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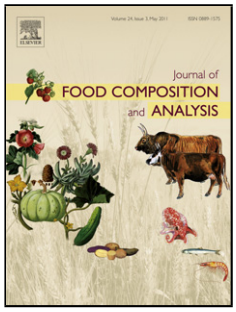

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TITLE: Revealing the relationship between vegetable oil composition and oxidative stability: a multifactorial approach

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HIGHLIGHTS

- 22 oils and fats samples showed a huge diversity in composition
- Oils and fats were grouped in 3 differentiated clusters by PCA
- TPC and SFA correlate positively with IP
- UFA, PUFA and total tocopherols correlate negatively with IP
- SFA, MUFA and PUFA account for 67% of variability of IP

ABSTRACT

A detailed composition analysis was performed for 22 diverse oils and fats and included determination of tocopherols (α, γ and δ), β-carotene, chlorophyll, total phenolic compounds (TPC) and fatty acid (FA) composition, as well as the determination of their oxidative stability (Rancimat test). Principal components analysis was applied to obtain an overview of the sample variations and to identify

behavioural patterns. Linear regression correlations and a multiple linear regression model were performed to quantify the relationship between the composition of oils and fats and their oxidative stability. The TPC and saturated FA were the main individual factors that correlated positively with oxidative stability (r^2 = 0.417, r^2 = 0.321 respectively, p < 0.01), whereas unsaturated FA, polyunsaturated FA and total tocopherols correlated negatively (r^2 = 0.304, r^2 = 0.264, r^2 = 0.223 respectively, p < 0.01). Saturated, monounsaturated and polyunsaturated FA together accounted for 67% of variability and are considered the most important parameters to affect oxidative stability. Results of this study provide a better understanding of the complex relationship between oil and fat composition and their oxidative stability, which is an essential step for designing strategies to increase stability and shelf-life of culinary oils.

ABBREVIATIONS

GAE, gallic acid equivalent

Keywords: Oxidative stability; Rancimat; PCA; regression model; oil; fat; food analysis; food composition.IP, induction period

MUFA, monounsaturated fatty acid

PC, principal component

PUFA, polyunsaturated fatty acid

TPC, total phenolic content

SFA, saturated fatty acid

UFA, unsaturated fatty acid

1. Introduction

Edible vegetable oils are commercially available as fully refined, partially refined, virgin or cold-pressed, depending on the processing steps involved in oil production. According to Codex Alimentarius (2015), virgin oils are obtained by mechanical procedures (e.g., expelling or pressing) and the application of heat only. Cold-pressed oils are obtained by mechanical procedures only without the application of heat. Both types (virgin or cold-pressed) may have been clarified by washing with water, settling, filtering and centrifuging. No food additives are permitted in virgin or cold-pressed oils. Refined oils are typically subjected to several chemical and physical refining processes, including degumming, neutralization, bleaching and deodorization. Consequently, they suffer losses of phenolic compounds, tocopherols, phytosterols, and carotenoids and as a result are more susceptible to oxidative deterioration (Chaiyasit et al., 2007); refined vegetables oils are often fortified with additives, including synthetic or natural antioxidants, to compensate for losses of endogenous compounds during the various steps of the manufacturing process (Aladedunye, 2014). An increase of carbonyl compounds and triglyceride dimers is observed during the refining process; meanwhile a reduction in oxidizable compounds, such as free fatty acids and oxidised triglyceride monomers and total polar compounds, is typically observed (Farhoosh et al., 2009). The quality of the oil should be determined holistically by simultaneously considering the industrial process involved, the chemical composition of the product and its resulting oxidative stability (Castelo-Branco et al., 2016).

Oxidative stability is an important parameter for evaluating the quality of oils and fats; it refers to the ability of oils and fats to resist oxidative rancidity (or deterioration) over processing and storage periods (Hu & Jacobsen, 2016). Lipid oxidation is one of the major causes of oil and fat degradation during processing and storage, resulting in an alteration of major quality parameters such as color, flavor, aroma, and nutritive value, due to essential fatty acids degradation and production of toxic compounds. Many of the oxidation products are highly reactive and may be responsible or contribute to undesirable *in vivo* effects in human health, such as cancer, atherosclerosis, heart disease and allergic responses (Yanishlieva & Marinova, 2001). These processes affect shelf life and their suitability

for consumption. The process of oxidation depends mainly on exposure to light, temperature, availability of oxygen, glyceridic composition, and the nature and concentration of the anti-oxidants and pro-oxidants (Kochhar, 2016; Choe & Min, 2006). It has been established that oxidation of edible oils and fats takes place through a chain reaction mechanism that essentially involves an induction stage; specifically, the time before a dramatic increase in the rate of lipid oxidation is a measure of oxidative stability and is referred to as the induction time or induction period (Tan et al., 2002). Rapid and reliable methods are required to assess the stability of edible oils and fats. The Rancimat method developed by Hadorn & Zurcher (1974), as described in the AOCS Official Method Cd 12b-92, is used to assess the oxidative stability index (AOCS, 1998). The Rancimat method is a well-established method to assess the oxidative stability of oils, which is based on the conductometric determination of volatile degradation products generated by the thermally-induced oxidation of the oils. The end point of Rancimat is determined by the induction period (time before rapid deterioration of fat occurs), which is a numerical value used to assess the relative stability of oils and fats. Rancimat is based on the release of volatiles, indicating the onset of advanced oxidation (termination). This method correlates with specific measures of advanced oxidation, such as differential scanning calorimetry (Tan et al., 2002), but also with measures of primary oxidation, such as peroxide value (Gordon & Mursi, 1994) and electron spin resonance spectroscopy (Velasco et al., 2004). Finally, induction period correlates with sensory evaluations of rancid flavors and odors in oils (Coppin & Pike, 2001).

