Journal of Food Composition and Analysis 148 (2025) 108208

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Oxidation of fatty acids in oils subjected to mild temperature stress: The case of grapeseed oil

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A R T I C L E I N F O

Keywords:
Grapeseed oil
Oxidation
Mild temperatures
Oxidated fatty acids
Oxidative indices

A B S T R A C T

Vegetable oils are among the most widely used ingredients and foods globally, with production ranging from artisanal to highly automated systems, making them a widespread commodity. Continuous evaluation of oxidative parameters is crucial to improving their sensory, qualitative, and environmental aspects. Grapeseed oil, due to its characteristics and supply chain, is a suitable matrix for oxidation studies with a relatively abundant dataset. This study investigates the physicochemical properties and oxidative stability of edible oils, specifically grapeseed oil, under mild temperature stresses. Various quality and oxidation indexes were assessed, including peroxide value, *p*-anisidine value, fatty acid composition, oxidized fatty acids content, volatile compounds, and general oxidative resistance. Analytical and instrumental methods, such as gas chromatography and OXITEST®, were employed. Results show that in an unsaturated matrix like grapeseed oil, oxidative degradation under mild temperatures follows complex kinetics that cannot be fully described by a single index. This is due to varying reactivity among fatty acids and simultaneous formation and inactivity of markers like peroxides and *p*-anisidine, respectively. The analysis of oxidized fatty acids proved to be a valuable tool for evaluating minimally stressed matrices and represents an additional parameter to enhance qualitative analysis of vegetable oil products.

1. Introduction

Vegetable oils are one of the most important components of the dietary intake of worldwide population. According to the United States Department of Agriculture (USDA), 210.3 million metric tons of vegetable oils were produced globally during the 2022/2023 season. Furthermore, the global production of vegetable oils continues to rise and studies on oils represent one of the main areas of research today, especially as consumers become increasingly careful and informed to nutritional and health aspects (Madhujith and Sivakanthan, 2019). Lifestyle-related diseases, including those associated with diet, such as coronary heart diseases, are the leading cause of death in developed and developing countries alike. In this context, oils play a crucial role in maintaining human well-being. Oils differ in their characteristics based on their composition, both in terms of fatty acids and minor compounds, and are utilized as cooking oils and ingredients in a wide variety of foods.

Grape seed oil (GSO) is an important emerging vegetable oil and it is a by-product of the wine industry that is one of the most important agro-economic activities globally (FAOSTAT, 2022). Grape seeds constitute 20–26 % of the grape berry and contain 10–20 % of oil, depending on the grape variety, environmental and extraction conditions (Crews et al., 2006). GSO is composed on average of 90 % monounsaturated and polyunsaturated fatty acids, particularly linoleic acid (58–78 %), followed by oleic acid and a smaller amount of saturated fatty acids. The high level of linoleic acid, progenitor of the essential omega-6 fatty acids, make this oil able to decrease triglycerides and cholesterol levels in the blood. GSO is also a rich source of bioactive compounds with various biological effects, such as tannins, oligomeric proanthocyanins (Xagoraris et al., 2021), carotenoids, tocopherols and phytosterols (Kiralan et al., 2019) that explain its potential health benefits (Garavaglia et al., 2016; Martin et al., 2020). For commercial vegetable oils, the hot extraction with solvents, mainly hexane, remains the simplest and most economical approach to date. Therefore, for food application, vegetable oils undergo various processes, primarily thermal treatments that can partially undermine their qualitative stability, closely linked to storage conditions, fundamental aspect to consider in the food industry supply chain. All chemical changes related to oils and fats subjected to high temperatures promote phenomena such as oxidation, hydrolysis, polymerization, isomerization, or cyclization.

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https://doi.org/10.1016/j.jfca.2025.108208
Received 29 April 2025; Received in revised form 22 July 2025; Accepted 15 August 2025
Available online 16 August 2025
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These reactions, in turn, influence the sensory, nutritional, and safety properties of oils. Moreover, these mechanisms can be triggered by various factors, including the presence of oxygen, moisture, trace metals, and free radicals, as well as other factors such as air contact, oil unsaturation levels, presence of oxidants and antioxidants, in addition to temperature and time of thermal treatment. Oxidation is the most significant cause of deterioration in oils and fats (Butinar, 2008). The primary products of oxidation are hydroperoxides, highly unstable molecules that further react to form secondary products such as hydrocarbons, alcohols, ketones, and aldehydes, which can be oxidized to carbonyl acids. Changes in oils or fats following thermal treatment are the subject of numerous studies and experiments. When referring to oxidative damage produced by intense thermal treatments over extended periods, such as frying (where temperatures of at least 180°C are reached), the available scientific literature is extensive and covers many chemicals, as well as nutritional and health-related aspects. Most of the organizations and food safety organs of various countries implement, in the panorama of safety indicators, the analysis of specific parameters strictly related to oxidation processes, such as the peroxide value (PV) that assess the amount of products originated from the first phases of oxidation; another common index is the *p*-anisidine value (*p*-AV), which is a spectrophotometric evaluation of the anisidine content, a product related to the secondary and ternary phases of oxidation. Although these parameters are simple and reliable and therefore widely used for routine analyses in most of food laboratories, they are not able to describe the evolution of a lipid substrate and, often, the analysis of only these parameters is not sufficient to describe the oxidation kinetics that occurs inside an oil. For these reasons, the lipid oxidation assessment is still a challenging task, and other oxidative methods and parameters could be found. As previously mentioned, the high unsaturation of the GSO makes it a suitable candidate in oxidation studies, not only for the presence of multiple polyunsaturated fatty acids, like α-linolenic acid (C18:3 n-3) and eicosadienoic acid (C20:2 n-6), but also for its product standardization, that makes it a stable matrix for analysis over different laboratories, finally it also has a well-established supply chain, that also gives information regarding the processes undertaken and the quality of the raw material.

