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PII: S2590-1575(23)00351-6
DOI: https://doi.org/10.1016/j.fochx.2023.100908
Reference: FOCHX 100908

To appear in: *Food Chemistry: X*

Received Date: 28 March 2023
Revised Date: 8 September 2023
Accepted Date: 27 September 2023

Please cite this article as: Q. Li, M. Wang, M. Belén Fernández, A. Sagymbek, Y. Dong, Y. Gao, X. Yu, Indication of the color change on the oxidation properties of fragrant rapeseed oil during shelf storage, *Food Chemistry: X* (2023), doi: https://doi.org/10.1016/j.fochx.2023.100908

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Indication of the Color Change on the Oxidation Properties of Fragrant Rapeseed Oil during Shelf Storage

Qi Li[a], Mengmeng Wang[a], María Belén Fernández[b], Altayuly Sagymbek[c], Yaoyao Dong[a], Yuan Gao[a], Xiuzhu Yu[a]*

a. Shaanxi Union Research Center of University and Enterprise for Functional Oil Engineering Technology, College of Food Science and Engineering, Northwest A&F University, 22 Xinong Road, Yangling 712100, Shaanxi, P. R. China

b. Universidad Nacional del Centro de la Provincia de Buenos Aires, Av. Del Valle 5737, Olavarría, Buenos Aires, Argentina.

c. Saken Seifullin Kazakh Agrotechnical University, Department of Food Science, Astana, Kazakhstan.

*Corresponding author. Tel.: +86-29-87092275; fax: +86-29-87092486. E-mail address: xiuzhuyu@nwafu.edu.cn (X. Yu).

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Abstract: The cause and trend of color change and their links to oxidative properties were investigated by simulating shelf storage conditions for fragrant rapeseed oils (FROs). Under illumination, the L* value gradually increased with the storage time. The a* and b* values showed different trends depending on brands. The photodegradation rates of chlorophylls were 8.6~15 times higher than those of carotenoids. The change in color of FROs was mainly caused by the light-induced photodegradation of chlorophyll. Compared with the hydroperoxides, the contents of some secondary oxidation products [i.e., 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E, E)-2,4-heptadienal, and (E)-2-decenal] were more closely associated with the color variation with correlation coefficients of 0.6~0.94. Significant negative correlation was found between α-tocopherol content and oil color difference. Therefore, illumination was the main reason for the color degradation of the FROs. The varying degree of color difference was strongly linked to the quality deterioration caused by oxidation.

Keywords: Fragrant rapeseed oil; Color; Oxidation; Tocopherol

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Abbreviations

FROs, fragrant rapeseed oils; PET, polyethylene terephthalate; PV, peroxide value; AV, acid value; p-AnV, anisidine value; PCA, principal component analysis; BQ, Bangqi; JLY, Jinlongyu; LH, Luhua; GC, gas chromatography; ΔE, color differences; UV-Vis, ultraviolet–visible; HS-SPME, headspace solid phase microextraction; GC-MS, gas chromatography-mass spectrometry; HPLC, high performance liquid chromatography; k, rate coefficient; R^2, coefficient of determination.

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1. Introduction

Given their flavor characteristics and nutritional advantages, fragrant rapeseed oils (FROs) have been increasingly favored in the edible oil market. To retain the rich fragrance, limited refining operations are applied in the processing of FROs. Thus, pigments, such as chlorophyll and carotenoids, and lipid concomitants (e.g., tocopherols) are substantially retained (Chew, 2020; Jing, Guo, Wang, Zhang, & Yu, 2020). Different from highly refined rapeseed oils, fragrant rapeseed oils not only possess strong flavor and high nutritional value, but are also dark in color in general.

The natural pigments in rapeseed oil are affected by several factors, such as rapeseed varieties and processing techniques. The total amounts of chlorophyll and carotenoid in rapeseed oil preprocessed using microwave roasting or roasting treatment were 18.84–27.16 and 7.22–11.51 mg/kg, respectively (Rękas, Wroniak, & Scibisz, 2017). In cold-pressed rapeseed oils obtained from 203 varieties of rapeseed in China, the chlorophyll, lutein, and β-carotene contents were 0.9–51.0, 28–352, and 1.4–6.7 mg/kg, respectively. Significant differences were also found in the pigment contents among the different varieties (Yang et al., 2013). The interaction of pigment–lipoprotein complexes in the thylakoid membrane was impaired due to the general stir–frying of high temperature during the processing of FROs, promoting the dissolution of pigments (Rabadán, Gallardo-Guerrero, Gandul-Rojas, Alvarez-Ortí, & Pardo, 2018). Therefore, stir-fried treatment of rapeseeds and a low degree of refining resulted in the deep color of FROs.

To date, limited knowledge is available on the quality defect of discoloration in the shelf storage of FROs. Illumination has a significant promoting effect on the degradation of chlorophyll. Such a process occurs on the cyclopentanone ring via epimerisation, demethylation and oxidation (Indrasti, Andarwulan, Purnomo, & Wulandari, 2018). The chlorophyll content of rapeseed oil decreases with prolonged illumination but is basically unchanged in a dark environment (Li et al., 2019). Moyano, Meléndez-Martínez, Alba, & Heredia (2008) reported the relationship between the chlorophyll content of virgin olive oil and L* value with a partial correlation coefficient as high as −0.989. The color evolution of virgin olive oil under an accelerated oxidation condition at 100 ℃ was investigated. A markedly negative correlation was identified between chlorophyll and carotenoid contents with L* values in the initial and final stages of oxidation (Ceballos, Moyano, Vicario, Alba, & Heredia, 2003). There was a positive correlation between b* value and chlorophyll content in virgin olive oil prepared from olive fruits under different irrigation treatments (Sena-Moreno et al., 2017). The a* and b* values of virgin olive oil of different Italian varieties were highly positively correlated with carotenoid contents, and the R^2 values were higher than 0.97 (Cerretani, Motilva, Romero, Bendini, & Lercker, 2008). Therefore, illumination presented a remarkable effect on the pigments, affecting the color change in edible oil.

In addition to affecting the color rendering of edible oil, chlorophylls are also typical

photosensitizer molecules, facilitating the occurrence of photooxidation by the excitation of light. The oxidation reaction is accompanied by the loss of nutrients and even the accumulation of harmful substances, resulting in the degradation of quality (Choe & Min, 2006; Huvaere & Skibsted, 2015; Esposto et al., 2017; Trypidis et al., 2019). The photooxidation of edible oil harms the aroma constituents, generally resulting in bland and unpleasant flavors. After the storage of olive oils at 600 lux for 90 days, the volatile compounds of C7–C11 aldehyde (i.e., 2-heptenal, E-2-heptenal, E, E-2, 4-heptadiene) in the sample aldehydes, E,E-2,4-nonadienal, and E,E-2,4-decadienal accumulated in large amounts, reaching 1000 μg/kg (Esposto et al., 2017).

FROs are prone to oxidation reactions due to their rich unsaturated fatty acids. Hence, the shelf storage conditions possibly alter their quality characteristics (Caponio, Bilancia, Pasqualone, Sikorska, & Gomes, 2005). However, considering the intuitive attraction for customers, FROs are mostly packaged in colorless and transparent polyethylene terephthalate (PET). They are also displayed on the shelves under direct light in the actual production and sales process. After being placed in such an environment for some time, contrary to that in the dark, the color instability of FROs probably leads to the apprehension of consumers about the quality of edible oils.