Despite the fact that fatty acid composition and other minor compounds such as antioxidants are known to be of fundamental importance for the process of lipid oxidation, consistent quantifications of the magnitude of their relative contribution to oxidative stability have proved elusive in edible oils and fats. Furthermore, although the association between fatty acid composition (saturated *vs* unsaturated) and oxidation is well documented, studies have usually demonstrated substantial deviations from the simple expectation that “the higher the content of unsaturated fatty acids the lower the corresponding oxidative stability” (Kerrihard et al., 2015). Non-saponifiable components, naturally present in fats and oils, such as tocopherols or phenol compounds, could also significantly

affect oxidative stability (Kamal-Eldin, 2006). Previous studies could not detect correlations between chemical composition and oxidative stability of edible oils (Ayyildiz et al., 2015; Bozan & Temelli, 2008); meanwhile others reported significant differences between refined and cold-pressed oils (Castelo-Branco et al., 2016). The compositional diversity of edible oils and fats, often subjected to variable processing steps during the manufacturing process, leads to inconclusive or misinterpreted data.

The aim of this study was to elucidates the complex relationship between composition and oxidative stability of vegetable oils and fats. To meet this objective a high number of products was analysed for potential components that could singly or in combination affect the induction period of the vegetable oils. Primarily 22 types of oils and fats were analyzed for fatty acid composition, tocopherols, β-carotene, chlorophyll, total phenolic content (TPC) and oxidative stability. Secondly, a statistical evaluation that allows the identification of behaviour patterns (principal components analysis, PCA) and signifies the relationship between oils' and fats' composition and oxidative stability (linear regression correlations and a multiple linear regression model) was applied. Results generate valuable information for the oxidative stability of edible vegetable oils and fats, which is one of the critical factors determining their shelf life.

2. Materials and methods

2.1. Samples

Details of the oils/fats purchased are presented in Table 1. Products without the addition of tocopherols were selected. Oils and fats were stored in a dark cool place and butter at –6 ºC to prevent oxidation. Methanol, cyclohexane, ethanol, $FeCl_3$, TPTZ reagent, HCl, $FeSO_4$, Folin-Ciocalteu reagent, sodium carbonate and gallic acid were purchased from Sigma-Aldrich (St Louis, MO). All reagents used were of analytical grade. Stripped corn oil was purchased from MP Biomedicals LLC (Santa Ana, CA).

2.2. Determination of Total Lipids as Fatty Acid Methyl Esters (FAMEs)

The fatty acid composition is determined by analyzing methyl ester derivatives with gas chromatography (Liu, 1994). Analysis of the fatty acid methyl esters (FAMEs) was carried out using a gas chromatograph (HP6890, Hewlett Packard, Avondale, PA) using 50 m × 20 mm Chrompac CP7488 CP Sil-88 capillary column (film thickness 0.20 μm). Helium was used as carrier gas at a rate of 0.5 mL/min, and the split/splitless injector was used at a split ratio of 20:1. The injector and detector temperatures were 250 °C. The column oven temperature was maintained at 80 °C for 1 min after sample injection and was programmed to increase then at 25 °C/min to 160 °C where it was maintained for 3 min. Temperature was then increased to 190 °C at 1 °C/min and then to 230 °C at 10 °C/min. The temperature was maintained at 230 °C for 30 min. Data were analyzed using Chemstation software (Hewlett Packard, Avondale, PA). The FAMEs were identified by comparison to previously essayed standards. Measurements were taken in duplicate. Results are expressed as % of total fatty acids.

2.3. Tocopherol and β-carotene content

A reverse-phase HPLC method was used to quantify *β*-carotene, *α*-tocopherol, *γ*-tocopherol and *δ*-tocopherol in oils using fluorescence and visible detection according to Hess et al. (1991). The measurements were taken in triplicate.

β-Carotene and tocopherols were extracted from the oil phase as follows: 20 mg of oil were mixed with 280 μL H_2O and 400 μL ethanol. Each tube was vortexed for 10 seconds and 700 μL of hexane (containing BHT) and 100 μL of echinone were added and the samples were shaken for 10 min in a Vortex Genie before centrifugation for 5 min. The supernatant hexane layer (600 μL) was removed and dried down on a speed vacuum for 10 min. Each sample was then dissolved in 200 μL of DEA (20 % (*v/v*) 1,4 dioxan, 20 % (*v/v*) ethanol, 60 % (*v/v*) acetonitrile) and was shaken for 5–10 min before injected for HPLC analysis. The HPLC analysis was performed using a Waters 717 plus Autosampler Module (Waters Corporation, Milford, MA) equipped with a Waters 2475 scanning fluorescence detector, a 2487 UV/VIS absorbance detector and a C-18 silica (Beckman Ultrasphere ODS) analytical

column (250 × 4.6 mm ID, 5 µm particle size). The eluent used was 67.4% acetonitrile, 22% tetrahydrofuran, 6.8% methanol containing 1% (*w/v*) BHT, and 3.8% ammonium acetate. Elution flow rate was 1.1 mL/min, sample run was 30 min and injection volume was 150 µL. Measurements were determined with mixed standards containing carotenoids and tocopherols at appropriate concentrations and results were expressed in µg/g of oil. Echinone was used as an internal standard.

2.4. Total phenolic content (TPC)

Extraction and testing sample preparation was performed as follows: 1 g of oil was measured into a test tube and then 3 mL of methanol were added. The test tube was vortexed and then centrifuged at 6000 rpm using a CompactStar CS4 centrifuge (VWR International Ltd, East Grinstead, UK) for 5 min and the supernatant was collected. The oil residues were re-extracted twice with methanol (3 mL × 2). The three methanol extracts were combined and the final volume was brought to 10 mL with methanol to obtain the testing sample solutions. The resulting antioxidant solution was then kept at 4 °C in the dark for one night until the analysis. The TPCs of the samples were determined using the Folin-Ciocalteu reagent as described by Parry et al. (2005). In brief, the reaction mixture contained 50 µL of testing sample solutions, 250 µL of the Folin-Ciocalteu reagent, 0.75 mL of 20% sodium carbonate and 3 mL of pure water. After 2 h of reaction at ambient temperature, the absorbance at 765 nm was measured by a Pye Unicam UV-4 UV-Vis scanning spectrophotometer (Spectronic Camspec Ltd., Leeds, UK) and was used to calculate the phenolic contents of oils using gallic acid as standard. Measurements were taken in triplicate. The results were expressed as gallic acid equivalents (GAEs) in micrograms per gram of oil.

