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Modeling the impact of residual fat-soluble vitamin (FSV) contents on the oxidative stability of commercially refined vegetable oils

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ABSTRACT

Fat-soluble vitamins (FSVs) may prevent or delay bulk lipid oxidation by exerting antioxidant action. However, literature data obtained from storage tests on commercial edible oils do not necessarily confirm a direct correlation between FSV contents of bulk oils and their measured oxidative stability. This, of course, may be predominantly due to their refining history, which can strip them of much of their FSV contents and/or standardize these values. The main goal of this study was to quantify the magnitude of the role of FSVs in hindering commercial edible lipid oxidation. Fatty acid composition and FSV content data were collected on a large mixed set of commercial vegetable oils devoid of added antioxidant stabilizers ($n = 123$) in order to establish baseline values for these constituents. Next, a random subset of these oils ($n = 50$) was then subjected to the oil stability index test (OSI at 120 °C), as well as accelerated storage testing over time (60 °C) whilst monitoring a host of classical methodologies used to monitor oxidation progress. A new aggregate parameter (i.e., a sum area under the lipid oxidation curves, or 'All Area') was introduced to better capture the total quantity of primary and secondary oxidation products accumulated in the samples tested over the storage period. Multivariate regression modeling was used to correlate the fatty acid composition of the samples with their oxidative stability data both including and excluding FSV contents in order to determine a magnitude for this relationship. As noted herein, the addition of FSV data improved the fitting of the model from $R^2_{Adj.}$ 0.877 to 0.925 using OSI data alone and from $R^2_{Adj.}$ 0.938 to 0.960 using the 'All Area' parameter. Correlations between specific FSVs and fatty acid compositional parameters exhibited a strong relationship with lipid category. Furthermore, principal component analysis of FSV contents revealed clustering of lipids based both on lipid category and refining history.

1. Introduction

Various studies have reported that the oxidative stability of vegetable oils is highly impacted by their fatty acid composition (Warner, Frankel, & Mounts, 1989; Neff et al., 1992; Neff, Mounts, Rinsch, Konishi, & El-Agaimy, 1994; De Leonardis & Macciola, 2012; Marmesat, Morales, Velasco, & Carmen Dobarganes, 2012; Kerrihard, Nagy, Craft, Beggio, & Pegg, 2015). As a first approximation, it is commonly accepted that edible oils containing a high quantity of unsaturated fatty acids are more susceptible to undergo oxidation reactions (i.e., low stability). For instance, soybean oil should be comparatively less stable than coconut oil due to its lower percent saturation (14 vs 84% w/w, respectively). Furthermore, oxidation rates of individual fatty acids have been shown to be impacted with respect to their degree of unsaturation. For example, the oxidation rates for oleic (C18:1), linoleic (C18:2), and α-linolenic (C18:3, ω − 3) acids have been reported as 1:12:25, respectively (Min & Boff, 2001). According to this assumption, high-oleic sunflower oil should exhibit greater oxidative stability than normal sunflower oil, because it contains about 40% less linoleic acid (w/w), respectively.

Indeed, whilst some of the aforementioned suppositions may hold as general guidelines, the comparative oxidative stabilities of bulk vegetable lipids used in food industry often prove more complex. For instance, an increased degree of unsaturation does not always correlate well with bulk lipid stability. In fact, the opposite has been reported (Marmesat et al., 2012). This is due to the fact that the oxidative stability of bulk oils is multifaceted and influenced by other pro- and anti-oxidant factors. Notable explanations given in the scientific literature for observed discrepancies between fatty acid composition and oxidative stability include: contents of endogenous or added antioxidants (e.g., either refining aids or declared stabilizers); contents of metal-ion oxidation catalysts inherent to the oils; and the prevalence of more polar lipid constituents in certain vegetable oils (Hoffmann, 1989; Kochhar, 2001; Marmesat et al., 2012).