The color change of FROs indicates the variation of pigments in these oils. This variation is most likely due to photooxidation, because the main pigments, i.e., chlorophyll, could act as photosensitizers during oxidation (Ludačka, Kubát, Bosáková, & Mosinger 2022; Yang et al. 2022). The quality of FROs would gradually deteriorate with the increasing degree of oxidization. Therefore, the reflection of color change on the oxidation of FROs and whether the degree of color difference was closely related to some oxidation-related characteristics need further research.

This study was performed to investigate the color stability of FROs and their relationship with oil oxidation during shelf storage under light and dark conditions. The variation of FRO colors was characterized by chromaticity values, transmittance, chlorophyll and carotenoid levels. Oxidation-related qualities were reflected by changes in the peroxide value (PV), acid value (AV), anisidine value (p-AnV), volatile products, and tocopherol content. Correlation analysis and principal component analysis (PCA) were applied to explore the intrinsic relationship between color change and oxidative properties.

2. Materials and methods

2.1. Materials

Three FROs of different brands (BQ, Bangqi; JLY, Jinlongyu; LH, Luhua) were purchased from local markets. They are classified as third grade rapeseed oil, according to relevant standards in China (GB/T 1536-2021). n-Hexane (gas chromatography, GC grade), 2-octanol (GC≥99.5%), and n-alkane (C7-C30) mixed standard (GC grade)

were obtained from TeleChem International, Inc. (Sunnyvale, CA, USA), Shanghai Yuanye Bio-Technology Co. Ltd. (Shanghai, China), and Merck & Co., Inc. (Kenilworth NJ, USA), respectively. Other chemicals were of analytical grade.

2.2. Methods

2.2.1. Storage of FRO samples

Three kinds of FRO (90 g) were individually packed in 100 mL transparent PET bottles. The storage conditions simulated the shelf storage of edible oil in ordinary supermarkets. An LED light (T5E03 4W- 4000K, Huizhou Laishi Photoelectric Technology Co., Ltd.) with a color temperature of 4000 K was used. The illuminance of the top and body of bottles was adjusted to 1300 lux and 400 lux, respectively. In addition, the storage temperature was 26±2 °C. The lighting time was 14 h/day for 50 days. The control group was stored in the dark at the same time.

2.2.2. Chromaticity value and transmittance analysis

The colors of FROs were analyzed with an X-rite colorimeter (Ci7600, X-Rite Inc. in Michigan, USA) by using the total transmission method (Wibowo et al., 2015). The maximum transmission aperture was selected as 25 mm. After calibration, petroleum ether was used as the standard for measurement. The CIELab chromaticity space was employed to represent the colors of the oil samples, in which L* was related to luminosity. The negative and positive coordinates of a* value represented green and red, respectively. The negative and positive coordinates of b* value corresponded to blue and yellow. Color differences (ΔE) were used to evaluate the degree of color change during light/dark storage of the FROs:

$$\Delta E = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2}. \qquad (1)$$

The transmittance of oil samples was determined using a colorimeter in the wavelength range from 360 nm to 750 nm.

2.2.3. Determination and degradation kinetics of chlorophyll and carotenoid

The International Union of Pure and Applied Chemistry standard method for the analysis of chlorophyll content was applied to the FROs (Pokorny, Kalinová, & Dysseler, 1995). An ultraviolet-visible spectrophotometer (UV-1200, Shanghai Meixi Instrument Co., Ltd., Shanghai, China) was used for measurements. After homogenization and filtration, the absorbance of the FRO samples was measured at 630, 670, and 710 nm, and the chlorophyll contents were calculated as follows:

$$C(\mathrm{mg/kg}) = 345.3 \times （\mathrm{A}_{670} - 0.5 \times \mathrm{A}_{630} - 0.5 \times \mathrm{A}_{710}）/\mathrm{L}, \qquad (2)$$

where C is the chlorophyll content calculated as pheophytin a; A is the absorbance at the corresponding wavelength, and L is the optical path (mm) of the cuvette.

The carotenoids were determined using ultraviolet-visible (UV-Vis) spectroscopy (Benmoussa et al., 2016). A certain amount of oil sample was diluted with cyclohexane. The carotenoid content was measured using the absorbance at 470 nm and calculated as follows:

$$[C_{\text{carotenoid}}](\text{mg/kg}) = \frac{\text{A}_{470} \times 10^6}{2000 \times 100 \times \text{density}}, \quad (3)$$

where $C_{\text{carotenoid}}$ is the carotenoid content; A was the absorbance at 470 nm; $E_{1cm}^{1\%}$ of lutein, the main component in carotenoid, was 2000 (Ceballos et al. 2003; Yang et al., 2013); and density was the ratio of the oil sample mass (g) to the final dilution volume (mL).

The degradation of chlorophylls and carotenoids conforms to first-order reaction kinetics (Chen & Huang, 1998; Psomiadou, & Tsimidou, 2002; Aparicio-Ruiz & Gandul-Rojas, 2014). Hence, the following kinetic equation was used to fit the changes in the chlorophyll and carotenoid contents in the FROs:

$$c = c_0 e^{-kt}, \quad (4)$$

where c is the pigment content after t-day light storage; c_0 is the initial pigment content; and k is the reaction rate of degradation of the chlorophylls and carotenoids.

2.2.4. Estimation of oxidation parameters and fatty acid composition

The PV reflects the level of hydroperoxides produced during the primary oxidation. The AV is used for quantitative analysis of the number of milligrams of KOH required to neutralize the free fatty acids (FFA) in 1 g of oil. Thus, AV indicates the rancidity. The p-AnV is a measure of aldehyde content, which is formed as a secondary oxidation product of edible oils. The determination of PV, AV, and p-AnV were referred to GB 5009.227-2016, GB 5009.229-2016, and GB/T 24304-2009, respectively. The fatty acid compositions were analyzed using GC (GB/T 5009.168-2016).

2.2.5. HS-SPME/GC-MS analysis of the volatile components

The volatile components were extracted through headspace solid phase microextraction (HS-SPME) and were analyzed using gas chromatography-mass spectrometry (GC-MS, Shimadzu QP2010, Kyoto, Japan). The sample (5.0 g) was weighed in a 20 mL vial sealed with an aluminum crimp cap. Divinylbenzene/carboxene/polydimethylsiloxane fiber (Supelco Inc., Bellefonte, PA, USA) was applied to headspace sampling. The vials containing the oil samples were equilibrated in an incubator at a constant temperature of 50 °C for 30 min. The fiber was conditioned by heating in a GC injection port at 250 °C for 60 min before it was inserted in the vial. Then, it was immediately desorbed into the GC-MS injection port at 250 °C for 3 min.

Oil samples stored at different times were analyzed by GC–MS under splitless injection mode and an initial GC temperature of 40 °C. After holding for 3 min, the temperature

was increased to 120 °C at 4 °C/min, followed by heating to 240 °C at 6 °C /min. Mass spectrometry analysis was operated in electron ionization mode (70 eV) with the ion source temperature of 230 °C and scanning range of 35.00–500.00 m/z. The various volatiles (matching degree > 85%) were determined by referring to MS databases (NIST14 and NIST14s, Institute of Standards and Technology, USA) in the GC-MS solution (Shimadzu Corporation, Tokyo, Japan). The contents of volatile compounds in the FROs were calculated based on the internal standard method with 2-octanol acting as the standard.