2.5. Determination of chlorophyll

The chlorophyll content of oils samples was determined by the method of Minguez-Mosquera et al. (1991). Oil (7.5 g) was accurately weighed and dissolved in cyclohexane up to a final volume of 25 mL. Chlorophyll content was calculated from the absorption spectra of the oils at

670 nm, measured by a Pye Unicam UV-4 UV-Vis scanning spectrophotometer (Spectronic Camspec Ltd., Leeds, UK). Absorption at 670 nm is usually considered to be related to the chlorophyll fraction with pheophytin-a being its major component. The chlorophyll content was calculated as follows: Chlorophyll (mg/kg) = $A_{670} \times 106/(613 \times 100 \times d)$, where A is the absorbance and d is the spectrophotometer cell thickness (1 cm). Data is reported as mg of chlorophyll per kg of oil.

2.6. Rancimat - Induction period (IP)

Oxidative stability of oils was determined by the oxidation induction period (IP) in a 743 Rancimat apparatus (Metrohm Ltd., Herisau, Switzerland) according to the AOCS Official Method Cd 12b-92 (AOCS, 1998). Oil samples (3 g) were heated at 120 °C with a constant airflow of 20 L/h. The times required for a sharp increase in water conductivity is calculated automatically by the software and corresponds to the induction period in hours. Measurements were taken in quadruplicate.

2.7. Statistical analysis

All chemical analyses were performed in duplicate (FAME), triplicate or quadriplicate (the others). Results of this study were expressed as means with standard deviations. One-way ANOVA followed by Tukey's or Games-Howell post-hoc test was used to compare chemical composition and oxidative stability between oils or fats. These treatments were carried out using SPSS (v.21.0, IBM Corporation, USA) and the level of statistical significance was set at $p < 0.05$. Principal component analysis (PCA), linear regression correlation and multiple linear regression model were performed using Minitab (Release 17.1.0 for Windows).

3. Results and discussion

3.1. Composition of oils and fats

Details of the studied oils/fats are presented in Table 1, and the fatty acid composition of 22 oils and fats is presented in Table 2. As expected the fatty acid composition varied considerably between the

samples, which is attributed mainly to varietal and genetic differences among plant species, different stages of seed maturity, geographical and climatic conditions as well as processing effects during the production (Kamal-Eldin & Andersson, 1997). The fatty acid composition was in accordance with the *Codex Alimentarius* Standards (Codex Alimentarius, 2015, 2009) for olive, coconut, rapeseed, sesame and sunflower (both regular and high oleic acid) oils. The composition of the other oils and fats included in this study is not described in the *Codex Alimentarius*.

Coconut oil showed the highest saturated fatty acid composition (94.3 and 92.7% for virgin cold-pressed and refined respectively), followed by butter (65.2%), ghee (64.1%) and virgin red palm oil (49.3%). Distinctive differences in the distribution of saturated fatty acids were detected between the above products. Coconut oil was rich in lauric acid (C12:0), accounting for 52.2% and 47.2% of the total fatty acid composition for virgin cold-pressed and refined respectively. Meanwhile butter, ghee and red palm oil were rich in palmitic acid (C16:0), with distributions of 32.8%, 31.8% and 41.2% respectively. Rapeseed oils (both refined and VCP) were the richest source of α-linolenic acid (C18:3ω3) contributing 9.24% and 10.8% to the fatty acid composition, respectively. With respect to the polyunsaturated to saturated fatty acids ratio (PUFA/SFA), sunflower VCP and sunflower oil generated the highest values (6.48 and 5.23 respectively), whereas coconut VCP and coconut oil showed the lowest values (0.01 and 0.02 respectively). In addition, butter, ghee, red palm oil and all types of olive oils showed a low PUFA/SFA ratio.

Tocopherols, β-carotene, TPC and chlorophyll content of oils and fats are shown in Table 3. Tocopherol content was in accordance with the Codex Alimentarius standards for coconut, rapeseed, sunflower oils and small differences were observed for sesame and high oleic sunflower oil (Codex Alimentarius, 2009). Tocopherol content in oils may be affected by climate, genetic variety and is also largely dependent on the production process, as reported for Brazil-nut oil (Funasaki et al., 2013), flaxseed oil (Obranović et al., 2015) and olive oil (Špika et al., 2016). The highest amounts of total tocopherols without significant differences between

them were presented by sunflower and rapeseed oil in the following order: sunflower oil, sunflower oil VCP, rapeseed oil and rapeseed oil VCP. Szydłowska-Czerniak et al. (2008) analyzed the total tocopherol content of rapeseed and olive oils subjected to different grades of refining; data from rapeseed oils were in accordance with our results (between 555 and 690 mg/kg), but not for olive oils, which demonstrated lower levels (80–190 mg/kg) compared to our results. In agreement with Dauqan et al. (2011), tocopherols were not detected in coconut oils. Unsurprisingly, the lowest tocopherol levels were detected in stripped corn oil followed by butter and ghee. α-Tocopherol was the major tocopherol in all olive oils, without significant differences between them, whereas γ-tocopherol was the most abundant in rapeseed oils, sesame oils and corn oil. With respect to vitamin E activity, α-tocopherol is the most effective form because of the specificity of absorption and distribution within the human body (Galli et al., 2016). However, γ-tocopherol might be more effective in increasing oxidative stability (Seppanen et al., 2010) and antioxidant activity of oils (Castelo-Branco et al., 2016).

Red palm oil was the only sample to contain significant amounts of β-carotene (133 μg/g). Dauqan et al. (2011) reported an even higher content of β-carotene in red palm oil (542 μg/g). β-Carotene, a provitamin A molecule, is the main pigment that gives red palm oil its distinctive orange-red color. Bioavailability of β-carotene from red palm oil is higher compared to other vegetable sources and this type of oil is highly efficacious in improving vitamin A status among populations at risk of vitamin A deficiency (You et al., 2002).

