Title: **Oxidation Derived Flavor Compounds as Quality Indicators for Packaged Olive Oil**

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Running title: Flavors in packaged olive oil as markers of the oxidation.

Key words: auto-oxidation, flavour compounds, olive oil, packaging, oil quality, oxidation model, photo-oxidation, storage conditions.

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ABSTRACT: Aroma compounds in packaged extra virgin olive oil can be present naturally or be derived through oxidative degradation under favorable temperature, light, and oxygen availability conditions. In this study, the identity and quantity of flavor compounds were determined for extra virgin olive oil packaged in 0.5 L glass, PET, and PVC bottles and stored at 15^{o}C, 30^{o}C and 40^{o}C under fluorescent light or dark conditions for one year. A set of mathematical equations concerning the rates of the most fundamental oxidation reaction~~s~~ in the oil was prepared and numerically solved and the reaction constants were estimated for specific temperature values.

Mainly the presence of fluorescent light, followed by the elevated temperature, stimulated the oxidative alterations in olive oil. Separated and identified flavor compounds were recorded for all the olive oil samples. Based on their abundance and evolution in the oil samples, the most clearly describing the oxidation were: hexanal, nonanal, (E)-2-decenal, (E)-2-heptenal, 2-pentyl furan. It was assumed that these compounds might be used as markers of the oxidation process to quantitatively monitor and describe the quality of packaged olive oil.

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The availability of oxygen, elevated temperatures of storage, and action of light can create the conditions for some decomposition of olive oil's triglycerides. The initially-formed mono-hydroperoxides decompose following various pathways, producing off-flavors and unpleasant odors, thus diminishing the quality of the olive oil (1- 4). Oil quality changes related to the production of oxidized by-products that alter the sensory and nutritional characteristics of the oil include increased acidity, production of carbonyl compounds, and a decrease of the α-tocopherol concentration, and generation of off-flavor compounds (5). Volatile aldehydes are considered to be the most responsible for the off-flavor note of the oxidized oils due to their low threshold odor levels (6). The major aldehydes can be summarized as: 2-undecanal, decanal, 2-decenal, nonanal and octanal deriving from oleic acid; 2,4-decadienal, hexanal and 2-heptenal from linoleic acid; 2,4-heptadienal, 3-hexenal, 3-hexanal and propanal from linolenic acid; and 2,4-decadienal, 3-nonenal and hexanal, from arachidonic acid. Their presence depends on the relative amount of fatty acids on the triacyloglycerol molecules in each oil.

When vegetable oils are commercially stored under light, their natural photo-sensitizers (e.g. chlorophyll) can stimulate photo-oxidative deterioration (7). Free radicals may be formed when these sensitizers react directly with the substrate (pathway I - photolytic auto-oxidation) or with triplet oxygen to form singlet oxygen and singlet sensitizer, i.e. both compounds at a higher energy level (pathway II - photosensitized oxidation). The direction the reaction will proceed is based on the competition between triplet oxygen and substrate or photo-sensitizers when light is present. Electron rich compounds favor the type II pathway; the rate depends on the solubility of the oxygen present in the food system. Conjugated and non-conjugated hydroperoxides produced can cleave to initiate conventional free radical chain reactions that produce undesirable flavor compounds. Thus, protection from direct light is required for commercial olive oil (7-10).

The nature of the packaging material has a notable influence on the quality (11). Oil in bottles with high air permeability (polyethylene-PE, polypropylene-PP) should be sold within four weeks, in contrast to PVC bottles that could hold olive oil for three months without appreciable quality loss. Significant changes have been observed in the oil quality stored in transparent glass bottles and exposed to light (12), while oil samples in polyethylene bottles contained a higher amount of hydroperoxides than those in glass bottles. The peroxide concentration of oil in glass bottles in the dark was lower than oil stored in plastic bottles also in the dark; in any case samples stored in light showed higher peroxide concentration that those in the dark (13). Olive oil stored in polyethylene bottles and exposed to diffused light for three months developed an off-taste and lost most of its original color (14). Samples stored in glass or poly(vinyl chloride)-PVC bottles, under light, experienced greater changes in sensory characteristics than those stored in darkness (10).

Plastics offer limited protection against oxygen and chemical migration compared to steel and glass. PVC is a popular packaging material for edible oils in many countries, mainly due to its adaptability to all types of closure, transparency, total compatibility with existing packaging lines, and potential for personalized design features (15). Driven by issues like the protection of the environment, ample supply, plastic shaping, and mechanical properties, poly(ethylene terephthalate)-PET has been supplanting PVC in the edible oil market.

Despite the volume of experimental evidence on the oxidation of packaged olive oil, only rather limited modeling information can be found in the literature. Dekker et al. (16) calculated the level of primary oxidation products and oxygen concentration in the headspace of the package during storage at various temperature conditions, with varying packaging. Their model was based on the reaction kinetics of the food and the active ingredients, the film permeability, and the mass transfer rate within the product. Using the modeling approach, a good estimation of the product quality could be achieved prior to any actual shelf life experiments.