2.2.6. Determination of tocopherols

High performance liquid chromatography (HPLC, Dionex Ultimate 3000, Thermo Scientific, USA) was used to determine the tocopherols in FROs and referred to the AOCS Official Method Ce 8-89. The oil sample (1 mL) was mixed with n-hexane (1 mL), and the mixture was filtered using a nylon organic membrane (0.22 μm). Then, the filtrate was put into the liquid phase vial for sample loading. The mobile phase was n-hexane/isopropanol (98.5%/1.5%). Isogradient elution was adopted with a flow rate of 1.0 mL/min and an elution time of 15 min. The injection volume was 5 μL, and the column temperature was set to 25 °C. The target response signal values at a wavelength of 295 nm were monitored using a UV detector. The standard curves of the different tocopherol standard substances were plotted to quantify the tocopherols in the FROs.

2.2.7. Statistical analysis

All the measurements were repeated at least three times. Pearson correlation analysis and PCA were conducted using Origin 2021. Statistical analysis was performed using ANOVA with $p<0.05$ considered as significant. Statistical differences among values were indicated by different letters by the Tukey test.

3. Results and discussion

3.1. Chromaticity value analysis

The color of food is often analyzed using the CIELab color space, because this parameter could uniformly cover the entire visible spectrum to the naked eye. The chromaticity values of the FROs under light and dark conditions for different times are presented in Fig. 1.

L*, a*, and b* represent the chromaticity values of the FRO sample color, i.e., the corresponding coordinates in the CIELab color space. Parameter L describes the magnitude of brightness from black to white, while a and b are the relative amounts of red-green and yellow-blue, respectively. As shown in Fig. 1(a-f), the L* values of the FROs stored under light conditions increased gradually with storage time. After a 50-day storage, the L* values of the BQ, JLY, and LH FROs increased from 87.29, 83.62,

and 85.65 to 89.00, 87.03, and 88.90, respectively. The continued increase in brightness indicated the lightening color of the oil samples, which was consistent with the results observed with the naked eye. In addition, the L* values of the oil samples in the dark showed a small fluctuation with prolonged storage.

For the FROs stored under light conditions, the a* and b* values of the BQ oil samples increased and decreased, respectively. This indicated that their color deviated from green and yellow. The gradually decreasing a* and b* values showed that the oil colors of JLY and LH flipped from red to green and also deviated from yellow. During the 50-day storage of the FROs in the dark, the a* values decreased obviously in a short period and then fluctuated. The yellow-blue chromaticity was relatively stable, in which the b* values of oils fluctuated within a small range. Therefore, the L* and b* values of FROs under illumination showed downward trends with storage time, whereas the change of a* value varied with different brands.

The changes in the ΔE values of the FROs are shown in Fig. 1(g-i), which reflects the degree of color change of the oil samples during storage.

As depicted in Fig. 1(g-i), the ΔE values of the FROs under the light condition gradually increased with the extension of storage time. By contrast, the variation ranges fluctuated within 0–3 units after storage in the dark. Color differences have been reported to be perceived by general observers when the ΔE values were higher than 3–5 units (Ghidouche, Rey, Michel, & Galaffu, 2013). During the 50-day storage in the dark, the ΔE values of the different FROs did not exceed 3 units, indicating that the color changes observed by the naked eye were not significant. However, the difference in the FRO colors gradually became obvious under prolonged storage under light conditions. Correspondingly, the ΔE values exceeded 7 units after storage for 50 days. Therefore, storage under light had a significant effect on the color difference of FROs.

3.2. Transmittance analysis

The change in the light transmittance of FRO samples during storage is shown in Fig. 2.

As shown in Fig. 2, the obvious absorption peaks in the wavelength ranges of 375–500 nm and 625–700 nm can be observed in the visible spectra of the FROs. The peak in the wavelength range of 400–450 nm could be attributed to the common absorption of chlorophylls and carotenoids. The absorption peak at 470 nm was related to carotenoids, especially the characteristic absorption of lutein. Moreover, chlorophyll has characteristic absorption in the waveband of 625–700 nm (Ceballos et al. 2003; Moyano, Heredia, & Meléndez-Martínez, 2010; Sant'Anna, Gurak, Marczak, & Tessaro, 2013; Yang et al., 2013; Rabadán et al., 2018; Chew, 2020).

During the 50-day storage under darkness, the transmittance curve of FROs almost did not change. However, for the FRO samples under illumination, transmittances in the

band of red light (625–700 nm) increased with time. Chlorophylls, with distinct absorption in the blue-violet and red spectral regions, possessed photosensitivity and were prone to be oxidized by singlet oxygen. The porphyrin macrocycles were broken due to photodegradation. Therefore, the transmittance in the red region of oil samples was constantly elevated (Llewellyn, Mantoura, & Brereton, 1990a; 1990b; Yasuda, Oda, Ueda, & Tabata, 2019). The transmittance at approximately 470 nm also showed a small increasing trend over storage time. This could be attributed to the degradation of carotenoids under light conditions. In addition, the decrease in transmittance at 400–450 nm corresponded to the variation trend of the two types of pigments. Specifically, the downward peak around 420 nm was less obvious with the extension of storage time, as well as the light transmittance was increased here. This is due to the obvious degradation of chlorophyll. Meanwhile, because of the slow degradation of carotenoids, the peak intensity around 440 nm and light transmittance were changed slightly. After a 50-day light exposure, the maximum absorption peaks at 670 nm of the FROs basically disappeared. Thus, the chlorophylls had been substantially degraded.

3.3. Chlorophyll and carotenoid content analysis

Changes in the chlorophyll and carotenoid contents of FROs during light and dark storage are shown in Fig. 3.

As shown in Fig. 3, the chlorophyll contents of the three FROs remained basically unchanged under dark conditions. However, this parameter decreased continuously with prolonged storage, indicating that the stability of the chlorophyll in the FROs was significantly affected by light exposure. After 50 days of illumination, the chlorophyll contents of the BQ, JLY, and LH oil samples decreased from 3.86, 8.24, and 5.98 mg/kg to 0.48, 0.41, and 0.21 mg/kg, respectively. The corresponding chlorophyll losses were 87.6%, 95.0%, and 96.5%, with almost complete loss. These results were consistent with those of the transmittance analysis in Fig. 2.

Within 50 days of dark storage, like chlorophyll, the carotenoid content remained virtually unchanged. However, the carotenoid contents of the BQ, JLY and LH FROs decreased from 3.81, 6.55, and 5.14 mg/kg to 3.34, 5.61, and 4.56 mg/kg, respectively, due to the 50 days of storage under illumination. The corresponding loss ratios were 12.3%, 14.4%, and 11.3% concerning their initial contents. Thus, the stability of the carotenoids was significantly higher than that of the chlorophylls under light conditions.

A first-order kinetic rate equation was also fitted to the degradation trends of the chlorophylls and carotenoids in the FROs under light storage. The rate coefficient (k) and coefficient of determination (R^2) are shown in Table 1.

As indicated by the R^2 values in Table 1, the chlorophylls and carotenoids in the FROs were well-fitted using a first-order rate equation. The measured k values of the chlorophylls for BQ, JLY and LH were 12.4, 8.6, and 15 times higher than those of the carotenoids, respectively. Hence, consistent with the results in Fig.s 3 and 4, the

photodegradation rate of the chlorophylls was considerably higher than that of the carotenoids.

3.4. Oxidation analysis

3.4.1. Oxidation parameters

Variations in these values of FROs during light and dark storage for 50 days are shown in Table 2.