Surprisingly, refined coconut oil followed by virgin cold-pressed coconut oil showed the highest TPC, compared to all other samples. This is because they are different samples from different soil types. Marina et al. (2009) reviewed coconut composition and reported a higher TPC in virgin coconut oils compared to refined oils of the same source. It was concluded that TPC is highly variable depending on coconut varieties and the oil extraction processes, which could account for the opposing results of the present study. Arlee et al. (2013) reported relatively lower TPC data for cold-pressed coconut oil

from six varieties of coconut cultivars (486–579 μg GAE/g oil), which are not distinctively different from our results. Toasted sesame oil also showed higher TPC (501±55.1 μg GAE/g oil), compared to untoasted sesame oil. Toasted sesame oil is produced by pressing toasted sesame seeds at approximately 200 °C which gives oil its dark colour and characteristic flavour, mainly because of the generation of Maillard reaction-mediated products. It has been reported that TPC increased significantly with the roasting process of sesame seeds (Jannat et al., 2013). Virgin cold-pressed rapeseed oil (VCP) showed the lowest TPC value (137 μg GAE/g) which was even lower than the one determined for refined rapeseed oil (202 μg GAE/g). Koski et al. (2003) reported a decrease in the phenolic content detected in rapeseed oil with increasing degree of refining. This suggests that our results are most likely attributed to other variability factors (i.e. cultivar). When comparing the TPC of olive oil samples, virgin and extra virgin demonstrated higher values than the blended one with one exception (VA2). Olive oils showed TPC values between 294 and 459 μg GAE/g, which is in agreement with reported values (148 to 1,212 μg GAE/g) measured in 22 commercial extra virgin olive oils (Galvano et al., 2007).

Chlorophyll content is typically high in virgin olive oils and accounts for their distinctive light green color. Chlorophyll acts as antioxidant when the oils are kept in the dark at low temperatures and may have a pro-oxidant activity when samples are exposed to light (Giuliani et al., 2011). Concentration of chlorophyll pigments in virgin olive oil is strongly related to the ripening stage of the fruit at the time of harvest, regardless of the variety of olives. Oils produced from unripe olives show a higher content of chlorophylls than those obtained from fruits harvested when completely ripe (Giuliani, et al., 2011). In the present study, this is noticeably evident when comparing the chlorophyll content of Cornicabra variety made from 80% green olives (ECV2, 8.26 mg/kg) with the one from 100% ripe olives (VC1, 1.74 mg/kg).

Virgin vegetable oils contain different types of natural antioxidants in variable amounts. During the refining process, vegetable oils suffer a reduction of antioxidants (Chen et al., 2011). For example, the overall loss of total tocopherols during refining was reported to be 37.9% for sunflower oil (Naz et al.,

2011). In the present study, it was not feasible to directly compare refined and virgin versions of the same vegetable oil since the oils are not produced from the same source. Vegetable oil composition of the finished product including antioxidants, is dependent on several parameters, which are summarized by the extraction process and type of refining, olive or seed variety, edaphoclimatic conditions, harvesting period and technique, fruit ripening degree and others (Santos et al., 2013).

3.2. *Oxidative stability (IP) of oils and fats*

Data from induction period (IP) of 22 fats and oils are presented in Figure 1. Virgin cold-pressed coconut oil (VCP) showed the highest oxidative stability, which was significantly different ($p < 0.05$) compared to all other oils. The IP of coconut oil VCP was not calculated directly using Rancimat software because the apparatus failed to terminate the measurement automatically within a reasonable period of time. Instead measurements were taken at 140 ºC (16.44 $\pm$ 0.11 h), 160 ºC (3.16 $\pm$ 0.14 h) and 180 ºC (0.68 $\pm$ 0.01h) and IP at 120 ºC was calculated (65.01 $\pm$ 2.69) from the temperature acceleration factor, known as Q10. The determination of Q10 that based on the increase in oxidation rate produced by a 10 °C increase in temperature (Frankel, 2012).

Virgin olive oil from Cornicabra variety made with 80% green olives (ECV2), generated the second highest IP, which was significantly higher ($p < 0.05$) than the IP of all the remaining olive oils and even the refined coconut oil. Montaño et al. (2016) compared the IP of oils from seven varieties of olives (Arbequina, Cornicabra, Manzanilla Cacereña, Manzanilla de Sevilla, Morisca, Pico Limón and Picual) using a Rancimat apparatus under a different experimental set-up to the one of the present study (100 ºC, air flow 15 L/h). The highest IP values ($p < 0.05$) reported were for oils from Picual and Cornicabra olives, whereas Arbequina and Morisca varieties showed the lowest values. In the same study, olives were collected on three harvesting dates from at least three different groves in varied locations; hence, the results are conclusive with respect to the effect of olive variety and not the ripeness state. In the present study, the lowest IP ($p < 0.05$) between monovarietal virgin olive oils was found in Hojiblanca and the highest in Cornicabra olive oil.

Previous studies determined the IP oils and fats using the same experimental conditions as the present study (120 ºC, air flow 20 L/h) and the results are documented as follows: ghee – 10.57 h (Pawar et al., 2014); refined rapeseed oil – 4.10 h (Anwar et al., 2003) and 5.9 h (Kowalski et al., 2004); refined sunflower oil – 1.89 h (Anwar et al., 2003), 3.05h (Ayyildiz et al., 2015) and 3.5 h (Kowalski et al., 2004); butter – 5.00 to 6.03h (Anwar et al., 2003); olive oil – 6.42 h (Läubli & Bruttel, 1985); virgin olive oils – 3.7 to 48.3 h (Mateos et al., 2006). As a general rule, virgin oils showed a longer IP, due to the presence of minor antioxidant compounds (Chaiyasit et al., 2007); however, refined sunflower and rapeseed oils showed longer IP values than their respective virgin cold-pressed oils. Wroniak et al. (2008) also reported Rancimat data which suggest that cold-pressed rapeseed oils (5.08 h) were more readily oxidized in comparison with the same oil subjected to a full refining process (5.37 h).