For these reasons, GSO was chosen as a simple lipid model for the evaluation of the thermo-oxidative stability of fats after mild thermal treatments. In this study, the oil was stressed at 100°C for limited exposure times with the aim of simulating conditions closer to cooking or home preparations. The monitoring of the oxidative state of vegetable oils is of outmost importance, when taken into consideration that most of these are used not only as simple ingredients, but also as essential part of formulations for different kinds of products, such as sauces, biscuits, breads, ready-to-eat meals and much more. Nevertheless, some chemical parameters routinely considered to evaluate oxidation in thermal treated food lipids, namely peroxide number, hexanal concentration, and *p*-anisidine value, have been considered. Additionally, an innovative and rapid analysis of the content of oxidized fatty acids (OFA), often overlooked in assessing the oxidative state of a food item but of fundamental importance, has also been conducted. The obtained results will help understand whether the grapeseed oil tested, may undergo oxidative processes even under mild and controlled thermal stress conditions and subsequently compromise the sensory and nutritional quality of the final product.

2. Materials and methods

2.1. Chemicals and reagents

All solvents and reagents were analytical grade and unless specified were purchased from used were purchased from Sigma Aldrich (St. Louis, MO, USA): methanol, chloroform, *n*-hexane, iso-octane potassium hydroxide, methyl tri-decanoate, glacial acetic acid, potassium iodide, starch solution, sodium thiosulfate, *p*-anisidine and dilaurin. The standard mix GLC-463 was purchased from Nu-Check (Elysian, MN, USA). The technical nitrogen used (95 %≥ pure) was purchased from Sapio industries (Monza, Italy).

2.2. Samples

The GSO analysed was a commercial oil acquired through direct purchase in local Italian supermarket. Three bottles from the same batch were purchased and they were directly analysed. 10 g of sample were placed in different 100 ml bottles with Sovirel® caps, heated at 100° C in a thermostatic oven (PID system, type M 150 - VF, Instruments s.r.l. Bernareggio, MI, Italy) and in dark condition. The oil samples were then sampled and analysed at different treatment times as reported in Table 1.

2.3. Fatty acids determination by FAST-GC-FID

The determination of the fatty acid composition was carried out by gas chromatographic analysis of the relative methyl esters (FAMEs) obtained by cold basic transesterification of 20 mg of oil, according to the method of Christopherson and Glass (1969) with some modifications. Methyl tri-decanoate (C13:0; 1 mg/ml) was used as internal standard (IS). After a suitable dilution step with *n*-hexane, 0.30 µl of the upper phase was injected into a GC-2010 Plus gas chromatograph (Shimadzu, Tokyo, Japan) equipped with a flame ionization detector (FID) with a split injection port (1:100) set at 250 °C. The chromatographic separation was carried out using a BPX 70 column (SGE, Analytical Science. Ringwood, VIC, Australia, 10 m x 0.1 mm of internal diameter and 0.2 µm of thickness of the film with cyanopropyl phase, polarity equivalent to 70 % cyanopropyl-siloxane) and the chromatographic conditions described by Marzocchi et al. (2018). The fatty acids were identified based on the known retention times of a standard blend of fatty acids (GLC-463 NuCheck. Elysian, MN, USA) and were quantified by the internal standard method, expressing them as weight percentage of total FAME (mg/100 mg of FAME). The chromatograms were recorded and processed using the Shimadzu GC-2010 post-run software and each determination was carried out in triplicate (n = 3).

2.4. Determination of the peroxide value (PV) by iodometric titration

The method used in this research is in accordance with the provisions of EC Reg. N. 2568/91 and subsequent amendments. 2 g of sample was weighed into a 250 ml flask. Subsequently, 25 ml of an acetic acid / chloroform mixture (3:2, v/v) and 1 ml of a saturated potassium iodide solution were added, which was freshly prepared to avoid the presence of iodine and iodates. After mixing and five minutes in the dark, 75 ml of distilled water were added to extinguish the reaction and 2 ml of starch solution, as a specific indicator to reveal the presence of iodine. Finally, the solution was titrated with 0.01 N sodium thiosulfate until the equivalence point was reached. The PV, expressed as milliequivalent of oxygen for kg of oil, was calculated by Eq. 1:

$$PV(meqO_2/kg\ of\ oil\quad) = \frac{V * N * 1000}{m} \tag{1}$$

Table 1
Experimental sampling of the analysed GSO.

Working Tag	Sampling Time (h)	Temperature
GSO 0	00:00:00	100 °C
GSO 1	00:30:00	
GSO 2	01:00:00	
GSO 3	01:30:00	
GSO 4	02:00:00	
GSO 5	03:00:00	
GSO 6	05:00:00	

V = total volume of sodium thiosulfate used
N = the normality of the sodium thiosulfate solution
m = the mass of the sample analysed

2.5. Determination of the p-anisidine value (p-AV)

In accordance with the official ISO 6885:2006 procedure, 0.3 g of the oil was weighed into a 10 ml flask and dissolved in iso-octane. 2.5 ml of this solution were placed inside a glass cuvette and the absorbance was measured at 350 nm, against a blank as a pure iso-octane. Then 0.5 ml of *p*-anisidine solution (0.25 g of *p*-anisidine reagent in 100 ml of acetic acid) were added to the cuvettes of both iso-octane (blank) and sample solution, placed in the dark for 10 min and measured their absorbance at 350 nm. The *p*-anisidine value was then calculated as indicated by Eq. 2:

$$p - AV = \frac{v * \{1.2 * [(Absc2 - Absb2) - (Absc1 - Absb1)]\}}{w} \quad (2)$$

v = volume of iso-octane used
1.2= correction factor
Absc1= absorbance of the sample before adding the *p*-anisidine solution
Absc2= absorbance of the sample after adding the *p*-anisidine solution and waiting for 10 min in a dark place
Absb1= absorbance of the pure iso-octane before adding the *p*-anisidine solution
Absb2= absorbance of the iso-octane after adding the *p*-anisidine solution and waiting for 10 min in a dark place
w= exact weight of the sample used