As shown in Table 2, the PVs of the BQ, JLY and LH oil samples (i.e., 5.02, 1.32, and 3.56 meq O_2/kg, respectively) increased significantly after 10 days of light storage, reaching 8.82, 5.01, and 6.98 meq O_2/kg, respectively. The activation of photosensitizers, e.g., chlorophylls, under light conditions, promoted the generation of singlet oxygen. This molecule is highly reactive with electron-dense centers (e.g., unsaturated fatty acids), thus contributing to the oxidation rate of oils. However, the PVs of the FROs later exhibited a decreasing trend to varying degrees. This phenomenon was due to the further degradation of hydroperoxides, which are unstable intermediate products of lipid oxidation (Holse, Petersen, Maruatona, & Hansen, 2012). In the dark, PV gradually increased, showing the accumulation of hydroperoxides due to the relatively slow autooxidation of the FROs. After 40 days of storage, the hydroperoxide levels of the BQ and LH oil samples exceeded those in the light, consistent with the results of Caponio et al. (2005).

High concentrations of aldehydes generated by unsaturated fatty acids during oxidation were then converted to FFA. Hence, the noticeable presence of FFA indicated a high degree of oxidation (Morales, Luna, & Aparicio, 2005). The FFA contents of FROs slightly increased during 50 days of light and dark storage. No significant difference was observed in the AVs between light and dark storage conditions. The p-AnVs of the FROs showed an overall upward trend under light storage and increased slightly during the dark storage. The fatty acid composition also did not significantly change (Tables S1-S3). Therefore, the FROs have not yet reached the stage of deep oxidation.

3.4.2. Variation in the volatile components

The volatile components of the FROs mainly have nitriles and sulfur-containing derivatives generated by the thermal degradation of glucosinolates, and heterocycles (e.g., pyrazines and furans) produced by the Maillard reaction and Strecker degradation. And aliphatic compounds of small molecules (e.g., aldehydes, alkenals, alcohols, ketones, acids, esters, and hydrocarbons), generated by the oxidative cleavage of unsaturated fatty acids, were also included (Zhang et al., 2021). Changes in the volatile components of FROs during storage are shown in Fig.s S1-S3.

As shown in Fig.s S1-S3, nitriles accounted for the largest proportion and possessed the richest species among the volatile components (Wang, Duncan, Whalley, &

O'Keefe, 2020). The distributions of pyrazine and furan derivatives partly varied in the different FROs. The nitriles, isothiocyanates, pyrazines, furans, heterocyclic ketones, hydroxyketones, and bis-carbonyl compounds were stable enough in light and dark storage for 50 days.

The change in aliphatic compounds (e.g., 2-alkenal, 2,4-alkenal, alkane, and alkene compounds) was the most obvious among the volatile oxidation products of all FROs. Alkenals, alkanes, and alkenes of the BQ and JLY oils increased significantly during light storage, while only a small amount of 2-heptenal and 2,4-heptadienal was measured in the LH oil. This result was in good agreement with the change in p-AnV.

The type and abundance of volatile aldehydes were consistent with the fatty acid composition of fats and oils. (E)-2-Heptenal were mainly derived from the linoleic acid acyl groups. Octanal and (E)-2-decenal were produced from oleic acyl groups. (E)-2-butenal and 2,4-heptadienal mainly originated from the linolenic acid acyl groups (Goicoechea & Guillén, 2014; Poyato, Ansorena, Navarro-Blasco, & Astiasarán, 2014). More octane and 2-decenal from oleic acyls were present during photooxidation than autooxidation. The generation of 2-heptenal and 2-butenal was obvious in the photooxidation of linoleic and linolenic acids but was negligible during autooxidation (Choe & Min, 2006). In addition, some other volatiles detected only in light conditions, i.e., 2-octene, 2, 4-heptadienal, and 2, 4-Octadiene also could be considered as the main volatiles from singlet oxygen oxidation. Furthermore, the flavor of the FROs was seriously damaged by the continuous accumulation of volatile products during the oxidation process, especially the aliphatic carbonyl compounds with low thresholds (Esposto et al., 2017; Nogueira, Scolaro, Milne, & Castro, 2019; Wang et al., 2022). Thus, volatile aldehydes could act as a good indicator of the intensity of photooxidation.

3.5. Tocopherol content analysis

The oxidation of edible oils is closely related to the activity of its internal lipid concomitants and is affected by external factors, such as light, oxygen, and temperature (Holse et al., 2012). Tocopherols, the important concomitant in FROs, can provide hydrogen atoms (H·) to react with ROO· or RO· generated by oil oxidation. This process inhibits the chain initiation and propagation, thereby delaying oil oxidation. Tocopherols could also act as electron acceptors to scavenge singlet oxygen, retarding the photooxidation process (Caponio et al. 2005). However, tocopherols may also become pro-oxidants depending on their concentration, temperature condition, and other conditions (Choe & Min, 2006; Nogueira et al., 2019). Changes in the tocopherol contents of the FROs during storage are shown in Fig. S4.

As shown in Fig. S4, the tocopherols in the FROs mainly included α-tocopherol and γ-tocopherol and lesser amounts of δ-tocopherol. The FROs under dark storage showed little loss in α-, γ- and δ-tocopherol. However, after 50-day storage in light, the α-tocopherol contents in the BQ, JLY, and LH samples declined from 157.55, 204.67,

and 242.76 mg/kg to 75.13, 111.38, and 153.74 mg/kg, respectively. This resulted in corresponding losses of 52.3%, 45.6%, and 36.7%. During the photooxidation process, α-tocopherol can exert its antioxidant effect and be partially converted into oxidation products, such as 8a-hydroperoxy-α-tocopherone (Tanno et al., 2020). The initial α-tocopherol content of LH oil was the highest among the FROs and may be a crucial reason for its relatively lower content of volatile oxidation products and the slightly increased p-AnV.

After light storage for 50 days, the γ-tocopherol contents of the BQ, JLY, and LH samples decreased from 407.42, 454.15, and 432.27 mg/kg to 392.45, 435.81, and 414.44 mg/kg, respectively, with corresponding loss rates of 3.7%, 4.0%, and 4.1%. Therefore, under light conditions, α-tocopherol participated in the photooxidation reaction in preference to γ-tocopherol to exert its antioxidant protection. Thus, this tocopherol possessed better antioxidant activity, which was consistent with the results of Holse et al. (2012). Illumination accelerated the loss of tocopherols in the FROs, and the loss rate was closely related to the degree of oxidation. Thus, the tocopherols, a group of lipid concomitants, were an important indicator of oxidation reactions (Zajdenwerg, Branco, Alamed, Decker, & Castro, 2011; Nogueira et al., 2019).

3.6. Correlation analysis

The correlation heatmaps of color and oxidation parameters of FROs during the light/dark storage are shown in Fig. 4(a).

As shown in Fig. 4(a), the chlorophyll and carotenoid contents of the FROs had a significantly high negative correlation with the L* value and a positive correlation with the a* and b* values. The contents of α-tocopherol and γ-tocopherol showed significantly high and relatively lower negative correlation, respectively, with those of 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E,E)-2,4-heptadienal, and (E)-2-decenal. This further verified the involvement of tocopherols in the oxidation of FROs.