Farhoosh & Moosavi (2007) confirmed that oxidative stability of oils determined *via* the Rancimat test cannot guarantee or predict the actual frying performance of the oil, but it is considered that this method can be useful to act as a "screening" test and eliminate the possibility of introducing lower stability oils into the production area with its consequences. They proposed that assuming a value of 24% of total polar compounds that indicates the maximum permitted levels in frying oils (i.e. discard point level), the corresponding IP of the oil should be $\geq$ 2.32 h for frying oils (Farhoosh & Moosavi, 2007). According to the findings of the present study, sunflower VCP, sesame and sunflower oil are below this point (Figure 1). Hence it may be concluded that these oils not suitable for frying purposes. Stripped corn oil is also below the limit; however, this product is not intended for human or animal consumption and is supplied for laboratory use only.

3.3. Principal components analysis (PCA)

The following fourteen variables were used for statistical assessment: IP, α-tocopherol, γ-tocopherol, δ-tocopherol, total tocopherols, β-carotene, chlorophyll, TPC, saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA), unsaturated fatty acids (UFA), PUFA/SFA and UFA/SFA ratios.

PCA was applied to reduce the initial variables to a small number of principal components (PCs), in order to obtain an overview of the sample variations and identify behavioral patterns. Figure 2 shows the bi-dimensional representation of oils and fats (Figure 2A) and all the variables taken into consideration (Figure 2B) for the first two PCs. The variance explained by PC1 and PC2 is 66.6%. PC1 (46.3% of the total variance) showed positive loading mainly with total tocopherols, UFA/SFA ratio, UFA and PUFA/SFA ratio, and negative loading with SFA, TPC and IP. PC2, which explained 20.3% of the total variance, was positively correlated with MUFA and chlorophyll, and negatively with PUFA. Figure 2B describes the behaviour of the variables. The most remote properties of the 0.0 point are more important for describing PCs, and those closest to 0.0, as β-carotene, are less important.

Oils and fats are distributed into three major clusters (Figure 2A). Cluster 1 exclusively includes samples characterized by the presence of SFA, TPC and IP, and is low in UFA content. It can be shown that coconut oils are more separated from red palm oil, butter and ghee, due to the higher values in SFA, TPC and IP. All the samples included in Cluster 1 are solids at room temperature, due to their relative high content of SFA. Olive oils and high oleic sunflower oil are grouped in Cluster 2, due mainly to their high MUFA content. High oleic sunflower oil was separated from olive oils because of differences in chlorophyll content. Finally, seed oils (except high oleic sunflower oil), which are all high in PUFA content and tocopherols (primarily δ-tocopherol), are distributed in Cluster 3.

3.4. Influence of chemical composition on oxidative stability (IP)

Linear regression correlation analysis showed that TPC, SFA, UFA, PUFA and total tocopherols were the major contributors to the oxidative stability (IP), as indicated by the correlation values (Table 4). TPC and SFA were positively correlated with IP. A positive correlation between TPC and IP in virgin olive oils has been extensively documented (Montaño et al., 2016; Manai-Djebali et al., 2012; Martínez Nieto et al., 2010; Caponio et al., 2001). On the other hand, Ayyildiz et al. (2015) concluded that no correlation between the IP of six fully-refined edible oils and fatty acid composition or tocopherols content could be detected. Furthermore, Bozan & Temelli (2008) reported similar findings (no

correlation) between the oxidative stability of flax, safflower and poppy oils and their corresponding fatty acid composition, tocopherols or total phenolic compounds.

The UFA, PUFA and total tocopherols were negatively correlated with IP (Table 4). The antioxidant behaviour of tocopherols in vegetable oils is not yet fully understood and there is evidence that it is manifested in a concentration-dependent manner. The "loss of efficacy" of tocopherols at high concentrations, sometimes referred to as a "pro-oxidant effect", is witnessed by an increase in the rate of oxidation during the induction period. This effect is more profound for α-tocopherol, but is also evident for other tocopherols (Kamal-Eldin, 2006). A positive correlation was observed for tocopherols with UFA and PUFA (r = 0.665 and r = 0.613, respectively, $p < 0.01$), and a negative correlation with SFA (r = –0.664, $p < 0.01$). This suggests that tocopherols are predominantly present in oils or fats with high unsaturated fatty acid content to confer protection against oxidation. A multivariate analysis of 14 vegetable oils showed natural interrelations between α-tocopherol and linoleic acid (r = 0.549, $p <$ 0.05) and between α-linolenic acid and γ-tocopherol (Kamal-Eldin & Andersson, 1997). Kamal-Eldin (2006) suggested that vegetable oils which are more susceptible to oxidation (i.e. high unsaturated content), are privileged by nature to contain optimal tocopherol levels for their stabilization.

A multiple linear regression model approach was adopted to determine the quantitative importance of the combined presence of 9 variables (α-tocopherol, γ-tocopherol, δ-tocopherol, β-carotene, chlorophyll, TPC, SFA, MUFA, and PUFA) on the oxidative stability of the oils and fats. The equation for this model between the summary of analyzed compounds and oxidative stability (IP) was as follows:

IP = –1356 + 0.0125[*α*-tocopherol] + 0.0161[*γ*-tocopherol] – 0.02[*δ*-tocopherol] – 0.074[*β*-carotene] + 1.99[chlorophyll] – 0.0333[TPC] + 14.32[SFA] + 13.66[MUFA] + 13.51[PUFA]; r^2 = 0.765 (1)

The three variables that showed a higher coefficient in the equation (SFA, MUFA and PUFA) are the same that mainly grouped the three clusters in PCA analysis. Taking into account these compounds, the equation was further simplified in the form below:

IP = -904 + 9.49 [SFA] + 9.16 [MUFA] + 8.94 [PUFA]; r^2 = 0.670 (2)

Some notable exceptions for both equations include coconut oil (both refined and VCP) samples. The later samples exhibited a much higher stability which would not fit to the multiple linear regression model signified by the above equations.