2.6. Volatile compounds determination by SPME-GC-MS

The volatile compounds of the oil samples were analysed by headspace solid phase microextraction-gas chromatography/mass spectrometry (HS-SPME-GC/MS), using a GC-MS eQP2010 Plus (Shimadzu, Tokyo, Japan) equipped with an AOC 5000 autosampler (Shimadzu, Tokyo, Japan). The SPME was carried out using a fibre of 2 cm long x 0.11 μm in diameter, coated with divinylbenzene / carboxen / polydimethylsiloxane (DVB / CAR / PDMS) 50/30 μm thick (Supelco, Bellefonte, PA, USA). Samples, weighted in a 10 ml amber vial with an aluminium cap and silicon septum, were equilibrated for 10 min at 40 °C. Fiber was exposed in the head space of the vials for 40 min at the same temperature and subsequently desorbed at 250 °C for 10 min in the split mode. The chromatographic separation was obtained with a Zebron-Wax fused-silica capillary column (30 m x 0.25 mm i.d. x 1.0 mm f.t.) (Phenomenex, Torrance, CA, USA) and the following GC conditions: carrier gas: helium; column flow: 1 ml/min; split ratio: 1:10 v/v; injector temperature: 230 °C; programmed oven temperature: from 50 °C (kept for 10 min) to 200 °C at 3 °C/min and kept for 3 min; from 200 °C to 240 °C at 10 °C/min and kept the final temperature for 5 min; running time: 72 min. MS conditions: temperature of the ion source of the mass spectrum: 200 °C; scanning mass range: 30–250 *m/z*; acquisition mode: Total Ion Current (TIC) mode. The GC-MS solution software, version 2.50 SU1 (Shimadzu, Tokyo, Japan) was used, and the volatile compounds identification was performed by comparing their mass spectra with those reported in literature and the NIST Mass Spectral Database (NIST 08, National Institute of Standards and Technology, Gaithersburg, MD, USA). The results were expressed in μg/g of oil and quantified with calibration curve of hexanal.

2.7. Determination by gas chromatographic analysis of oxidized fatty acids (OFA)

The OFA analysis was carried out with the same trans methylation carried out to analyse the fatty acids composition and the subsequent injection into a gas chromatograph GC20–25 Shimadzu (Tokyo, Japan) with ionization detector of flame (GC-FID). Chromatographic separation was carried out using a Restek RXi5ms FAST column (low polarity phase; 5 % diphenyl, 95 % dimethylpolysiloxane Crossbond), length 10 m, internal diameter (ID) 0.1 mm, stationary phase with 0.10 μm film thickness (df). GC-FID conditions: carrier gas: hydrogen; injection volume: 0.30 μl; injector temperature: 325 °C; column flow: 1.80 ml/min; split ratio 1:50. The oven temperature program was: 130 °C for 0 min, then it was raised to 5 °C/min up to 250 °C and then at 20 °C/min up to 325 °C; total running time: 27.75 min. The OFA were identified as a zone of the chromatogram reuniting the fatty acids of interest, compromised for the most part of C18 fatty acids, which account approximately 88 % of the total fatty acids present on most of the vegetable oils used today in the food industry. Due to their higher molecular weight and the chromatographic conditions implemented, the OFA tend to elute after the unoxidized ones and this area of the chromatogram was elaborated not taking into account single peaks in virtue of the high similarities and possibility of signal interlaps between the single molecules.

The chromatograms were recorded and processed using the Shimadzu GC-2010 postrun software. The results were expressed in μg OFA/mg of oil, using dilaurin as internal standard.

2.8. Tocol analysis

For tocols determination, approximately 100 mg of oil was dissolved in 1 ml of *n*-hexane and filtered through a 0.2 μm nylon filter. The individual tocols were determined by HPLC 1200 series equipped with a fluorimeter detector (Agilent Technologies, Palo Alto, CA, USA) according to Marzocchi et al. (2022). The excitation wavelength was 290 nm and the emission one was 325 nm. The separation was performed by a HILIC Poroshell 120 column (3 x 100 mm, 2.7 μm particle size; Agilent Technologies, USA), in isocratic conditions, using an *n*-hexane/ethyl acetate/acetic acid (97.3: 1.8: 0.9 v/v/v) mobile phase. A calibration curve was constructed with α-tocopherol (Sigma-Aldrich, St. Louis, MO, USA), as previously reported (Ben Lajnef et al., 2017; Bombai et al., 2017; Marzocchi et al., 2022), and values expressed in mg/100g of oil.

2.9. OXITEST® analysis

The oxidative stability of the oil samples was evaluated using the OXITEST® instrument (Riciputi and Caboni, 2017). After optimisation of analytical conditions, 10 g of the different oil samples were placed in the two reactors (A and B) and stressed with a temperature of 90 °C and an oxygen pressure of 6 bar. The samples charged inside the system were GSO treated at 100 °C for 0 and 5 h. The instrument monitors the oxygen pressure inside the chambers until it collapses, recording the IP (induction period) which represents the ability, expressed in hours (h), of the oil to resist forced oxidation.

2.10. Statistical analysis

The samples were analysed in three replicates and the results were expressed as mean value ± standard deviation (s.d.). One-way analysis of variance, ANOVA (Tukey's honest significant difference multiple comparison) were evaluated using Statistica 8 software (2006, StatSoft, Tulsa, OK, USA). *p*-values lower than 0.05 were considered statistically significant.

