.0	0.7	0.6	–
POO	18.3	14.7	13.1	3.5	4.6	2.3	1.5	2.1	0.7
SOO	2.1	4.1	2.6	–	1.3	0.7	0.8	1.3	–
OOO	3.4	30.0	12.8	1.7	17.9	3.3	2.9	2.5	4.0
POL	11.1	8.1	17.6	11.0	5.7	10.1	6.7	8.7	4.5
SLO	0.7	0.9	4.2	1.6	2.2	1.6	2.9	2.3	1.9
PoOO	–	7.8	–	–	–	–	–	–	–
OLO	1.7	16.5	16.8	4.5	25.0	6.8	9.9	15.3	2.4
OOA	–	0.7	2.4	–	–	–	–	–	–
OOLn	–	3.6	–	–	–	–	–	1.3	5.2
PLL	2.2	1.9	4.2	22.8	1.2	13.4	9.1	11.3	2.4
SLL	–	–	1.1	4.1	–	7.9	7.2	2.2	–
OLL	0.7	6.3	14.8	12.7	8.5	20.1	25.2	16.3	5.8
LLL	–	–	3.2	18.0	1.2	20.1	29.2	18.5	7.3
PLnO	–	–	–	–	2.4	1.4	–	1.3	3.0
PLnL	–	–	–	1.0	0.7	1.1	–	2.2	3.8
OLnO	–	–	–	–	11.8	–	–	–	–
OLLn	–	–	–	–	6.1	–	–	–	–
LLLn	–	–	–	0.8	2.9	2.8	–	5.9	7.9
PLnLn	–	–	–	–	2.4	–	–	–	4.6
OLnLn	–	–	–	–	3.9	–	–	5.2	9.6
LnLLn	–	–	–	–	–	–	–	0.9	12.1
LnLnLn	–	–	–	–	–	–	–	–	24.8
Calculated fatty acid composition [relative %] and iodine value									
P	50.4	11.5	15.5	24.2	6.9	13.9	8.2	10.2	6.4
S	3.4	2.1	3.5	2.7	1.3	4.6	4.3	2.2	0.6
Po	–	2.6	–	–	–	–	–	–	–
O	35.8	68.3	49.6	17.0	56.5	21.8	23.1	27.4	17.9
L	10.3	14.4	30.5	55.5	23.1	58.0	64.4	52.6	26.4
Ln	–	1.2	0	0.6	12.2	1.8	0	7.6	48.7
A	–	–	0.8	–	–	–	–	–	–
I.V.[†]	53	89	96	112	122	124	131	135	189

[§] Oils: PO = palm oil; OO = olive oil; GNO = groundnut oil; CSO = cottonseed oil; RSO = rapeseed oil; CO = corn oil; SFO = sunflower oil; SBO = soybean oil; and FSO = flaxseed oil.

[$] Fatty acids: P = palmitic acid (16:0); S = stearic acid (18:0); Po = palmitoleic (16:1, Δ9); O = oleic acid (18:1, Δ9); L = linoleic acid (18:2, Δ6,12), Ln = α-linolenic acid (18:3, Δ9,12,15); A = arachidic acid (20:0).

[#] All data on triacylglycerol composition was estimated from [4], except rapeseed oil [5].

[†] Iodine values (I.V.) were calculated as (% monounsaturated fatty acids × 0 860 + % 18:2 × 1 732 + % 18:3 × 2.616).

contents [6] in Tab. 2. Rapeseed and linseed oils contain variable levels of plastochromanol-8, a special tocol derivative with a long unsaturated tail [7, 8]. The structures of tocochromanols and NMR chemical shifts for plastochromanol-8, isolated from linseed oil by column chromatography, are provided in Fig. 1. Cereal germs contain very high levels of tocopherols, mainly α-tocopherol, while the pericarp and endosperm parts of the grain

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Tab. 2. Tocopherol contents (ppm) of common edible vegetable oils.

Tocopherols/ Tocotrienols[$]	Vegetable oils[§]								
	PO	OO	GNO	CSO	RSO	CO	SFO	SBO	FSO
α-Tocopherol	377	96	141	403	180	222	671	116	–
β-Tocopherol	1	6	4	2	–	1	23	17	–
γ-Tocopherol	4	12	131	383	340	570	4	578	588
δ-Tocopherol	–	–	9	4	–	23	–	263	6
α-Tocotrienol	52	–	–	–	–	54	–	–	–
β-Tocotrienol	4	–	–	–	–	11	–	–	–

[§] Oils: PO = palm oil; OO = olive oil; GNO = groundnut oil; CSO = cottonseed oil; RSO = rapeseed oil; CO = corn oil; SFO = sunflower oil; SBO = soybean oil; and FSO = flaxseed oil.
[$] Mean values were obtained from literature [6]. Plastochromanol-8, present in rapeseed and flaxseed oil (Fig. 1), is often ignored when analyzing their tocopherol levels.