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In terms of predominant residual fat-soluble vitamin (FSV) contents, endogenous tocopherol (T) levels have been proven characteristic to vegetable oil types in supply for industry (Lechner, Reiter, & Lorbeer, 1999; Pinheiro-Sant'Ana et al., 2011; Wong et al., 2014) and can even be used to discriminate between their sources (Li et al., 2011). It has been suggested that the levels of Ts and fatty-acid profile both affect the ultimate oxidation rates of oils; thereby, explaining how two oils with a different PUFA content might demonstrate the same measured oxidative stability (Normand, Eskin, & Przybylski, 2006). Several past studies investigated the antioxidant potency and ranking of different T vitamers. It is generally accepted that α-T exhibits higher antioxidant activity in fats and oils at lower concentrations, but at higher concentrations, γ-T is the more active antioxidant (Seppanen, Song, & Saari Csallany, 2010). The experiments in this latter work were conducted with sunflower-seed oil, in which α-T accounts for greater than 90% of the total Ts. The authors thus concluded that substitution of α-T by γ-T can have a positive impact on oil stability.

Despite these promising preliminary observations, choosing refined oils with either higher residual levels of antioxidants, or selecting which natural (e.g. mixed T vitamers) or synthetic antioxidant stabilizers (e.g. butylated hydroxyanisole {BHA} and butylated hydroxytoluene {BHT}) to add to the bulk oils for quality maintenance is not so straightforward. This was illustrated by the study of Roman, Heyd, Broyart, Castillo, and Maillard (2013) showing that the presence of α-T in oils significantly increases stability, but no clear improvement in oil stability was observed when another natural antioxidant compound (chlorogenic acid) was added. Further, contradictive results appear regarding possible synergies among various T vitamers as a reported synergy was observed by Barrera-Arellano, Ruiz-Méndez, Velasco, Márquez-Ruiz, and Dobarganes (2002), yet no synergy was observed by Lampi and Kamal-Eldin (1998). Surely, likely explanations for this may include the complex interplay among several pro-/anti-oxidant factors impacting lipid oxidation progress in edible oils as well as the certainty that one sample is not fully representative of all lipids of a given origin/category due to the inherent variance in minor compounds (Marmesat et al., 2012).

The main goal of this study was to quantify the magnitude of the role of residual FSVs in promoting the oxidative stability of commercially refined vegetable oils. For this purpose, fatty acid composition and FSV content data were collected on a large mixed set of commercial oils and fats devoid of added antioxidant stabilizers (n = 123) in order to establish baseline values for these constituents. Next, a random subset of these oils (n = 50) was then subjected to the oil stability index test (OSI at 120 °C), as well as accelerated storage testing over time (60 °C) whilst monitoring a host of classical methodologies used to monitor oxidation progress. Multivariate regression modeling was then used to correlate the fatty acid composition of the samples with their oxidative stability data, both including and excluding FSV contents, in order to determine a magnitude for this relationship. It should be noted that the choice to implement assessments at these two widely different temperatures was in accordance with the frequent uses of these approaches in food industry and academic research, respectively. For a recent review of lipid oxidation methods, their common usage and underlying chemistry/principles see Kerrihard, Pegg, Sarkar, and Craft (2015).

2. Materials and methods

2.1. Materials

HPLC-grade *n*-hexane (article number 1.04391), methanol (article number 1.06007), and 2-propanol (article number 1.01040) were procured from Merck KGaA (Darmstadt, Germany) as well as analytical-grade chloroform (article number 1.02445), absolute ethanol (article number 1.00983), and tetrahydrofuran. Acetone (CHROMASOLV® Plus for HPLC, article number 650501) and 1,4-dioxane (article number 34857) were obtained from the Sigma-Aldrich Company (Steinheim, Germany) as were acetic acid (eluent additive grade for LC–MS, article number 49199), butylated hydroxytoluene (BHT, article number 34750), and glyceryl trioleate (article number T-7140). Deuterated standards $^{2}H_{6}$-cholecalciferol (vit. D3, lot number: AR4620213), $^{2}H_{4}$-phylloquinone (vit. K1, article number DLM-7702-0) and $^{2}H_{6}$-α-tocopherol (vit. E, article number OR 02-054) were purchased from Chemaphor Chemical Services (Ottawa, ON, Canada), Cambridge Isotope Laboratories Inc. (Andover, MA, USA), and Orphachem (Clermont-Ferrand, France), respectively. Labeled $^{13}C_{4}$-β-carotene standard (pro-vitamin A, lot nb. CAR-13C4-01129) was purchased from Buchem BV (Apeldoorn, Netherlands).