3. Results

3.1. Fatty acid composition

As shown in Table 2, 21 fatty acid methyl esters (FAMEs) were identified and quantified in GSO (Supplementary material 1). Polyunsaturated fatty acids (PUFAs) resulted as the main components of the

Table 2
Fatty acids composition of the analysed GSOs. Values with different superscript letters are significantly different (Tukey HSD, $p < 0.05$). Uppercase letters refer to separate statistical elaboration between the FAME classes.

Fatty acids	mg FA/100 mg FAME
C12:0	0.02 ± 0.00^{h}
C14:0	0.04 ± 0.00^{h}
C15:1	0.02 ± 0.00^{h}
C16:0	6.68 ± 0.00^{c}
C16:1c n−7	0.02 ± 0.00^{h}
C16:1c	$0.10 \pm 0.01^{g, h}$
C17:0	0.05 ± 0.01^{h}
C17:1	0.03 ± 0.00^{h}
C18:0	3.84 ± 0.08^{d}
C18:1t	0.10 ± 0.00^{h}
C18:1c n−9	18.87 ± 0.02^{b}
C18:2c n−6	69.26 ± 0.03^{a}
C19:1	0.02 ± 0.00^{h}
C18:3c n−3	0.29 ± 0.00^{e}
C20:0	$0.19 \pm 0.03^{f,g}$
C20:1	$0.25 \pm 0.00^{e,f}$
C20:2c n−6	0.04 ± 0.00^{h}
C22:0	0.07 ± 0.00^{h}
C22:1	0.04 ± 0.00^{h}
C22:2	0.02 ± 0.00^{h}
C24:0	0.03 ± 0.00^{h}
SFA	10.92 ± 0.60^{C}
MUFA	19.46 ± 0.10^{B}
PUFA	69.62 ± 0.50^{A}

fatty acid profile (69.62 %), with linoleic acid (C18:2 n-6) as the principal one (69.26 %). Among the other identified PUFA, α-linolenic acid (C18:3 n-3), eicosadienoic acid (C20:2 n-6) and docosadienoic acid (C22:2 n-8) were also identified, with a total concentration lower than 5 % of the total FAME content. Among the monounsaturated fatty acids (MUFAs), oleic acid (C18:1 n-9) showed almost all the content of this class with a percentage of approximately 19 %. Other minor MUFAs were found with a percentage lower than 1 %: C20:1 > C16:1c n-7 > C18:1 t > C22:1 > C17:1 > C16:1 t > C15:1 > C19:1. Saturated fatty acids (SFAs) were the least abundant class with a total content of about 11 % and the main component was represented by palmitic acid (C16:0, 6.68 %) followed by stearic acid (C18:0, 3.84 %). Other minor SFAs were identified, as reported in Table 2. The results obtained for these commercial GSO samples fall within similar ranges reported in literature (Al Juhaimi et al., 2017; Di Stefano et al., 2021; Kiralan et al., 2019; Lutterodt et al., 2011). Several authors have studied the fatty acid composition in GSO showing slight variation among cultivars, geographical origin and extraction methods. Al Juhaimi et al. (2017) reported the fatty acid profile of the GSO of eleven different varieties of grape with a PUFA range of 48–73 %, while MUFA and SFA were 14–29 % and 13–24 %, respectively. Di Stefano et al. (2021), studying the influence of the extraction methods (cold pressed vs. Soxhlet) and grape variety (red vs. white), reported linoleic acid as the major fatty acid (67.2–71.15 %) in all samples, followed by oleic acid (16.62–20.4 %) and palmitic acid (7.90–8.88 %). As a result, it can be stated that the linoleic acid is the key fatty acid in GSO. Moreover, the total sum of the unsaturated fatty acids represents the 88.55 % of the total fatty acids identified, and also the 99.4 % of the total unsaturated fraction of the oil; confirming once again how the C18 fatty acids population, and its relative oxidative state defines the FA quality of the GSO. Another consideration that has to be taken is related to the concentration of trans oleic acid (C18:1 t) found, for which the values obtained tend to be in agreement with the technology operated on the oil, being it a result of a refining process. PUFA represent a researched quality in crude consumable oils, mainly to the fact that their intake contributes to a significant lowering in risk of developing oxidation and inflammation related pathologies (Hu et al., 2014; Yanishlieva et al., 1999).

3.2. Oxidative indexes

As reported in Table 3, the values for the peroxide value (PV) and *p*-anisidine value (*p*-AV) showed a typical evolution during the treatment time. PV reached the maximum value of 6.38 $meqO_2$/kg of oil after 1 h of treatment at 100 °C (GSO2), following a rapid decrease towards values of 4.52 after 1 h and half (GSO3) and 5.27 after 5 h of heating (GSO6). The chemical kinetics of the peroxides formation clearly show how in the first phases of oxidation the peroxide concentration tends to increase following the first reaction of fatty acids with the oxygen present in the system; however, those same peroxides are also characterized by low chemical stability, which are prone to form more stable molecules by cleavage of the O-O σ-link of the molecules, with the formations of aldehydes and ketons (Frankel, 2012a). In all the treated samples, the content of the PV never exceeded the legal limits of 10 $meqO_2$/kg of oil for the refined oils.

The *p*-AV results showed how also the content of secondary oxidation products never rose above legal thresholds (usually set at values of 10, depending on the country), always maintaining values between 6.10 and 7.24. These data, reported in Table 3, describe how the oil samples never reached optimal temperature, humidity, and time conditions for the demolition of the hydroperoxides, leaving the levels of *p*-AV always constant during the different treatment time. Kiralan et al. (2019) reported higher PV values for cold-pressed unrefined GSO under accelerated thermal conditions, such as 60°C for a total of 6 days. These values varied from 12.2 $meqO_2$/kg oil at 0 days of storage to 64 $meqO_2$/kg oil at 6 days of storage. More similar results were found by Nyam and Chew (2014) that assessed the PV of a commercial GSO subjected to a domestic deep frying. In fresh grapeseed oil before frying process, PV was 1.10 $meqO_2$/kg oil and after 30, 60 and 90 min at 190 °C changed to 2.50, 3.53 and 4.63 $meqO_2$/kg oil, respectively. The same study assessed *p*-AV reporting a value of 9.40 for fresh oil and of 28.34, 31.37 and 32.67 for samples fried for 30, 60 and 90 min, respectively. These results confirm how the *p*-AV is a parameter susceptible only to very strong oxidation condition, as for frying. Indeed, looking at the data obtained it is clear how the PV and *p*-AV are parameters not sufficient to describe the oxidation evolution in samples under mild thermal oxidation condition.