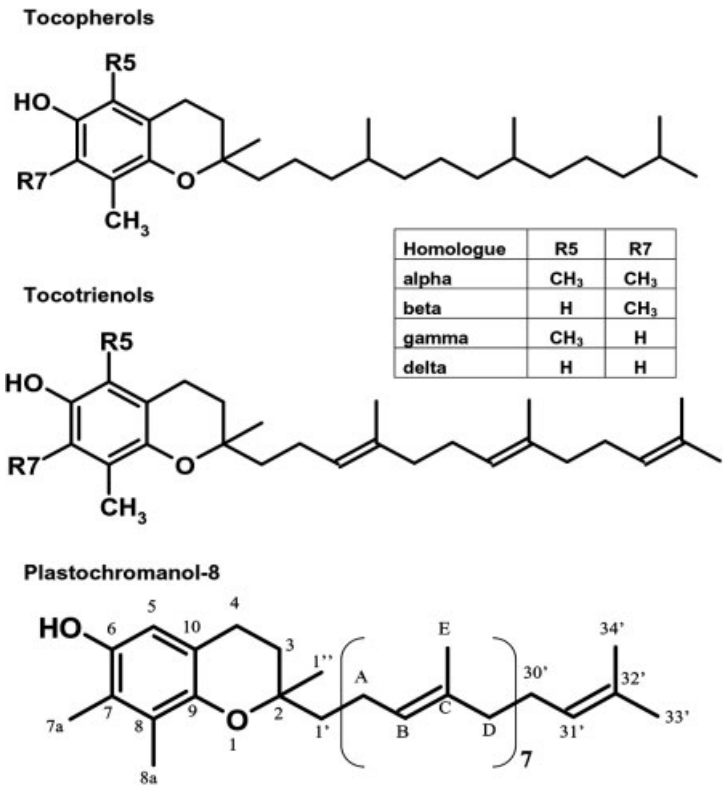

Fig. 1. Structure of tocopherols, tocotrienols, and plastochromanol-8 present in vegetable oils. Plastochromanol-8 (CAS Registry number 4382–43–8) was isolated from flaxseed oil and characterized by ^{1}H-NMR spectroscopy. Chemical shifts (ppm): 3 (1.76, 2H), 4 (2.68, 2H), 5 (6.37, 2H), 7a (2.13, 3H), 8a and 30' (2.12, 5H), 1" (1.26, 3H), A; 2'+6'+10'+14'+18'+22'+26' (2.06, 14H), B; 3'+7'+11'+15'+19'+23'+27' (5.11, 7H), D; 5'+9'+13'+17'+21'+25'+29' (1.99, 14H), 1', 33' and E; 4'a, 8'a, 12'a, 16'a, 20'a, 24'a+28'a (1.60, 25H), 31' (5.37, iH), 34' (1.68, 3H).

accumulate significant amounts of tocotrienols [9, 10]. Total tocopherol and tocotrienol contents in wheat germ oil varied between 2000 and 4000 ppm [11, 12].

3 Oxidation mechanism of unsaturated fatty acids

It is well known that lipid oxidation starts by the abstraction of a hydrogen atom from an allylic or *bis*-allylic position of an unsaturated fatty acid (LH) to generate an alkyl radical ($L^{\bullet}$), which combines with molecular oxygen at diffusion-controlled rate to produce a lipid peroxyl radical ($LOO^{\bullet}$). The $LOO^{\bullet}$, having longer lifetimes (ca. 7 s) than $L^{\bullet}$ (ca. 10^{-8} s), propagate the oxidation reaction by selectively abstracting hydrogens from LH to form lipid hydroperoxides (LOOH) and another $L^{\bullet}$:

$$LH + X^{\bullet} \rightarrow L^{\bullet} + XH \quad \text{(initiation)} \quad (1)$$

$$L^{\bullet} + O_2 \rightarrow LOO^{\bullet} \quad \text{(propagation)} \quad (2)$$

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$$LOO^{\bullet} + LH \rightarrow L^{\bullet} + LOOH \quad (3)$$

$$LOO^{\bullet} + LOO^{\bullet} \rightarrow \text{non-radical products (termination)} \quad (4)$$

$$LOO^{\bullet} + L^{\bullet} \rightarrow \text{non-radical products} \quad (5)$$

$$L^{\bullet} + L^{\bullet} \rightarrow \text{non-radical products} \quad (6)$$

Unsaturated fatty acids have different susceptibilities to hydrogen abstraction, depending on the dissociation energies of labile C-H bonds within the molecules. C-H bonds adjacent to a double bond or at a tertiary carbon atom are weaker and easier to break. For the fatty acid series $-CH_2-(CH{=}CH-CH_2)_n-CH_2-$ (n = 1–3), the relative oxidation rates increase in the order 1 : 40 : 80, respectively. It is well established that fatty acid oxidizability is much lower for monounsaturated substrates (*e.g.* oleic acid and cholesterol) than for polyunsaturated fatty acids (mainly linoleate and linolenate). Thus, the oxidizability of a fatty acid mixture is mainly dependent on the number of *bis*-allylic methylenes therein ([13, 14] and references cited therein).