The L* value had a significantly positive correlation with PV and δ-tocopherol content but was negatively correlated with γ-tocopherol content. PV was highly and negatively correlated with the a* value, b* value, chlorophyll and carotenoid contents, and had a low positive correlation with the ΔE value. The a* and b* values also exhibited a significant correlation with the contents of γ-tocopherol and δ-tocopherol. The positive correlation between p-AnV and AV was high, but these values had a low positive correlation with the a* value. In addition, the ΔE value had an obvious negative correlation with the α-tocopherol content but positively related to a part of the secondary oxidation products, i.e., 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E, E)-2,4-heptadienal, and (E)-2-decenal. Therefore, a remarkable association was found between the color and oxidation parameters of FROs. Furthermore, the primary oxidation products were still in the accumulation stage when

ΔE was less than 2~3, indicating the good quality of oil samples. The secondary oxidation products were significantly formed when ΔE exceeded 2~3, and the freshness and oxidation stability of oil samples were decreased. Therefore, ΔE may be a potential objective indicator to determine the quality of FROs.

3.7. PCA of color difference

The degree of ΔE of FROs was divided into different grades (a, ΔE<3; b, 3≤ΔE≤5; c, ΔE>5) according to the variation in color perception. The PV, p-AnV, AV, volatile aldehydes, and tocopherol contents of the oil samples stored in the light/dark for 0, 10, 20, 30, 40, and 50 days, were subjected to PCA for ΔE values. The results are shown in Fig. 4(b-c).

The variance contribution rates of PC1, PC2, and PC3 were 47.11%, 20.99%, and 8.23%, respectively, accumulatively reaching 76.33%. Thus, these rates could be evaluation factors for a fuzzy comprehensive assessment. As shown in Fig. 4(b), α-tocopherol, 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E,E)-2,4-heptadiene, and (E)-2-decenal possessed high matrices in PC1. Thus, PC1 mainly reflected the information of these parameters. PV, AV, p-AnV, γ-tocopherol content, and δ-tocopherol content exhibited relatively higher matrices in PC2, indicating that PC2 represented the information of these indicators to a large extent. PC3 reflected the main information of hexanal content.

As shown in Fig. 4(c), PC1 had an obvious distinguishing effect on the color difference of FROs. Thus, α-tocopherol and some secondary oxidation products, such as 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E,E)-2,4-heptadienal, and (E)-2-decenal, had a close association with the ΔE values. Furthermore, the α-tocopherol contents were negatively correlated with the ΔE values (the correlation coefficient of -0.73). And the secondary oxidation products were positively correlated with ΔE values (the correlation coefficients between 0.6 and 0.94). These findings were identical to the results in Fig. 4(a). The lower correlation (the correlation coefficient of 0. 37) between PV and ΔE showed no close relationship between changes in the content of primary oxidation products and the color difference of the FROs. Specifically, since the oxidation reaction was a dynamic equilibrium process, primary oxidation products were decomposed into secondary oxidation products. That would mean that the PV of FROs increased first and then decreased, while secondary oxidation products increased gradually. Meanwhile, the color parameters of oil samples generally exhibited a monotonous variation trend over time. As a result, some secondary oxidation products were more closely related to color change than PV. In addition, PC2 combined with PC3 exhibited a good classification effect on the brands of FROs. Hence, PV, AV, p-AnV, hexanal, γ- tocopherol content, and δ-tocopherol content were more significantly affected by the intrinsic properties (e.g., rapeseed variety and processing method) of the FROs.

The FROs of a-class, in which no perceptible color difference was observed, presented high similarity and good gathering effect. Oil samples of the same brand were reasonably close, while the discrimination of the FRO color was not obviously affected. For the FROs of c-class with the color difference that could be clearly perceived, the BQ and JLY oil samples could be distinguished well. The hardly qualified distinguishing effect of the LT oil sample may be due to its lower degree of oxidation (as indicated by p-AnV and volatile components) during storage under the influence of rapeseed and processing conditions.

4. Conclusion

In the present study, variations in the color characteristics, oxidative properties of FROs, and the connection between them were investigated. Illumination was the main factor that caused the color change of oils, which accelerated the degradation of chlorophylls. This phenomenon resulted in the significantly increasing L* values in the colorimetric analysis. The photodegradation rate constants of chlorophylls were substantially greater than those of carotenoids. During a 50-day storage in the dark, the contents of the two pigments in the FROs almost did not change, and the ΔE values were always less than 3, thus, no obvious color change was observed with the naked eye. In addition, the ΔE value of the FROs had a marked positive correlation with 2-butenal, octane, (Z)-2-octene, 2,4-octadiene, (Z)-2-heptenal, (E, E)-2,4-heptadienal, and (E)-2-decenal. In addition, this parameter had a significantly negative correlation with α-tocopherol content. The PC1, which mainly integrated important features of these oxidation-related parameters, presented a conspicuous discrimination result of the color difference of the FROs. Therefore, the visible change in FRO colors on the shelf indicated that the corresponding quality would be significantly reduced. The results may serve as the basis of successive research in the protection of the color stability of FROs.

Declaration of interests

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.

Acknowledgements

This work was supported by the Key Research and Development Projects of Shaanxi Province [2023-YBNY-161]; National Natural Science Foundation of China [32072260]; and Shaanxi Province Agricultural Collaborative Innovation and Promotion Alliance Major Science and Technology Project [LMZD202005].

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635 Table caption:

636 Table 1. Rate constants (k) and determination coefficients (R^2) estimated for the kinetic mechanism
637 of the photo-decoloration of the chlorophylls and carotenoids in the fragrant rapeseed oils.

638 Table 2. Peroxide value, acid value and anisidine value of FROs during 50-day storage in the
639 light/dark.

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644 Table 1. Rate constants (k) and determination coefficients (R^2) estimated for the kinetic
645 mechanism of the photo-decoloration of the chlorophylls and carotenoids in the fragrant rapeseed
646 oils[a]

	Samples	k/d^{-1}	R^2
Chlorophyll	BQ	0.036±0.002[a]	0.96
	JLY	0.030±0.004[a]	0.84
	LH	0.036±0.004[a]	0.89
Carotenoid	BQ	0.0029±0.0001[b]	0.98
	JLY	0.0035±0.0001[a]	0.94
	LH	0.0024±0.0001[c]	0.96

647 [a] For each pigment fraction, different letters in the same column indicate significant differences
648 ($p<0.05$).

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656 Table 2. Peroxide value, acid value and anisidine value of FROs during 50-day storage

657 in the light/dark[a]

	Storage time /d	PV/meq·kg^{-1}		AV/mg·g^{-1}		p-AnV/-	
		Light	Dark	Light	Dark	Light	Dark
BQ	0	5.02±0.03^{d}	5.02±0.03^{e}	0.375±0.015^{a}	0.375±0.015^{a}	5.03±0.07^{e}	5.03±0.07^{a}
	10	8.82±0.11^{a}	5.12±0.01^{d}	0.370±0.014^{a}	0.385±0.007^{a}	5.78±0.04^{d}	4.98±0.12^{a}
	20	8.05±0.13^{b}	4.92±0.20^{de}	0.405±0.021^{a}	0.395±.013^{a}	6.00±0.05^{c}	5.28±0.06^{a}
	30	8.16±0.11^{b}	5.73±0.01^{c}	0.405±0.007^{a}	0.400±0.016^{a}	6.91±0.07^{b}	5.27±0.19^{a}
	40	7.66±0.14^{c}	8.15±0.13^{b}	0.380±0.005^{a}	0.395±0.008^{a}	7.02±0.11^{b}	5.40±0.09^{a}
	50	7.73±0.07^{c}	9.41±0.07^{a}	0.400±0.014^{a}	0.385±0.019^{a}	7.34±0.15^{a}	5.60±0.17^{a}
JLY	0	1.32±0.03^{d}	1.32±0.03^{c}	0.400±0.019^{b}	0.400±0.015^{a}	6.58±0.37^{c}	6.58±0.37^{a}