3.3. Volatile compounds analysis

The SPME-GC-MS analysis of the GSO samples reported a total of 23 volatile compounds, as shown in Supplementary Material 2. Most of the compounds found were identified in previous studies by being markers of "rancid", "oxidized", "nutty", "mold" and "oily" flavours that can occur in different type of vegetable oils, notably extra-virgin olive oils, sunflower oils, rice oils and grapeseed oils extracted by cold mechanical pressing (Hu et al., 2014; Yanishlieva et al., 1999). Most of the molecules were attributed to the category of ketones and aldehydes, compounds usually originated from the demolition of the hydroperoxides during the advanced phases of the lipid oxidation (Frankel, 2012a). This observation is in line with the results previously obtained with the other indexes, demonstrating that the GSO undergoes significant changes and oxidation kinetics during treatment time, especially between the 3 (GSO5)

Table 3
Oxidative indices (PV and *p*-AV) after the different heating treatment of the analysed GSOs. Values with different superscript letters in each column are significantly different (Tukey HSD, $p < 0.05$).

Sample	PV ($meqO_2$/kg of oil)	*p*-AV (n)
GSO0	$4.88 \pm 0.68^{b,c}$	7.24 ± 0.42^{a}
GSO1	5.50 ± 0.12^{b}	$6.51 \pm 0.1^{a,b}$
GSO2	6.38 ± 0.18^{a}	$6.36 \pm 0.28^{a,b}$
GSO3	4.52 ± 0.13^{c}	$6.46 \pm 0.02^{a,b}$
GSO4	5.69 ± 0.01^{b}	6.10 ± 0.12^{b}
GSO5	$5.24 \pm 0.69^{b,c}$	$6.56 \pm 0.32^{a,b}$
GSO6	$5.27 \pm 0.48^{b,c}$	$6.73 \pm 0.17^{a,b}$

and the 5 h (GSO6) of heating. As reported in Table 5, five specific molecules (2-octene, 2-heptanal, hexanal, 2-pentanone, and hexanoic acid) were discussed here because of their constant evolution during the treatment period and because they are flavour and aroma-related markers of lipid oxidation (Hu et al., 2014; Kiralan et al., 2019). Molecules like the 2-heptanal, 2-octene and hexanal usually derive from the first break of the linolenic acid hydroperoxide, which tends to form intermediates of reaction with carbon chains of 6 or 7 atoms of carbon; this phenomenon is explained by the favourite attack point on the fatty acid in positions 9 and 12 on the carbonic chain, in correspondence to the π bonds (Frankel, 2012a). The further reactions of polymerization and condensation of alcohols and aldehydes tends to produce firstly intermediates like epoxy, peroxides, and poly-alcohols, which then undergo hydrolysation and isomerization with the usual formation of short chain, highly volatile products like acrolein, alkanes and terpenes. The studied compounds, as shown in Table 5, have different trend during the heating treatment: in particular, the concentration of aldehydes (hexanal and 2-heptanal) increased significantly after 2 h of heating (GSO4), with a maximum hexanal content after 2 h (13.29 μg/g) of treatment and after 5 h for 2-heptanal (24.20 μg/g). This trend suggests a gradual demolition of hydroperoxides over time, which was not confirmed in the PV data obtained, where stable levels were found during the last three treatment times. Similar results were recorded by Multari and co-workers in lupin and sunflower oils subjected to thermal stress and frying process (Multari et al., 2019). The same consideration can be made for ketons (2-pentanone), which also follow the kinetics described and reached the maximum value after 5 h of treatment (37.32 μg/g). Different evolutions were recorded for organic acids, where hexanoic acid showed a maximum concentration after 1 h (GSO2), 2 h (GSO4) and 3 h (GSO5), with a content almost equal to zero at the end of treatment (GSO6). The same trend was observed by Zhang et al. (2022) for organic acids in rapeseed oil after roasting process of seeds: hexanoic acid increased from 0.05 mg/kg to 0.14 mg/kg after treatment at 150 °C for 0, 15 and 30 min, whereas not identifiable was the concentration in samples heated for 45 and 60 min, suggesting the demolition of the organic acids in smaller volatile compounds, responsible for the more “pungent”, “rancid” and “bitter” flavours. In the case of 2-octene a decreasing concentration was registered from GSO0 to GSO2, reaching a minimum of 5.49 μg/g, then a slight turnover up until GSO5 (13.77 μg/g) succeeded by another significant decrease after 5 h of heating (GSO6). Alkanes are products originated by oxidation process involving singlet oxygens. Li et al. reported how the content of 2-octene in rapeseed oil was negatively correlated with the content of natural antioxidants of oils such as α-tocopherol and carotenoids, while it was positively related to other oxidation markers such as 2,4-heptadienal and 2-decenal, highlighting its importance as oxidative marker of oils (Li et al., 2023).

The total content of these specific volatile compounds showed a significant increase after 2 h of heat treatment at 100°C, with a content of approximately 73 μg/g for GSO4 and GSO5 and approximately 76 μg/g for GSO6, values three times higher than those found in the first hour and a half of heating (GSO1, GSO2 and GSO3).

Table 4
OFA content after the different heating treatment of the analysed GSOs. Values with different superscript letters are significantly different (Tukey HSD, $p < 0.05$).