Linear regressions suggest that TPC is the most important individual factor (explaining 41.7% of variability); when all the parameters are considered, SFA, MUFA and PUFA in combination appear to be the most important factors (explaining 67% of variability). These results are in agreement with previously published studies aiming to correlate oxidative stability of 50 refined plant-based oils and fats with fatty acid composition (Kerrihard et al., 2015). According to the findings of this study, the concentrations of MUFA, di and tri-unsaturated fatty acids (DiUFA and TriUFA, respectively) in combination correlate strongly ($r^2 = 0.915$) with the oxidative stability of the samples. The contributions of MUFA, DiUFA and TriUFA in the present study were also assessed by a multiple linear regression model approach, resulting in a lower correlation value ($r^2 = 0.401$). When refined, non-refined and cold-pressed oils and fats are studied, the presence of minor compounds (e.g., phenolic compounds) also impacts on the oxidative stability. This may at least partially explain the lower correlation observed between fatty acid composition and IP in the present study. Castelo-Branco et al. (2016) described that α- and γ-tocopherol in combination correlated ($r^2 = 0.916$) with oxidative stability of 17 samples (9 different oils, refined and cold-pressed). In the present study α- and γ-tocopherol explained significantly lower variability ($r^2 = 0.223$).

4. Conclusions

The selected oils and fats (*n* = 22) showed a huge diversity in composition, which helped to better understand distinctive differences in their oxidative stability. PCA enabled us to group samples into three different clusters according to their compositional data and oxidative stability:

1. high in SFA, fats (solids at ambient temperature),

2. high in MUFA, olive oils and high oleic sunflower oil,

3. high in PUFA, seed oils.

Edible oils and fats contain natural compounds that could act as antioxidants or pro-oxidants. Linear regressions suggested, on one hand, that TPC and SFA were the most important individual factors (explaining 41.7% and 32.1% of variability, respectively), which correlated positively with IP. On the other hand, UFA, PUFA and total tocopherols showed a negative correlation with oxidative stability (30.4%, 26.4% and 22.3%, respectively). When all the parameters were taken in account, nine compounds (SFA, MUFA, PUFA, chlorophyll, *β*-carotene, TPC, *δ*-, *γ*- and *α*-tocopherol) explained 76.5% of total variability (equation 1), whereas SFA, MUFA and PUFA combined explained 67% of variability (equation 2). This suggests that the type of fatty acid is critically important for the oxidative stability of oils and fats, but to a lesser extent than previously described for refined oils (Kerrihard et al., 2015). The study of a diversity of oils and fats (refined, but also non-refined and cold-pressed) leads to a better understanding of the behavior of their oxidation stability.

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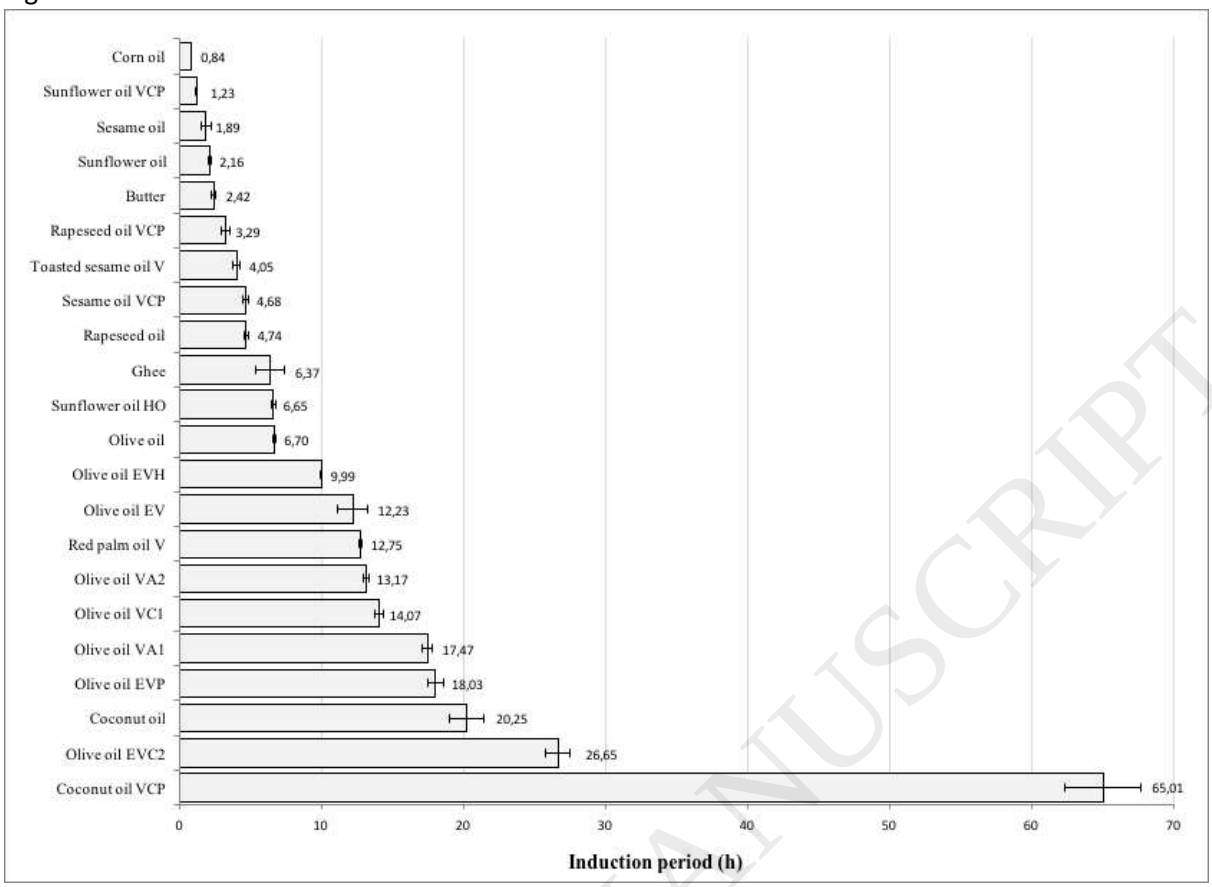
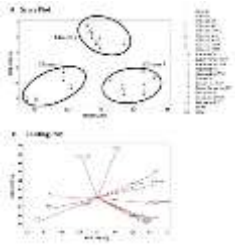
Figure Caption