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	10	5.01±0.04[a]	1.33±0.04[c]	0.395±0.007[b]	0.410±0.014[a]	7.07±0.24[b]	6.85±0.27[a]
	20	4.13±0.10[c]	0.74±0.03[d]	0.405±0.10[b]	0.412±0.018[a]	7.45±0.47[b]	6.86±0.16[a]
	30	4.38±0.03[b]	1.51±0.16[c]	0.395±0.011[b]	0.414±0.009[a]	7.79±0.15[b]	6.75±0.13[a]
	40	4.18±0.08[c]	2.27±0.09[b]	0.430±0.008[a]	0.415±0.002[a]	7.90±0.06[b]	6.61±0.25[a]
	50	4.19±0.04[c]	2.85±0.10[a]	0.440±0.015[a]	0.415±0.007[a]	8.40±0.13[a]	6.77±0.10[a]
L H	0	3.56±0.03[e]	3.56±0.03[f]	0.320±0.014[b]	0.320±0.014[b]	4.62±0.16[b]	4.62±0.16[a]
	10	6.98±0.11[a]	3.82±0.02[e]	0.325±0.009[b]	0.343±0.008[a]	4.60±0.14[b]	4.30±0.12[b]
	20	6.08±0.20[d]	4.03±0.04[d]	0.355±0.005[a]	0.371±0.005[a]	4.83±0.08[a]	4.29±0.09[b]
	30	6.40±0.06[c]	5.90±0.14[c]	0.365±0.012[a]	0.352±0.013[a]	5.42±0.35[a]	4.83±0.20[a]
	40	6.61±0.01[b]	8.10±0.03[a]	0.370±0.011[a]	0.362±0.009[a]	4.89±0.14[a]	4.75±0.13[a]
	50	6.93±0.13[a]	7.89±0.04[b]	0.365±0.006[a]	0.370±0.007[a]	5.00±0.16[a]	4.70±0.08[a]

658 [a]Statistical differences ($p < 0.05$) among values in the same column are indicated by different letters.

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662 Figure caption:

663 Fig. 1. Chromaticity values (Light: a, Bangqi [BQ]; c, Jinlongyu [JLY]; e, Luhua [LH]; Darkness:
664 b, BQ; d, JLY; f, LH) and color differences (g, BQ; h, JLY; i, LH) of the fragrant rapeseed oils
665 (FROs) during 50 days of storage.

666 Fig. 2. Transmittance spectra of the FROs during the 50-day storage in the light (a, BQ; c, JLY; e,
667 LH) and darkness (b, BQ; d, JLY; f, LH).

668 Fig. 3. Chlorophyll (Chl) and carotenoid (Caro) contents in the FRO during 50-day storage in the
669 light and darkness (a, BQ; b, JLY; c, LH).

670 Fig. 4. Correlation heatmap and principal component analysis (a, $\Delta E<3$; b, $3\leq\Delta E\leq5$; c, $\Delta E>5$) of
671 observation indicators for FROs stored in the light/darkness for 0, 10, 20, 30, 40, and 50 days.

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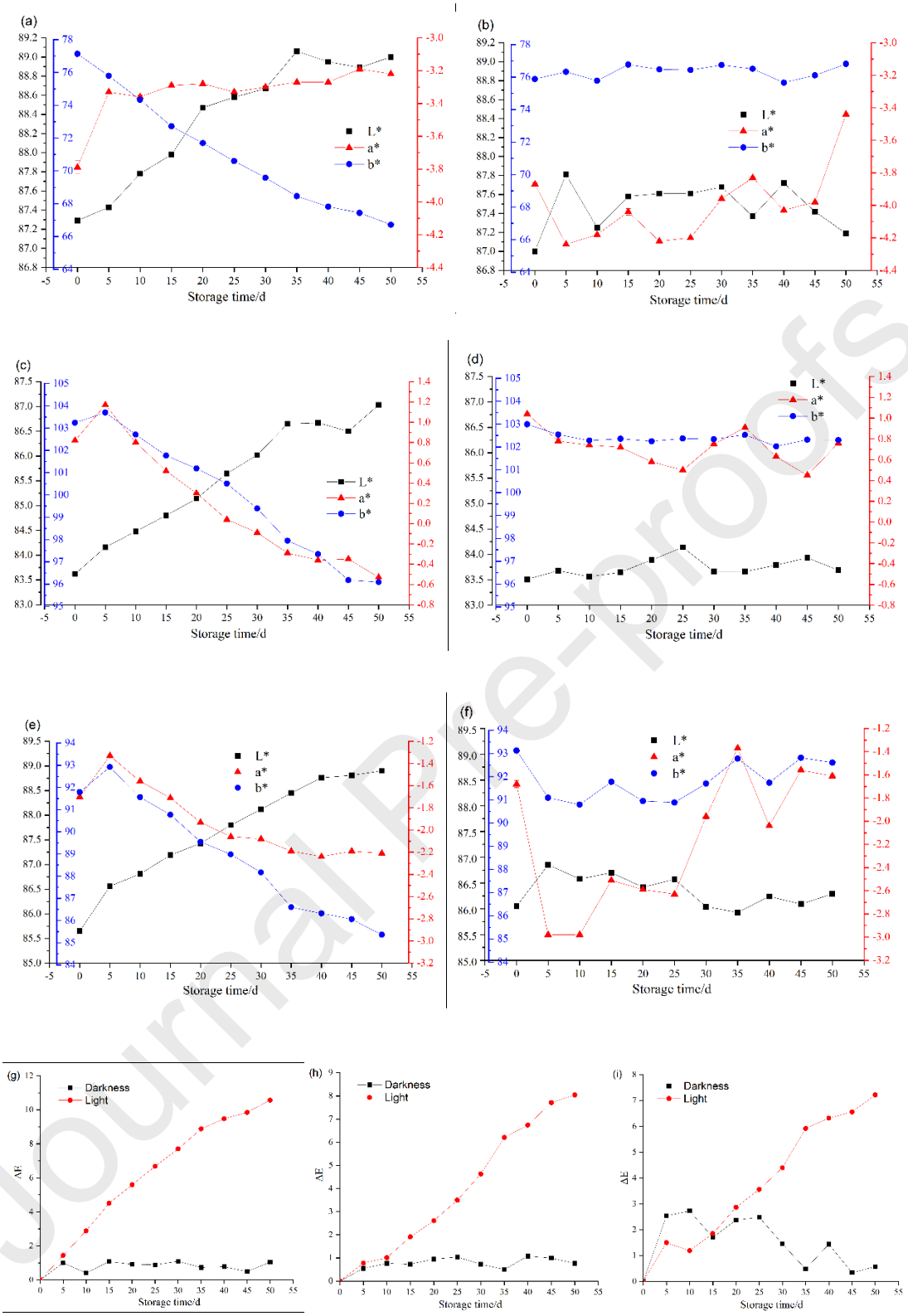