Sample	OFA μg/g
GSO0	0.00 ± 0.00^{d}
GSO1	10.23 ± 1.33^{c}
GSO2	28.51 ± 1.20^{a}
GSO3	24.04 ± 0.90^{b}
GSO4	27.84 ± 0.60^{a}
GSO5	29.70 ± 0.10^{a}
GSO6	31.96 ± 1.15^{a}

3.4. Oxidated fatty acid (OFA)

A widely used analysis to evaluate the general quality of a fat is the content of Free Fatty acids (FFA), which is an analysis normally conducted with gas-chromatographic systems that highlights the products of the first phases of the oxidation process, which normally partake with the hydrolysis of the bond between a fatty acid and the glyceridic structure (Frankel, 2012a). These procedures, however, tends to give different results between one analysis and another mainly to the fact that FFA are unstable molecules, and also due to the analysis being only an estimation of the lipid hydrolysis; these reactions are particularly favoured when high temperatures are reached (150 °C and above) (Frankel, 2012b). Considering this information, it could be implied that, in the chromatographic analysis of FFA a portion of the analytes can undergo reaction, due to the high temperatures of injection that the instrument normally reaches (≈230 °C). The oxidation of fatty substances can generate volatile compounds that impact the sensory characteristics of the vegetable oils, but also forms oxidized compounds, like oxidized fatty acids (OFA), with negative biological effects (Dobarganes & Márquez-Ruiz, 2003). OFA are molecules with the same molecular dimensions as the parent fatty acids but with a higher molecular weight due to oxidation. OFA are characterized by having at least one extra oxygen in the carbon chain and it is possible to divide them into three principal types: epoxy-FAME, keto-FAME and hydroxy-FAME. Due to the huge number of oxygenated compounds which may be formed from the different fatty acyl chains of a triglyceride, the separation and quantification of OFA with specific functional groups is difficult and requires the derivatization of triglycerides into simpler derivatives such as FAME. Exploiting this characteristic, in this study OFA were trans-methylated and analysed by GC-FID using a column with a low polarity phase. Under these conditions, OFAs were separated in a specific region of the chromatogram after the elution of the corresponding fatty acids, as a function of their molecular weight, due to the fact that they tend to have a higher molecular weight when compared to the unoxidized ones. As reported before, since it was not possible to identify the individual oxidized compounds, OFAs were quantified as the sum of the peaks in their elution zone. The OFA content showed a demarked change after heating treatment, with a substantial increase after 1 h at 100 °C. In fact, as reported in Table 4, the total OFA content was already 10.23 μg/g of oil after 30 min (GSO1) and it increased more than double (28.51 μg/g) after 1 h of heating (GSO2). As reported for PV, the maximum content was reached after 1 h of treatment, followed by a significant decrease at 1 h and half (24.04 μg/g, GSO3). No significant increases and differences in OFA were observed during at subsequent heat treatment times, but it’s important to take notice that the absolute value of the measurement was increasing over the last samples, probably indicating, a first pace change between initiation and propagation. As reported by Buettner, 1993), this trend could be explained by the greater affinity of the initiation products with oxygen rather than with lipid molecules, by the fact that most of the oxygen present in the system had already been used in the reactions to obtain the hydroperoxides.

3.5. Tocol analysis

According to literature, in GSO samples the α- and γ-isomers were the principal tocopherols and tocotrienols (Supplementary Material 3) (Laqui-Estaña et al., 2024; (Fiori et al., 2014). The α-forms were the most abundant with a range from 8.71 to 11.23 mg/100 g of oil for α-tocopherol and from 6.32 to 8.17 mg/100 g of oil for α-tocotrienol. γ-Forms were found in lower amount and tocotrienol were more concentrated (4.48–5.72 mg/100 g) compared to tocopherol (2.34–5.22 mg/100 g). It is widely reported in the bibliography how the presence of tocols highlights antioxidant properties, due to their ability to donate phenolic hydrogens to lipid free radicals and peroxide free radicals. They can also act as single line oxygen and nitrite peroxide anion quenchers, to form hydroperoxydienone, tocopheryl quinone, and

Table 5
Volatile compounds content after the different heating treatment of the analysed GSOs. Values with different superscript letters in each column are significantly different (Tukey HSD, $p < 0.05$).

Sample	2-octene	2-pentanone	hexanal	2-heptanal	hexanoic acid	Total
	μg/g					
GSO0	23.38 ± 2.61^{a}	20.97 ± 3.44^{b}	10.78 ± 0.75^{a,b}	9.29 ± 0.24^{c,d}	n.d.	64.42 ± 1.82^{b}
GSO1	11.43 ± 2.61^{c}	4.26 ± 0.55^{c}	5.70 ± 0.31^{c}	5.72 ± 0.61^{d}	n.d.	27.11 ± 2.11^{c}
GSO2	5.49 ± 1.76^{e}	2.92 ± 0.50^{c}	7.79 ± 0.10^{b,c}	4.75 ± 0.35^{d}	5.14 ± 0.87^{a}	26.08 ± 0.85^{c}
GSO3	8.19 ± 0.73^{d}	n.d.	5.37 ± 0.55^{c}	5.07 ± 0.73^{d}	3.49 ± 0.05^{b}	22.12 ± 0.61^{c}
GSO4	16.06 ± 1.44^{b}	26.38 ± 2.03^{b}	13.29 ± 0.18^{a}	12.10 ± 0.51^{b}	5.46 ± 0.98^{a}	73.29 ± 1.24^{a}
GSO5	13.77 ± 1.04^{b,c}	30.12 ± 0.85^{a,b}	12.05 ± 0.92^{a}	11.30 ± 1.82^{b,c}	5.35 ± 0.73^{a}	72.60 ± 0.36^{a}
GSO6	4.96 ± 0.55^{e}	37.32 ± 2.35^{a}	8.86 ± 0.63^{b}	24.20 ± 1.12^{a}	0.33 ± 0.06^{c}	75.66 ± 3.61^{a}