Discovery DSC 18, 6 mL, 500 mg solid phase extraction (SPE) cartridges were acquired from Supelco Inc. (Bellefonte, PA, USA, cat. nb. 56604-U). A Hypersil GOLD™ silica analytical HPLC column (2.1 × 200 mm; 1.9 μm particle size, cat. nb. 25102-202130) was obtained from Fisher Scientific AG (Reinach, Switzerland). The UPLC-Xevo ultra performance liquid chromatograph-triple quadrupole tandem mass spectrometer was from Waters Corporation (Milford, MA, USA). All-rac-α-tocopherol, all-rac-β-tocopherol, RRR-γ-tocopherol, and RRR-δ-tocopherol (article number 613424-1SET) were obtained from Merck Chemicals—Calbiochem (Darmstadt, Germany). Tocopherol vitamers α-tocotrienol, β-tocotrienol, γ-tocotrienol, and δ-tocotrienol (article numbers 20112375, 20110516, 201123069, and 20110702, respectively) were purchased from Davos Life Science Pte Ltd. (Singapore). Phylloquinone (article number 4-7773) was procured from Supelco, Inc. (Bellefonte, PA, USA). β-Carotene (article number 22040) was purchased from the Sigma-Aldrich Chemical Company (Steinheim, Germany).

A commercial fully-refined bulk vegetable oil sample set (n = 123 total) comprising common oil categories found in food industry was procured from a pool of global suppliers to Nestlé including: cocoa butter (n = 13), coconut oil (n = 9), olive oil (n = 14), palm oil (n = 13), palm kernel oil (n = 3), palm olein faction (n = 15), rapeseed oil (n = 15), soybean oil (n = 21), sunflower oil (n = 10), and high-oleic sunflower oil (n = 10). An additional amount of palm stearin samples (n = 9) was procured later in this study from the same supplier pool in order to develop relationships between the palm oil and its fractions (olein/stearin). The oil samples for examination were transferred to 500-mL aluminum containers, nitrogen-flushed, and stored at −20 °C until analyzed; all analyses were completed within 10–11 months. The lack of added natural antioxidants in these samples was stated during procurement from the oil suppliers. All oils were verified to be devoid of added synthetic antioxidants by high-performance liquid chromatography (HPLC) according to AOAC Official Method 983.15 (AOAC, 2012).

2.2. Fatty acid composition by GC-FID

Fatty acid profiles of the initial lipid samples set (n = 123) were quantified by gas chromatography–flame ionization detection (GC–FID) according to AOCS Official Method Ce 1a-13 (AOCS, 1998) and appear in Table 1. Calculated iodine values (CIV) for the various lipids were determined according to AOCS Official Method Cd 1c-85 (AOCS, 1998) utilizing the fatty acid composition data contained in Table 1.

2.3. Analysis of fat-soluble vitamins (FSVs) by HPLC–MS

2.3.1. Sample preparation

Vegetable oils were removed from the freezer (T = −20 °C) and thawed out in ambient conditions. Aliquots (100 μL) of oils from the initial sample set (n = 123) were then placed in a 10 mL volumetric flask and then brought up to the mark with a solution of acetone:chloroform 1:1 (v/v) containing 0.1 mg/mL of BHT. A 100 μL aliquot of this solution was then mixed with 0.2 mL of an internal standard solution (corresponding to 62.5 ng of labeled internal standards — Table 2) and diluted to 10 mL with CH_3OH including 2.5 mg/mL of BHT. Ten milliliter aliquots of these sample solutions were then loaded onto SPE cartridges that