Fig. 1. Chromaticity values (Light: a, Bangqi [BQ]; c, Jinlongyu [JLY]; e, Luhua [LH]; Darkness: b, BQ; d, JLY; f, LH) and color differences (g, BQ; h, JLY; i, LH) of the fragrant rapeseed oils (FROs) during 50 days of storage

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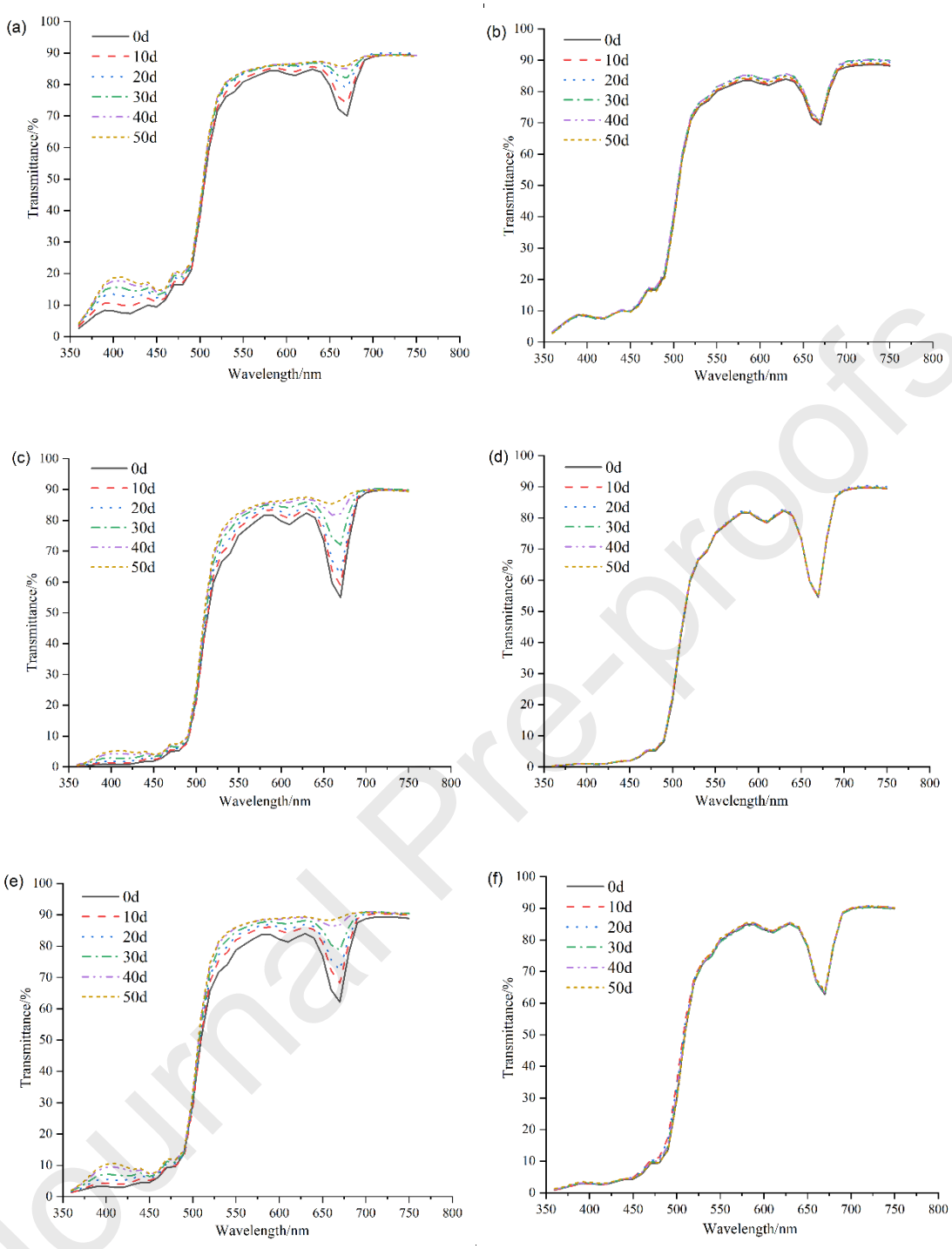

Fig. 2. Transmittance spectra of the FROs during the 50-day storage in the light (a, BQ; c, JLY; e, LH) and darkness (b, BQ; d, JLY; f, LH)

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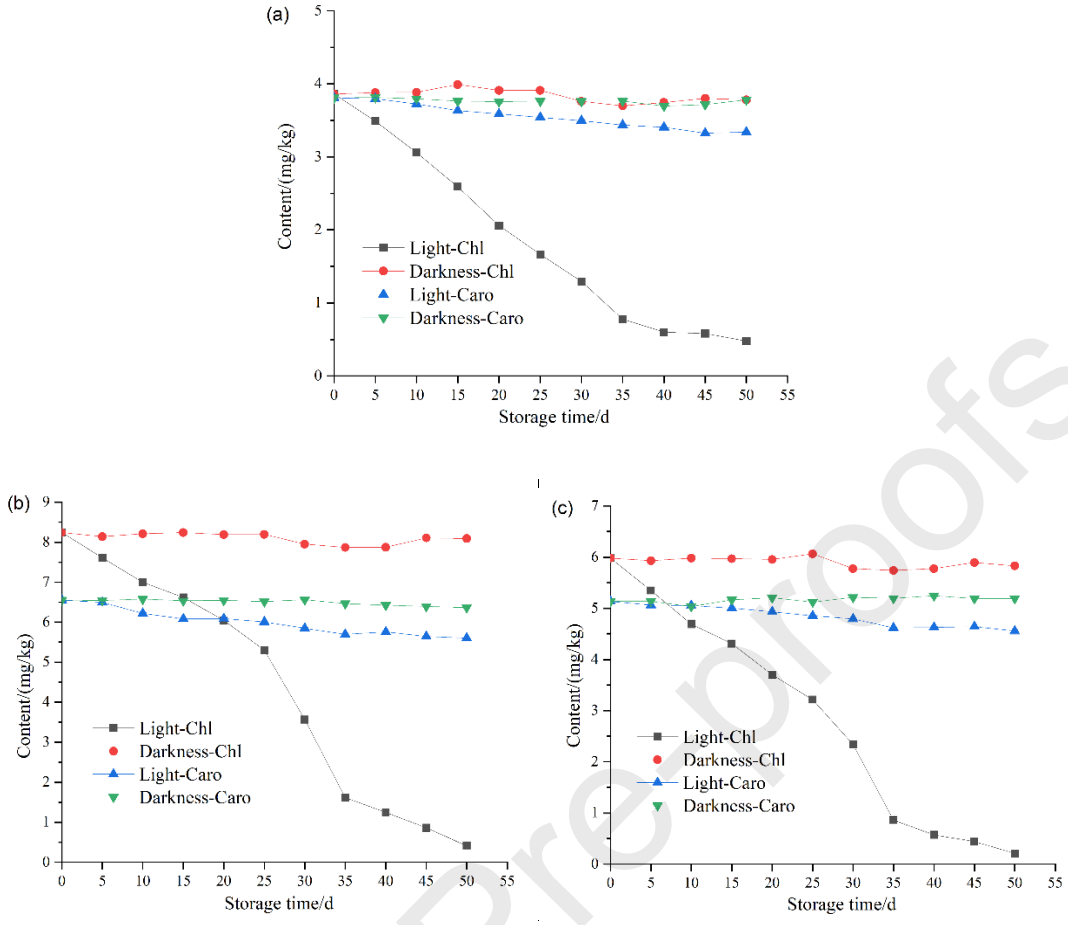