quinone epoxide, which retard photosensitive oxidation (Kamal-Eldin, 2006). The contents of the individual tocols did not show significant differences among samples (Table 6), showing how the conditions used were indeed mild temperature stress. In a similar study, conducted by Bruscatto et al. (2019), the research group conducted different thermal treatment on chemically and physically refined rice bran oils which were stored in conditions of absent light at temperatures ranging from 100 to 180°C for periods of time ranging from 0 to 1368 h. Their results showed how the concentration of the α-tocopherol, in chemically refined samples, started to significantly change, when stored at 100°C only after 768 h of treatment, dropping from 18.43 to 14.46 mg/100 g of oil, meanwhile for the γ-tocopherol significant changes were not recorded, with the most abrupt change at 768 h, from 6.82 to 6.07 mg/100 g of oil (Bruscatto et al., 2019). Although the absolute values of tocols showed a slight decrease during heating, it is possible to observe a relative stability of these compounds during the treatment. Only the GSO3 sample (1.5 h) gave slightly different results, with the highest concentrations recorded for both α-tocopherol and γ-tocopherol (Table 6), confirming the lower values found in the oxidative parameters for the same sample. The total content of tocols was in line with the bibliography (Gliszczyńska-Świgło et al., 2007) and with the content of vitamin E reported on the label (10 mg/100 ml of oil).

3.6. OXITEST® analysis

The accelerated oxidation analysis gave results regarding the oxidative stability of the analysed GSOs during the applied heating treatment. Fig. 1 shows how the oxidation stability of GSO remained constant during the heating treatment with an IP (Induction Period) value of approximately 4:30 h. Sample GSO3, after 1 h and half of heating, showed the highest IP (5:25 h) compared to the other samples, in line with the trend observed for the other oxidation parameters, such as PV, OFA and volatile compounds with the lowest content in GSO3. On the contrary, after 5 h of heat treatment (GSO6), GSO showed a significant decrease of the IP value (equal to 2:57 h) and therefore a lower stability to the lipid oxidation.

The reduction of the IP of the oil is primarily retraceable to the natural decrease of antioxidant molecules in the system that are the first to react with the oxygen, inducing the formation of free radicals and reactive species of oxygen (ROS); they tend to be gradually less stable with the increase of temperature storage and during shelf-life, being susceptible to the presence of atmospheric oxygen (Firestone, 1999). No studies on the OXITEST® analysis on GSO was found but compared to other vegetable oil, the IP is very low. In an article published by (Grimaldi et al., 2022), low oleic sunflower oil, which is known for its high content of linoleic acid and relative low content of oleic acid, was subjected to similar analysis conditions of OXITEST® and the IP was registered at 8 h and a half. It is to consider that sunflower oil tends to differ from grapeseed oil for its relative abundance of monounsaturated and saturated species of fatty acids, that in turn lower the oxidative resistance to the oxidation processes.

4. Conclusions

The study, which covered conditions of mild thermal stress in grapeseed oil, showed how the consideration of normally recognised chemical parameters, such as PV, *p*-AV and volatile compounds are not sensitive enough in describing the general overview of the oxidation process, especially in the phases between initiation and propagation. The hydroperoxides can undergo various decomposition reactions that constitutes the real propagation phase, however, results indicated that in grapeseed oil the concentration of peroxides remain stable during treatment time, failing to describe how and if the oxidation was increasing or not in our samples. Following this general rule, it is understandable how the only consideration of the PV as a quality indicator is not representative of the reality, given the fact that a matrix with a low value could indicate a situation in which either the oxidation process must take place or has already taken place in full. Even the adoption of other parameters such as *p*-AV was not sufficient in describing the qualitative state of the oils, due to the low values registered. In fact, *p*-AV tends to stay constant in oils which undergo mild thermal stress (e.g., 100 °C), and the parameter do not describe equally each category of oil, mainly to the fact that the secondary products, are different based on the different initial structure of the OFA taken into account. If the analysis of the OFA is also considered, then it is possible to make some additional considerations, since the concentration of OFA is directly related to the lag period between initiation and propagation, and showed how the oils were beginning to oxidize, based on the absolute increase of the parameter. By taking in account different categories of molecules developed, and by not considering only a select few, to monitor the

Table 6
Tocol content after the different heating treatment of the analysed GSOs. Values with different superscript letters in each column are significantly different (Tukey HSD, $p < 0.05$).

Sample	α-tocopherol	α-tocotrienol	γ-tocopherol	γ-tocotrienol	Total
	mg/100 g				
GSO0	10.50 ± 0.94^{a}	8.17 ± 0.45^{a}	3.32 ± 0.25^{b}	5.72 ± 0.64^{a}	27.71 ± 2.27^{a}
GSO1	10.25 ± 0.81^{a}	7.09 ± 0.21^{a}	2.53 ± 0.12^{b}	4.96 ± 0.13^{a}	24.82 ± 1.01^{a}
GSO2	9.28 ± 0.64^{a}	6.32 ± 0.14^{a}	2.34 ± 0.36^{b}	4.48 ± 0.25^{a}	22.42 ± 0.39^{a}
GSO3	11.23 ± 0.41^{a}	6.49 ± 0.71^{a}	5.22 ± 0.39^{a}	4.65 ± 0.44^{a}	27.58 ± 1.13^{a}
GSO4	9.81 ± 0.92^{a}	7.61 ± 1.32^{a}	2.70 ± 0.34^{b}	5.12 ± 0.46^{a}	25.24 ± 3.05^{a}
GSO5	8.88 ± 1.28^{a}	7.27 ± 0.22^{a}	2.43 ± 0.33^{b}	5.02 ± 0.04^{a}	23.40 ± 1.63^{a}
GSO6	8.71 ± 1.22^{a}	7.74 ± 0.15^{a}	2.49 ± 0.043^{b}	5.05 ± 0.31^{a}	23.70 ± 0.40^{a}