The presence of antioxidants in the fatty mixtures inhibits their oxidation, mainly by scavenging peroxyl radicals:

$$LOO^{\bullet} + AH \rightarrow A^{\bullet} + LOOH \quad (7)$$

$$A^{\bullet} + LOO^{\bullet} \rightarrow \text{non-radical products} \quad (8)$$

The antioxidant radical ($A^{\bullet}$) is stabilized by resonance and does not propagate oxidation. Several phenolic compounds, having electron-releasing substituents in the *ortho*- and *para*-positions of their phenolic function, effectively participate in radical interception reactions. Because of their relatively high lipid solubility, tocopherols are recognized as the main antioxidants responsible for the stability of natural lipids [15], although other antioxidants may also play an important role. However, as vegetable oils generally contain adequate tocopherol contents, the fatty acid composition is more important for their oxidative stability than the tocopherol level [16, 17]. These aspects will be discussed in more details *vide infra*.

4 Fatty acid composition and oxidative stability

Fig. 2 presents the relative oxidation rates of purified triacylglycerols of sunflower and soybean oil at room temperature (from [18]), which illustrates the importance of fatty acid composition for their oxidative stability. The resistance of purified oils from different soybean germplasms to oxidation at 60 °C, measured as peroxide value, correlated positively with the average number of double bonds (R = 0.81), linolenic acid (R = 0.85), and linoleic acid (R = 0.63), and negatively with oleic acid (R = 0.76) [19]. It has been shown that oleate behaved as an inert diluent during the oxidation of linoleate at low temperatures [20]. Oils with modified fatty acids, *e.g.* high-oleic oils of peanut [21], sunflower [22], corn [23], and canola [24], were proven to have improved stability compared to the original oils.

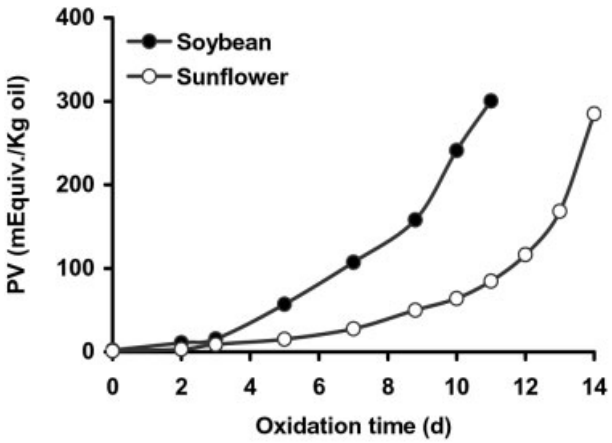

Fig. 2. Oxidation of purified soybean and sunflower oils at 25 °C. The fatty acid composition of soybean and sunflower oils, respectively, was: palmitic (9.7 and 6.2%), stearic (3.8 and 3.4%), oleic (22.7 and 26.4%), linoleic (55.2 and 62.8%), linolenic (8.6 and 0%) (data from [19]).

The distinct differences in oxidizability between oils with different degree of unsaturation are minimized as the oxidation temperature increases [25–27]. This is because the increase in oxidation rate induced by high temperatures is by far greater than the difference in oxidizability between oleate and linoleate, especially as oxidized linoleate radicals act as initiators for the oxidation of oleate [28]. Experimental results agree with the general empirical chemical rule that with each temperature increase of 10 °C, the rate of a chemical reaction is approximately halved. Studies have confirmed this temperature effect, *e.g.* Hess and Hara's results [29] on the oxidation of flaxseed oil at 80–130 °C (Fig. 3) and the results of Tan et al. [30] on the oxidation of ten different oils at 110–140 °C. With a wider difference in temperature, other factors will interfere with the reaction rates. For example, the solubility of oxygen in the oil decreases by ca. 25% for every 10 °C rise in temperature [31], and the initiation mechanisms differ between low and high temperatures *inter alias* due to degradation of hydroperoxides [30]. The importance of temperature for the oxidation rates of fatty acids becomes clear by considering the quantitative relationship between oxidation rate constant and temperature described by the Arrhenius equation:

$$k = A \times e^{-Ea/RT} \quad (9)$$

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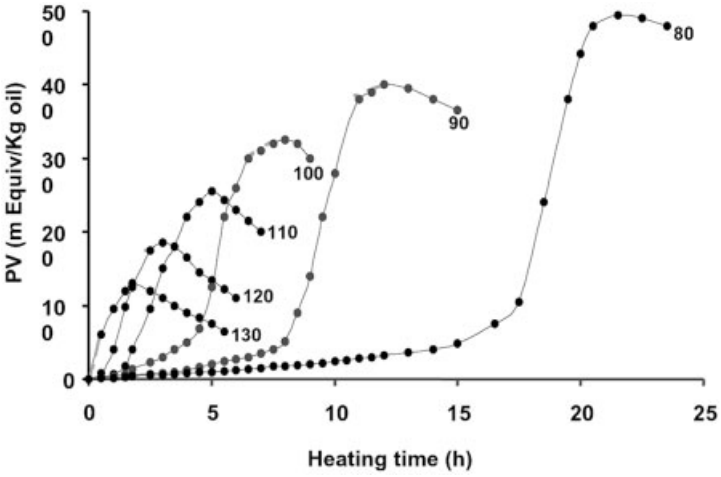

Fig. 3. The effect of temperature on the induction period (IP) and maximum attainable peroxide value (PV) in the oxidation of flaxseed oil. Note that the IP doubles with every 10 °C increase in temperature from 90–130 °C (Redrawn from [29]).

where A, the so-called pre-exponential factor, is a constant related to the geometry of the reaction medium, e is a constant (ca. 2.7281), E_a is the activation energy, R is the universal gas constant (8.314 JK^{-1} mol^{-1}), and T is the absolute temperature (in degrees Kelvin). The activation energy (E_a) correlates with the C-H bond dissociation energy (BDE) by the equation given by Korcek et al. [32]:

$$E_a = 0.55\ [\mathrm{BDE(C\text{-}H)}–62.5] \quad (10)$$

Since BDE is about 83 kcal/mol for the *bis*-allylic hydrogens of linoleate and linolenate and is approximately 10 kcal/mol higher for the allylic hydrogens in oleate [33], E_a is about 11 and 17 kcal/mol for linoleate and oleate, respectively. Thus, as the oxidation temperature increases, the effect of E_a in Eq. (9) becomes less significant.

Mateos et al. [34] performed a study on the relation between oxidative stability and triacylglycerol composition of olive oils spiked with the antioxidants α-tocopherol and hydroxytyrosol using the Rancimat at 100 °C. At the same concentration of antioxidants, the oxidative stability decreased with increased unsaturation of the triacylglycerols (Tab. 3). In this study, the triacylglycerols provided a better parameter than fatty acids for the estimation of the oxidative stability of olive oils.

Besides the degree of unsaturation of the triacylglycerol, the position of the fatty acids in the glycerol moiety might affect their oxidizability at low temperatures. In the oxidation of soybean oils at 60 °C, volatile formation was especially related to the concentration of linolenate at the exterior 1,3-positions and the concentration of linoleate at the interior 2-position of the glycerol [19]. Similar results were obtained with canola oil triacylglycerols [35] and with interesterified blends of soybean oil and palmolein [36, 37]. The explanation of the effect of the position

Tab. 3. Contribution of different triacylglycerol species of olive oil to its Rancimat stability at 100 °C.

Triacylglycerol species	Relative oxidation rate
POS, POP	–
POO, SOO, POPo	0.2
PLP	0.5
OOO, PLO, PoOO	0.7
SOL	0.8
POLn	1.5
PLL	2.0
PLLn, OOL	2.2
OLL, OOLn + PoOL	2.3
OLLn + PoLL	2.8
LLL	3.0

Data from [34].

of linoleate on its oxidative stability was confirmed using synthetic triacylglycerols. Oxidations performed at 60 °C in the dark showed that LnLnL oxidized faster than LnLLn and LLnL oxidized faster than LLLn [38, 39]. Similarly, LPL was more stable than PLL and PLP was more stable than PPL [40]. The effect of the triacylglycerol structure and composition on their thermal oxidative stability has also been studied using synthetic triacylglycerols containing palmitate, oleate, linoleate, and linolenate, at 150 or 180 °C [41]. The mixture of PPP/LLL (2 : 1 mol/mol) was more susceptible to thermal oxidation than PPP/PLL (1 : 1 mol/mol) and PPL. Similarly, the mixtures PPP/OOO and PPP/LnLnLn (2 : 1 mol/mol) were less stable than PPO and PPLn, respectively. The facts that unsaturated fatty acid synthesis increases at lower growing temperatures and that they preferentially occupy the 2-position of the glycerol in the vegetable oils [42] seem to emphasize the purposeful biosynthesis

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strategies in plants. Nevertheless, the effect of the triacylglycerol structure on the oxidative stability merits further research aiming towards the production of tailored stable nutritional vegetable oils.