688

689 Fig. 3. Chlorophyll (Chl) and carotenoid (Caro) contents in the FRO during 50-day storage in the
690 light and darkness (a, BQ; b, JLY; c, LH)

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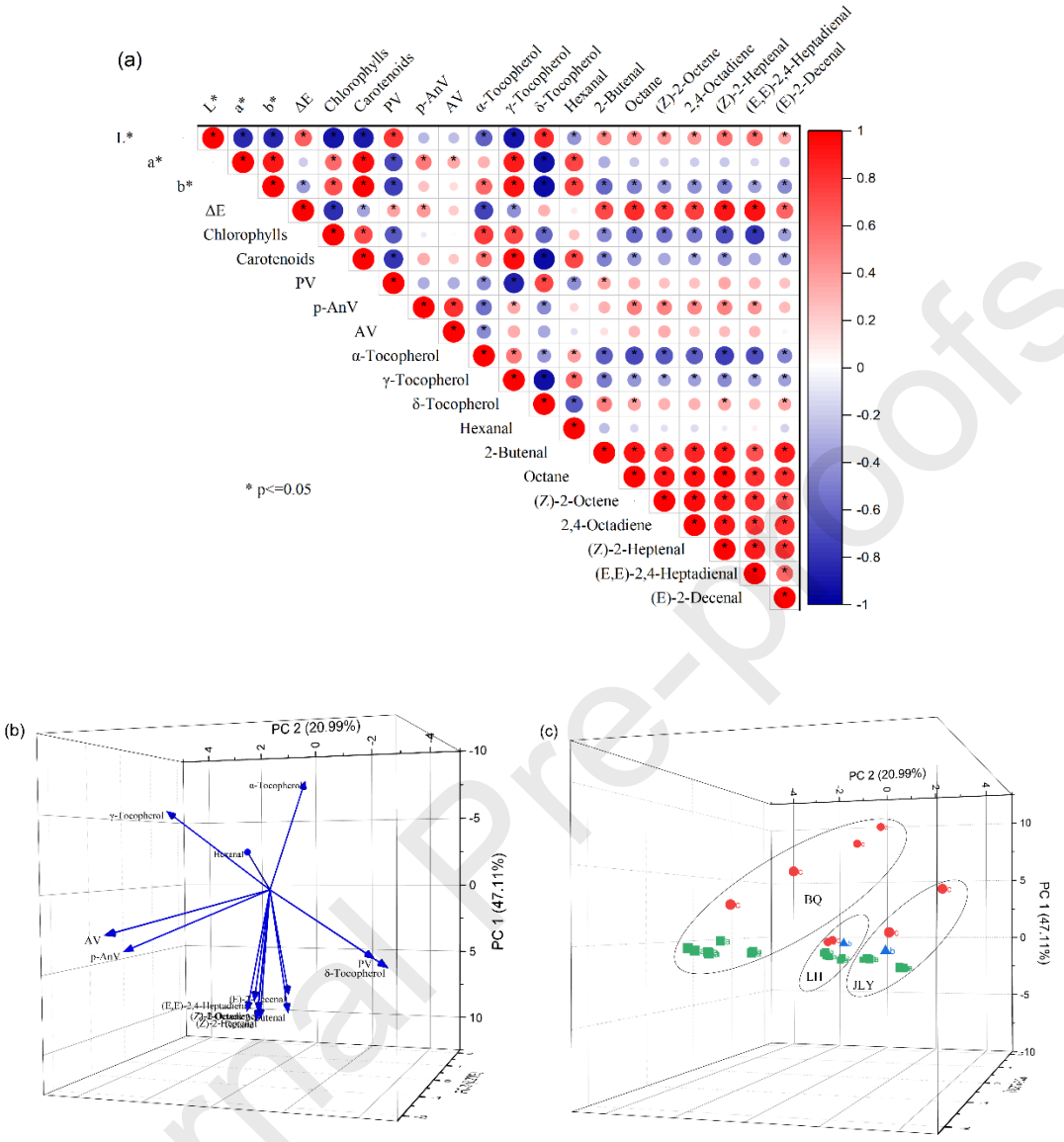

Fig. 4. Correlation heatmap and principal component analysis (a, ΔE<3; b, 3≤ΔE≤5; c, ΔE>5) of observation indicators for FROs stored in the light/darkness for 0, 10, 20, 30, 40, and 50 days

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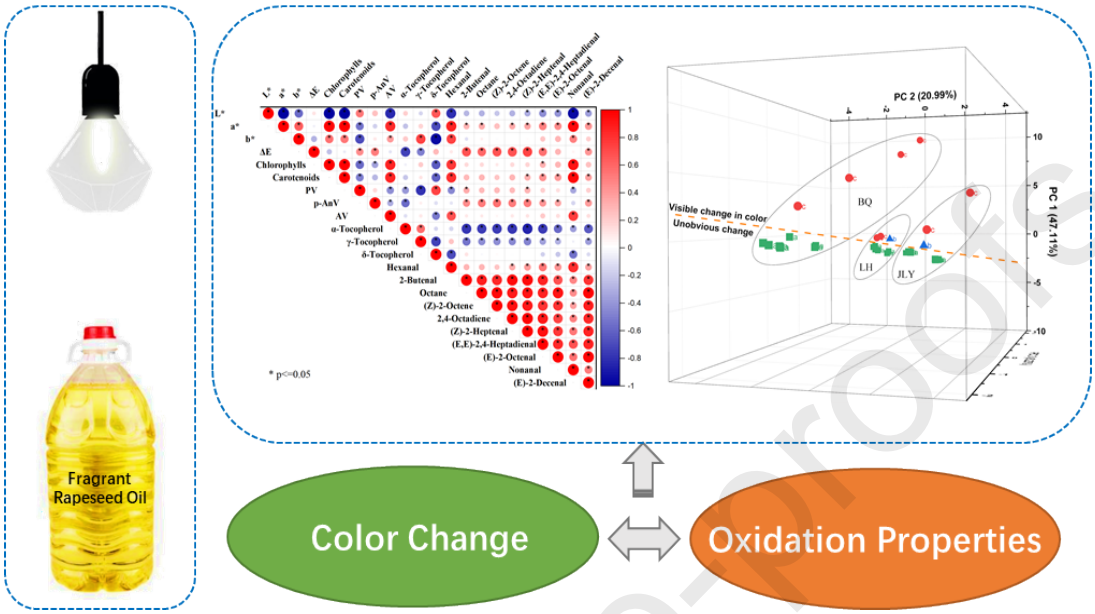
Graphical abstract



Highlights

1. Connection between color variation and oxidative properties of FRO were investigated.

2. The degradation rate of chlorophyll was considerably larger than that of carotenoid.

3. The ΔE value had a significantly negative correlation with α-tocopherol content.

4. Some secondary oxidation products were more closely related with color change than PV.

Credit authorship contribution statement

Qi Li: Conceptualization, Methodology, Writing-Original draft preparation. **Mengmeng Wang**: Data curation, Investigation, Software. **María Belén**

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716 **Fernández**: Writing-Reviewing and Editing. **Altayuly Sagymbek**: Writing-
717 Reviewing and Editing. **Yaoyao Dong**: Software, Validation. **Yuan Gao**:
718 Visualization, Formal analysis. **Xiuzhu Yu**: Conceptualization, Writing-Reviewing
719 and Editing, Supervision.

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