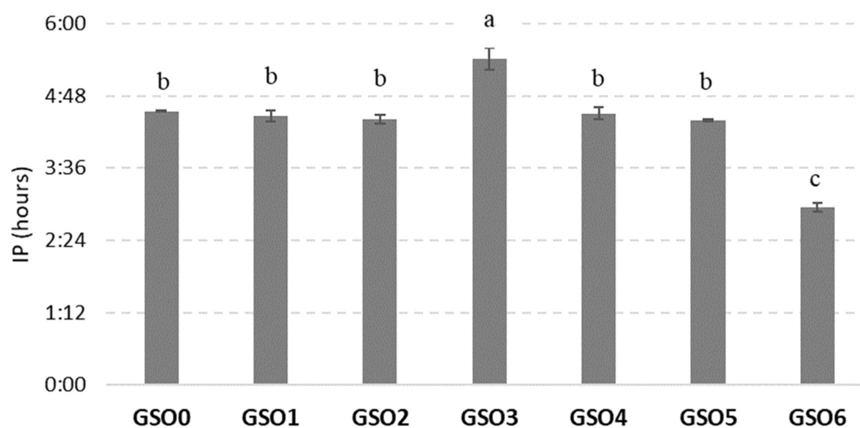

Fig. 1. IP (Induction Period) values recorded for the different heating treatment of the analysed GSOs. Bars with different letters are significantly different (Tukey HSD, $p < 0.05$).

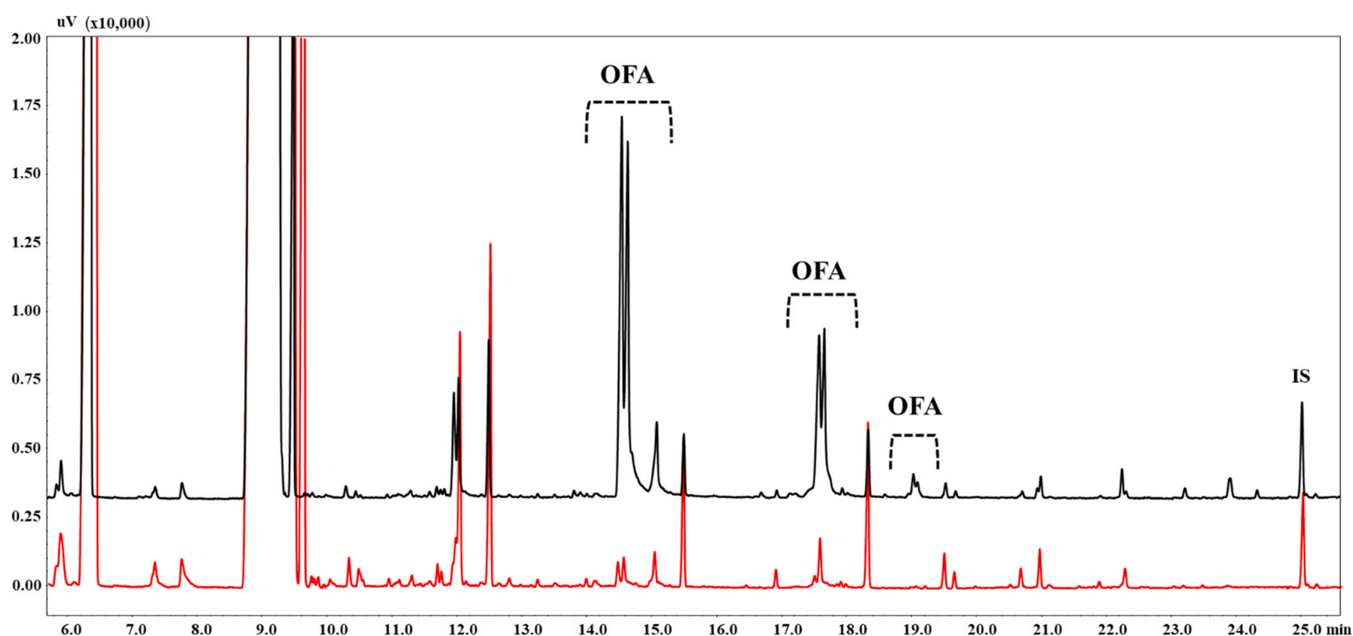

Fig. 2. Chromatogram of the oxidated fatty acids (OFA) for the sample GSO0 (red line) and GSO6 (black line). The dotted brackets show the oxidated fatty acid peaks, with one, two and three degrees of unsaturation respectively from left to right.

oxidative evolution of the samples, the evaluation of the oxidative state of the oils can be more precise. In this context, the evaluation of the general stability of an oil, using physical analyses is useful in the general assessment of the situation in which the sample is in, and gives more depth to the chemical characterization. It is to be noted that the study followed thermal oxidation relative to low temperatures, that puts the results obtained into perspective, as the general reaction dynamics are not easily distinguishable, and the products obtained may differ between one sample and the other based on the different probabilities of reaction. It is also to consider that the ability to detect slight changes in the chemical composition of oils can be especially important when looking at them as ingredients of further processes and formulations. In conclusion, the results showed a much more complicated situation regarding the oxidative stability of refined vegetable oils The oxidation processes are, in fact, diverse and strongly dependant on the conditions applied, and notable changes in the sensorial and aromatic profiles can be detected even in conditions of apparent safety.

Funding

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

CRediT authorship contribution statement

Cesare Ravagli: Writing – review & editing, Writing – original draft, Investigation, Formal analysis, Data curation. **Maria Fiorenza Caboni:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **pasini federica:** Writing – review & editing, Visualization, Supervision, Methodology, Investigation. **Silvia Marzocchi:** Writing – review & editing, Visualization, Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2025.108208.

Data Availability

Data will be made available on request.

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