5 Tocopherol contents and oxidative stability

Generally, tocopherols are recognized as the important antioxidants in vegetable oils, mainly because of their lipophilicity [43], although this might not apply to all oils. In this section, focus will be paid to the antioxidant mechanisms of tocopherols, with particular emphasis on α- and γ-tocopherols, the major tocopherols in vegetable oils. The addition of tocopherols to triacylglycerols increases their activation energies (E_a) and inhibits their degradation. For example, E_a was found to be ca. 42, 46, and 51 for trilinolein containing 0, 250, and 500 ppm of α-tocopherol, respectively, and E_a/T was directly proportional to the induction period [44]. The inhibition of vegetable oil oxidation is usually associated with a critical minimal concentration of antioxidants [45], *e.g.* 60–70 ppm of α-tocopherol in olive oil [46]. Complete tocopherol consumption is not always a necessity for the transition from the induction period to the rapid oxidation phase. As suggested by Witting [47], this transition is determined by the ratio of tocopherols to the degree of oxidation already reached, *i.e.* the amount of hydroperoxides present.

It has been known for a long time that it is difficult to stabilize vegetable oils by supplementing them with tocopherols, because there seems to be an optimal level of tocopherols for maximal protection [43]. Several studies were performed on the contribution of tocopherols to the stability of purified vegetable oils. Fortification of purified olive oil triacylglycerols with α-tocopherol revealed 100 ppm as the concentration that provided the highest stability at 40 °C in the dark [45]. The antioxidant properties of α- and γ-tocopherols (5–500 ppm) were studied during the oxidation of purified rapeseed oil triacylglycerols at 40 °C in the dark [48]. At concentrations ≤50 ppm, α-tocopherol was more stable, *i.e.* consumed at a lower rate, and more efficient as antioxidant than γ-tocopherol, while at concentrations >100 ppm, γ-tocopherol was more stable and more efficient as antioxidant than α-tocopherol. In sunflower triacylglycerols oxidized at 55 °C, α-tocopherol was a more efficient antioxidant than γ-tocopherol at up to 50 ppm, but started to lose efficacy at 200-ppm levels [49]. The antioxidant behaviors of α- and γ-tocopherols (5–2000 ppm) were also compared in purified triacylglycerols of sunflower and soybean oils at 100 °C and at room temperature. At concentrations above 400 ppm in soybean and 700 ppm in sunflower oil at 100 °C, α-tocopherol participated in side reactions and witnessed loss of antioxidant activity, a feature that was exhibited by γ-tocopherol at much higher concentrations [50]. In summary, studies with purified triacylglycerols showed that very high levels of tocopherols, especially α-tocopherol, increase the peroxidation rate during the induction period (Fig. 4).

Antioxidant effectiveness is dependent on the extent to which the antioxidant participates in side reactions, *i.e.* reactions with species other than peroxyl radicals. These reactions will consume the antioxidant as well as lead to the formation of active radicals able to initiate new oxidation chains. Kinetic analysis of oxidation rate data has been a useful tool in interpreting the differences in antioxidant actions of α- and γ-tocopherols [50]. When the induction period is linearly dependent on the initial concentration of the antioxidant, the antioxidant is effectively consumed in reactions with peroxyl radicals, and when this relation is not linear, it is an indication that the antioxidant participates in side reactions. These studies showed that tocopherols lose their antioxidant efficacy at high concentrations because they participate in a number of reactions that increase the rate of initiation of new oxidation chains. The rates of these side reactions are higher in soybean than in sunflower purified triacylglycerols [18, 50]. α-Tocopherol as well as its radicals participated more readily in side reactions than γ-tocopherol and its radicals. Both α- and γ-tocopherols (AH) react with lipid hydroperoxides (LOOH), leading to the production of alkoxyl radicals [51]:

$$LOOH + AH \rightarrow A^{\bullet} + LO^{\bullet} + H_2O \quad (11)$$

Alkoxyl radicals ($LO^{\bullet}$) consume tocopherols and initiate new reaction chains because of their low selectivity (Fig. 5). This leads to partial loss of antioxidant activity,

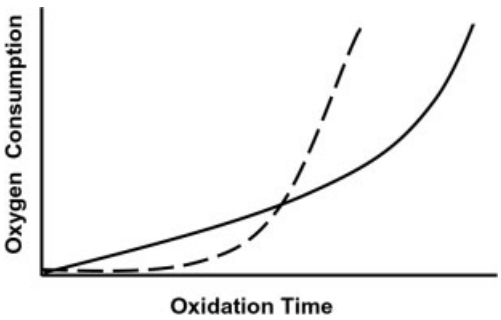

Fig. 4. Schematic description of the loss of efficacy of α-tocopherol: (- - -) oxidation in the presence of low tocopherol concentration (generally <200 ppm) *versus* (—) oxidation at high tocopherol concentration (generally >500 ppm). This behavior has been referred to as "pro-oxidant effect" in the literature, but this remains a matter of definition of this complex phenomemon (for more details, see [50] and references cited therein). This phenomenon is important for shelf life storage.