Figr-1





Figr-2

Table 1

Abbreviated names, description and origin of oils and fats

Oil or fat	Characteristics	Brand	Place of purchase
Corn oil	Tocopherol stripped, for laboratory use only	MP Biomedicals	Sigma–Aldrich, Co Ltd (Dorset, UK)
Olive oil	Blended (refined and virgin)	Tesco	Tesco supermarket (Aberdeen, Scotland)
Olive oil EV	Extra virgin	Tesco	Tesco supermarket (Aberdeen, Scotland)
Olive oil VC1	Virgin, from Cornicabra olives (100% ripe)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Olive oil EVC2	Extra virgin, from Cornicabra olives (80% green)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Olive oil VA1	Virgin, from Arbequina olives (70% green)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Olive oil VA2	Virgin, from Arbequina olives (10% green)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Olive oil EVP	Extra virgin, from Picual olives (50% green)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Olive oil EVH	Extra virgin, from Hojiblanca olives (10% green)	Villajos	Villajos, Agrovillasierra S.L. (Spain)
Sunflower oil	Refined	Tesco	Tesco supermarket (Aberdeen, Scotland)
Sunflower oil VCP	Virgin cold pressed, organic	NaturGreen	Sabor del Monte, Valencia (Spain)
Sunflower oil HO	High oleic, refined, organic	Spectrum	iHerb (USA)
Rapeseed oil	Refined	Goldenfields	Tesco supermarket (Aberdeen, Scotland)
Rapeseed oil VCP	Virgin cold pressed	Tesco	Tesco supermarket (Aberdeen, Scotland)
Sesame oil	Refined	Spectrum	iHerb (USA)
Sesame oil VCP	Virgin cold pressed, organic	Sabor del Monte	Sabor del Monte, Valencia (Spain)
Toasted sesame oil V	With toasted seed, virgin, organic	Spectrum	iHerb (USA)
Coconut oil	Refined	KTC	Tesco supermarket (Aberdeen, Scotland)
Coconut oil VCP	Virgin cold pressed, organic	Dr. Goerg	Sabor del Monte, Valencia (Spain)
Red palm oil V	Virgin, organic	Nutiva	iHerb (USA)
Butter		Tesco	Tesco supermarket (Aberdeen, Scotland)

Ghee	East End	Tesco supermarket (Aberdeen, Scotland)

Table 2

Fatty acid composition (expressed as % of total fatty acids) of 22 oils and fats:

	OIL/FAT	12:0	14:0	16:0	18:0	18:1ω9	18:2ω6	18:3ω3	MUFA	PUFA	UFA	SFA	PUFA/SFA	UFA/SFA
1	Corn oil	0.0	0.03 ±0.0	11.1± 0.02	1.98± 0.0	28.3± 0.01	55.8± 0.06	1.17± 0.01	28.5	57.2	85.7	14	4.09	6.14
2	Olive oil	0.0	0.02 ±0.0	11.2± 0.02	3.67± 0.01	74.7± 0.03	7.36± 0.05	0.94± 0.0	75.8	8.59	84.3	15.6	0.55	5.40
3	Olive oil EV	0.0	0.01 ±0.0	10.5± 0.01	3.80± 0.01	76.6± 0.01	6.05± 0.01	0.92± 0.0	77.7	7.22	84.9	15.0	0.48	5.65
4	Olive oil VC	0.0	0.01 ±0.0	7.24± 0.18	3.08± 0.09	82.7± 0.43	4.40± 0.11	0.84± 0.03	83.8	5.61	88.4	11.4	0.49	8.00
5	Olive oil EV	0.0	0.01 ±0.0	10.6± 0.01	3.17± 0.0	79.4± 0.10	3.57± 0.05	0.88± 0.0	80.5	4.81	85.1	14.7	0.33	5.81
6	Olive oil VA	0.0	0.02 ±0.0	12.8± 0.03	2.21± 0.01	74.3± 0.01	7.30± 0.01	0.75± 0.0	75.7	8.28	84	15.8	0.53	5.34
7	Olive oil VA	0.0	0.02 ±0.0	12.4± 0.01	2.09± 0.0	74.5± 0.05	7.61± 0.02	0.77± 0.0	75.9	8.65	84.5	15.3	0.57	5.55
8	Olive oil EV	0.0	0.01 ±0.0	11.0± 0.03	3.61± 0.01	78.2± 0.01	4.21± 0.0	0.84± 0.0	79.2	5.31	84.5	15.4	0.35	5.51
9	Olive oil EV	0.0	0.02 ±0.0	13.2± 0.01	3.02± 0.01	70.9± 0.02	9.24± 0.03	0.93± 0.0	72.4	10.4	82.8	17.0	0.61	4.87
10	Sunflower o	0.0	0.08 ±0.0	6.61± 0.04	3.46± 0.01	27.8± 0.16	60.2± 0.25	0.0 ±0.0	28.2	60.6	88.8	11.1	5.23	7.66
11	Sunflower o VCP	0.0	0.07 ±0.0	5.98± 0.01	3.50± 0.0	19.5± 0.04	69.4± 0.08	0.0 ±0.0	19.6	69.5	89.0	10.7	6.48	8.31
12	Sunflower o HO	0.0	0.05 ±0.0	4.07± 0.01	2.97± 0.0	81.7± 0.40	8.40± 0.40	0.34± 0.0	82.4	9.45	91.8	8.72	1.08	10.5
13	Rapeseed oi	0.0	0.08 ±0.04	4.97± 0.76	1.97± 0.43	62.4± 0.83	18.4± 0.44	9.24± 0.23	63.9	28.9	91.1	9.25	3.12	11.4
14	Rapeseed oi VCP	0.0	0.05 ±0.0	4.38± 0.12	1.59± 0.02	62.2± 0.25	18.5± 0.09	10.8± 0.06	63	29.8	92.3	7.29	4.09	12.9
15	Sesame oil	0.0	0.04 ±0.01	10.4± 0.06	4.27± 0.0	40.8± 0.31	41.6± 0.76	0.72± 0.19	41.4	43.5	83.7	15.7	2.77	5.34