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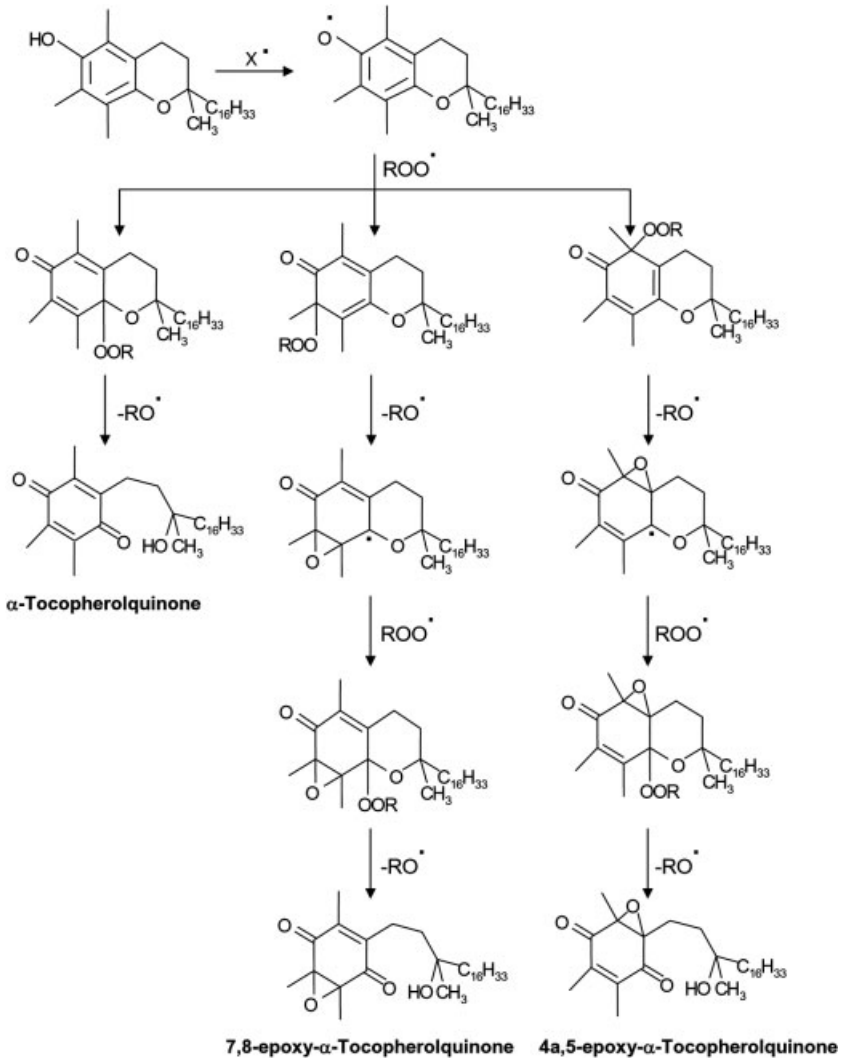

Fig. 5. Scheme for loss of antioxidant efficacy of tocopherols due to the generation of alkoxyl radicals (LO•) resulting from the reaction of its tocopheroxyl radical with peroxyl radicals (LOO•).

which is greater for α- than for γ- and other tocopherols (Fig. 6). In addition to this reaction, α-tocopheroxyl radicals, generated *inter alias* in reaction (7), propagate chain reactions by abstracting hydrogens from unsaturated lipids and their hydroperoxides ([52] and references therein):

$$A^{\bullet} + LH \rightarrow L^{\bullet} + AH \quad (12)$$

$$A^{\bullet} + LOOH \rightarrow LOO^{\bullet} + AH \quad (13)$$

A study on the effect of tocopherols on the stabilities of cold-pressed olive and linseed oils, performed using the Rancimat at 120 °C, showed that the addition of γ-tocopherol at up to 8000 ppm provided a fourfold stabilization to olive oil initially containing 210 ppm α-tocopherol and 45 ppm γ-tocopherol [53]. Linseed oil initially containing 80 ppm α-tocopherol and 590 ppm γ-tocopherol benefited less from the addition of γ-tocopherol, with a max-

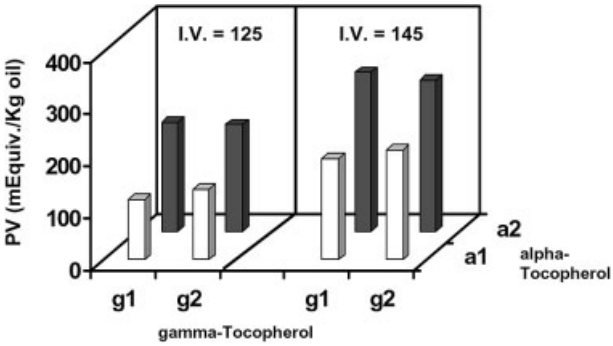

Fig. 6. Effect of fatty acid unsaturation and of mixed α- and γ-tocopherol concentrations on the peroxidation of vegetable oil triacylglycerols (iodine value of 125 and 145) after 7 days at 50 °C. The tests were performed at two tocopherol concentrations; γ-tocopherol (g1 = 600 ppm, g2 = 1100 ppm) and α-tocopherol (a1 = 350 ppm, a2 = 850 ppm).

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imum stabilization of <2-fold upon supplementation with 1000 ppm. α-Tocopherol did not provide stabilization to any of the two oils. There is a wide variation in the levels of γ-tocopherols and plastochromanol-8 in the oilseed rape [54] and in the genus *Linum* [8]. The antioxidant contribution of plastochromanol-8 to the stability of rapeseed and flaxseed oil has not been studied yet. Germ oils contain high levels of tocopherols, but also of free fatty acids. The later oxidize faster than acylated fatty acids due to the pro-oxidant effect of free carboxylic groups [55].

The existence of a correlation between tocopherols and fatty acids in vegetable oils has been discussed by many authors during the years [56–59]. Multivariate analysis of 14 vegetable oils showed natural interrelations between α-tocopherol and 18:2, on the one hand, and between 18:3 and γ-tocopherol, on the other hand [6]. The work of Nagao et al. [60] showed no correlation between α-tocopherol and linoleic acid contents in sunflower seeds produced in Japan. Analyzing oils from seeds of sunflower, wheat, canola and soybean, Dolde et al. [11] questioned the suggested correlation between tocopherols and fatty acids and considered it non-causal. Results obtained by these authors on the soybean samples provided evidence that low-linolenate oils are associated with reduced tocopherol contents. Goffman et al. [61] studied the fatty acid and tocopherol composition of oils from 91 accessions of Brassicaceae and, likewise, showed that total tocopherol and γ-tocopherol levels are positively correlated with the sum of monounsaturated fatty acids and negatively correlated with the sum of saturated fatty acids and the sum of polyunsaturated fatty acids. In summary, the tocopherol contents in vegetable oils are close to their optimal amounts needed for the stabilization of these oils.

6 Fatty acids and tocopherol composition and stability of frying oils

The chemistry of degradation of vegetable oils under frying conditions is notably different from that at storage conditions, mainly because of the effects of high temperature on the degradation of peroxides leading to very high initiation rates, the low availability of oxygen leading to increased contribution of radical-radical polymerization reactions and formation of non-polar dimers and oligomers, as well as interferences from components of the fried food [1]. The fatty acid unsaturation of frying oils is of great significance, and saturated and hydrogenated vegetable oils are mostly used for frying, despite the hazardous nutritional effects of saturated and *trans* fatty acids. Triacylglycerols purified from sunflower, rapeseed and high-oleic sunflower oils were much less stable than their non-purified forms at 180 °C, and part of the protection against oxidative polymerization was provided by α- and γ-tocopherols [62]. Tocopherols degrade fast in frying oil, with the degradation being faster in less unsaturated oils at very high temperatures [17]. Comparing degradation of α-tocopherol in several oils (coconut, palm, tallow, olive, high-oleic sunflower, sunflower, corn, soybean, and flaxseed), a linear correlation ($y = 3.72x + 137.5$, $R^2 = 0.9463$) was obtained between residual tocopherol content (y) and iodine value (x) [63]. Oxidation at high temperature causes α-tocopherol to degrade to a wide range of oxidation products. Three oxidation products (7,8-epoxy-α-tocopherolquinone, 4a,5-epoxy-α-tocopherolquinone, and α-tocopherolquinone) were identified during the oxidation of triolein and tripalmitin, but several of which were not easy to analyze due to broad HPLC peaks and lack of strong fluorescence because of impaired chromanol structures [64]. To understand the role of tocopherols in stabilizing frying oils, it is important to identify their major oxidation products, especially those resulting from reactions with alkyl radicals.