16	Sesame oil VCP	0.0	0.03 ±0.01	9.63± 0.16	5.9 ±0.03	39.2± 0.01	43.2± 0.16	0.54± 0.00	39.3	44.1	83.2	16.7	2.64	5.04
17	Toasted sesa oil V	0.0	0.04 ±0.01	10.4± 0.07	3.88± 0.01	39.1± 0.05	43.8± 0.10	0.75± 0.00	39.4	45	84.3	15.6	2.88	5.44
18	Coconut oil	47.2± 1.81	19.2 ±0.76	10.7± 0.48	3.47± 0.01	7.99± 1.01	1.86± 0.13	0.0 ±0.0	9.25	2.11	10.1	92.7	0.02	0.11
19	Coconut oil VCP	52.2± 0.13	20.0 ±0.2	8.79± 0.12	3.39± 0.06	5.23± 0.04	0.94± 0.01	0.0 ±0.0	5.27	0.95	6.17	94.3	0.01	0.07
20	Red palm oi	0.51± 0.28	0.95 ±0.09	41.2± 0.47	4.97± 0.19	40.8± 0.45	10.2± 0.08	0.0 ±0.0	41.5	10.6	51.5	49.3	0.21	1.07
21	Butter	3.68± 0.00	11.5 ±0.16	32.8± 0.15	11.8± 0.14	24.1± 0.00	2.09± 0.05	0.83± 0.00	29.1	4.00	32.4	65.2	0.06	0.50
22	Ghee	3.75± 0.04	11.7 ±0.11	31.8± 0.04	11.5± 0.08	24.6± 0.10	1.79± 0.01	0.92± 0.04	29.8	3.86	32.9	64.1	0.06	0.52

Results are expressed as mean ± SD (standard deviation). *Abbreviations*: MUFA; monounsaturated fatty acid, PUFA; polyunsaturated fatty acid, UFA; unsaturated fatty acid, SFA; saturated fatty acid. The most abundant fatty acids are selected for presentation in the table

Table 3

α-Tocopherol, γ-tocopherol, δ-tocopherol, total tocopherol, β-carotene, total phenolic and chlorophyll content in 22 oils and fats:

	oil or fat	**α-tocopherol**	**γ-tocopherol**	**δ-tocopherol**	**total tocopherols**	**β-carotene**	**total phenolic content**	**chlorophyll**
		µg/g	µg/g	µg/g	µg/g	µg/g	µg GAE/g	mg/kg
1	Corn oil	2.19±0.07	19.9±0.77	0.68±0.04	22.78±0.29	n.d.	149±37.8	0.00±0.02
2	Olive oil	220±21.1	15.2±1.43	0.83±0.10	236±7.55	0.10±0.02	306±30.8	0.53±0.03
3	Olive oil EV	209±16.8	19.2±1.54	0.88±0.09	229±6.13	0.45±0.01	361±30.2	1.88±0.05
4	Olive oil VC1	168±9.44	10.7±0.57	0.91±0.06	180±3.35	0.23±0.03	344±24.5	1.74±0.04
5	Olive oil EVC2	182±9.49	11.6±0.42	1.27±0.05	195±3.32	1.72±0.13	459±11.3	8.26±0.02
6	Olive oil VA1	177±8.74	4.57±0.26	0.95±0.08	182±3.03	1.24±0.07	457±27.9	7.02±0.01
7	Olive oil VA2	121±10.8	3.93±0.21	0.58±0.05	126±3.70	1.20±0.09	294±37.8	6.78±0.12
8	Olive oil EVP	169±8.80	20.7±1.15	0.89±0.09	190±3.35	0.76±0.07	389±10.1	3.95±0.03
9	Olive oil EVH	244±25.3	16.2±1.72	0.87±0.03	261±9.00	0.81±0.12	411±14.8	3.28±0.05
10	Sunflower oil	578±20.4	25.4±1.01	6.66±1.77	610±7.73	n.d.	309±19.8	0.04±0.02
11	Sunflower oil VCP	449±28.1	22±1.27	8.17±0.56	480±9.99	0.09±0.02	329±14.9	0.22±0.02
12	Sunflower oil HO	387±25.1	17.8±1.10	4.58±0.24	410±8.82	n.d.	179±9.62	0.03±0.02
13	Rapeseed oil	214±7.33	335±12.7	9.28±0.33	558±6.79	n.d.	202±27.4	0.08±0.02
14	Rapeseed oil VCP	179±13.0	374±29.8	14.8±1.21	568±14.7	1.13±0.06	137±22.1	0.39±0.30

15	Sesame oil	78.7±10.1	244±29.3	9.27±0.92	332±13.43	n.d.	269±40.2	0.04±0.03
16	Sesame oil VCP	n.d.	418±10.9	8.90±0.85	427±5.88	n.d.	304±12.8	0.09±0.01
17	Toasted sesame oil V	65±2.78	372±20.1	11.1±0.30	448±7.73	n.d.	501±55.1	1.01±0.03
18	Coconut oil	n.d.	n.d.	n.d.	n.d.	n.d.	881±171	0.13±0.02
19	Coconut oil VCP	n.d.	n.d.	n.d.	n.d.	n.d.	681±100	0.02±0.02
20	Red palm oil V	122±5.52	1.35±0.07	7.14±0.21	131±1.94	133±10.4	499±10.4	0.31±0.03
21	Butter	22.8±2.50	0.40±0.03	n.d.	23.2±1.26	3.50±0.11	226±9.37	3.29±0.31
22	Ghee	42.4±2.74	0.68±0.05	n.d.	43.1±1.90	5.64±0.40	326±35.7	0.44±0.03

Results are expressed as mean ± SD (standard deviation). *Abbreviations*: GAE; gallic acid equivalent, n.d.; not detected.

Table 4

Correlations between chemical composition of oils and fats and oxidative stability (IP) for $p < 0.05$:

	Correlation coefficient (*r*)	**Coefficient of determination (r^2)**	***p***
TPCs	+ 0.646	0.417	0.001
SFAs	+ 0.566	0.321	0.006
UFAs	- 0.551	0.304	0.008
PUFAs	- 0.514	0.264	0.014
Total tocopherols	- 0.472	0.223	0.027
UFA/SFA ratio	- 0.424	0.180	0.049

Abbreviations: TPC; total phenolic compound, SFA; saturated fatty acid, UFA; unsaturated fatty acid, PUFA; polyunsaturated fatty acid.