7 Interaction between tocopherols and other components of vegetable oils

The non-saponifiable constituents of vegetable oils include a wide range of low-molecular-weight lipophilic and amphiphilic components, metals, and proteins, which might affect the rate of oxidation of these oils. Virgin olive oil is a good example of an oil rich in several of these components, notably phenolic compounds, chlorophyll and carotenoid pigments. Examples of the polyphenols of olive oil include tyrosol, hydroxytyrosol, caffeic acid and oleuropein [65]. Chlorophylls a and b, and pheophytins a and b are abundant in virgin olive oil, with pheophytin a being the predominant pigment, while the carotenoid fraction included lutein, neoxanthin, violaxanthin, luteoxanthin, antheraxanthin, mutatoxanthin and β-cryptoxanthin [66]. The chlorophyll pigments are known to act as antioxidants in the dark, but as singlet oxygen sensitizers and pro-oxidants in light [67–70]. Carotenoids, on the other hand, are efficient singlet oxygen quenchers and prominent antioxidants in the light [71]. However, both chlorophylls and carotenoids, having a highly conjugated double bond system, add radicals, resulting in unstable radical adducts leading *inter alias* to the decolorization of these pigments and initiation of new lipid oxidation reaction chains. The same phenomenon was reported for squalene [72]. In the presence of tocopherols and other phenols, there is an outstanding synergism between these highly conjugated pigment molecules and the phenolic-led radical interception.

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Chlorophylls and carotenoids are removed during bleaching and therefore are present at very low levels in refined vegetable oils. Refined vegetable oils, however, contain residual phenolic compounds, phospholipids, and other polar compounds [73]. The phytosteryl ferulate esters of rice bran oil, γ-oryzanols, are important antioxidants in this oil [74]. Other lipid-soluble compounds, such as menadione (vitamin K3), are also found to exert protective effects against lipid oxidation and tocopherol degradation in vegetable oils [75]. The effects of natural antioxidants, such as phenolic acids, lignans, lecithins, and oryzanols on the stability of frying oils have already been discussed [76].

One vegetable oil known for superior oxidative stability, despite its rather unsaturated fatty acid composition (semi-drying oil), is roasted sesame oil. Fig. 7 presents results from the study of Tan et al. [30] that has evaluated the oxidative stability of different vegetable oils, applying Arrhenius kinetics to oxidation data obtained by isothermal differential scanning calorimetry at 110, 120, 130 and 140 °C. The relation between iodine value and expected shelf life at 30 °C was linear and highly significant for palm kernel oil (PKO), peanut oil (PNO), rapeseed oil (RSO), corn oil (CO), and soybean oil (SBO) (y = 98.9–0.611x I.V., R^2 = 0.9874, p <0.01). This sesame oil (SO), extracted from roasted seeds, stands as an outlier as it is rich in melanoidins with high antioxidant potential [77]. The extra stability of sesame oil merits further research to attempt increased oxidative stability of vegetable oils by processing, *e.g.* roasting of seeds. Indeed, roasting may affect the sensory qualities of the oil in a way that might offend consumers used to oils with bland flavor and color.

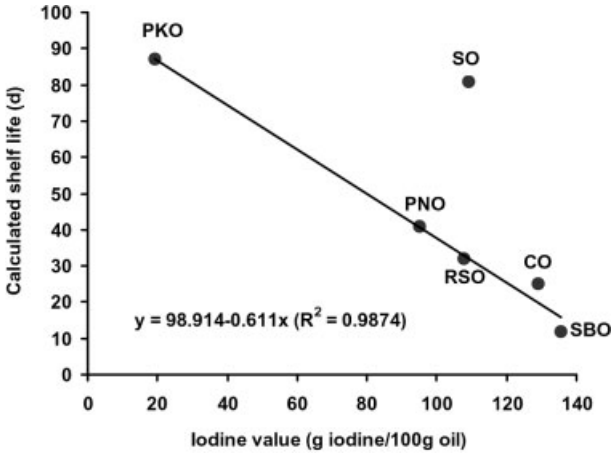

Fig. 7. The correlation between shelf life (days at 30 °C) predicted by Arrhenius kinetics from data obtained for different refined oils by differential scanning calorimetry at 110, 120, 130, and 140 °C. Oils: PKO = palm kernel oil, PNO = peanut oil, RSO = rapeseed oil, CO = corn oil, SBO = soybean oil, SO = sesame oil. SO, standing as an outlier, is extracted from roasted seeds usually rich in melanoidins (data from [30]).

8 Concluding remarks

The oxidative stability of vegetable oils is determined in a complex way by their fatty acid composition and tocopherol contents. More unsaturated fatty acids are most susceptible to oxidation, but this susceptibility is affected by their position within the triacylglycerol molecules, with the intermediate position (*sn*-1) being slightly protected. Among the tocopherols, α-tocopherol is the most efficient in scavenging peroxyl radicals, but its antioxidant activity in vegetable oils is partially minimized because of participation in side reactions leading to increased rates of initiation. With the identification of efficient synergists, the stability of vegetable oils might be improved.

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