The main objective of this work was to describe the oxidative deterioration of extra virgin olive oil when it is packaged in glass and plastic containers and stored in light or in the dark, using the alteration of the volatile compound profile over time. A group of flavor compounds was selected as indicators of the quality of the olive oil. A simple model based on the evolution of hexanal inside the oil was also applied to estimate the reaction constants under various storage conditions of light and temperature.

EXPERIMENTAL PROCEDURES

Portuguese organic extra virgin olive oil was packed under nitrogen gas, without headspace, in cleaned and dried 500 mL PET drinking water bottles, in 500 mL PVC bottles (Novapack, Co. Paris, IL, USA), and in 500 mL glass bottles (Fisher Scientific Co. New Jersey, USA). The oxygen transmission rates for PET and PVC were to be approximately 8 cc/m^2/day and 9.8 cc/m^2/day at 0.21 atm driving force, respectively. Both materials seem to be effective barriers to wavelengths shorter than 340 nm while visible light was almost equally highly transmitted through either PET or PVC materials. The percentage of light transmitted (% T) through PET and PVC increased as λ increased with the most marked changes occurring between 300 and 350 nm. The average thickness for PET bottles was 400 μm and for PVC bottles 640 μm (17). Bottles were sealed tightly with standard polypropylene threaded caps. Half of the bottles were covered with aluminum foil and placed inside fiberboard boxes and the other half were exposed to fluorescent light. Filled bottles were stored in controlled environment chambers at 15, 30 or 40^{o}C and 60% RH. During the experiment, four 40 W fluorescent light bulbs were placed at 30 cm above the bottles. Weekly rearrangement of the bottles was applied to ensure uniform exposure to light. Two bottles per treatment were analyzed in triplicate monthly up to 12 months. Values of peroxide concentration, namely peroxide value (PV), were collected according to IUPAC Method 2-501. The concentration of the conjugated dienes deriving during oxidation, were recorded as K_{232} values as they were obtained from 0.02 g of oil diluted in 10 mL iso-octane (Merck, Darmstard, Germany) and analyzed at 232 nm using a Perkin Elmer Lambda 25 UV-VIS spectrophotometer. Data was recorded by the UV-WIN-Lab software the K_{232} values were calculated from absorbency readings. An automatically operating stripping apparatus (Dynatherm 1000, Dynatherm Analytical Instruments Inc., Kelton, PA) was used to strip volatile compounds out of the oil, kept at 37ºC, into a Tenax-TA trap (Supelco, Bellefonte, PA). Compounds were desorbed using a desorption unit (Model 890 from Dynatherm Analytical Instruments Inc. Kelton, PA) connected to a gas chromatography apparatus (Hewlett Packard 5890 Series II, Hewlett Packard, Philadelphia, PA) with a 30 m x 0.32 mm ID x 0.25μm film thickness, fused silica capillary column (SPB-5, Supelco, Bellefonte, PA). The temperature program was: initial temperature, 35°C for 5min, increased to 80°C at a rate of 3°C/min, held for 1 min, then increased to 180°C at 10°C/min, held for 1 min, and finally increased to 220°C at 4°C/min where it was held for 10 min. The carrier gas was maintained at a flow rate of 1.75 mL/min at 40°C. Identification of compounds was performed with a Varian 2000 mass spectrometer (Varian, TX, USA) interfaced with the Dynatherm desorption unit. The tuning value for the ITMS was 100, using cedrol as the tuning standard. Other parameters were: tune sensitivity, 9000; acquisition parameters: full scan, scan range: 41-300 amu, scan time: 1.0 sec, threshold: 1 count, multiplier from 1500 to 2300 V depending on multiplier conditions; transfer line temperature, 240ºC; exit nozzle 240ºC; manifold 240ºC. In addition, the following standard compounds were injected in the GC to be analyzed for their retention times: pentane, 1-hexene, ethyl acetate, 1-penten-3-ol, 2-propanol, 1-pente-3-one, n-pentanal, 2-pentanol, heptane, 2-methyl-1-butanol, 1-propanol, 2-butanone, ethyl-iso-butyrate, pentanol, (E)-2-hexenal, (Z)-3-hexenol, heptanal, 6-methyl-5-hpten-2-one, octanal, 3-hexenyl acetate, (Z)-3-nonen-1-ol, 2-nonanone, nonanal, 2-phenyl-ethyl alcohol, (E)-2,4-decadienal, dodecane, (E)-2-nonenal, (E,E)-2,4-decadienal, and undecanal.

Statistical analysis of volatile aroma compounds was performed using commercial software (SAS^{TM} Proprietary Software Release 8.2, TS2M0, SAS Institute Inc., Cary, NC, USA) to determine differences between treatments for the rate of evolution for each flavor compound. GLM analysis was applied and the Tukey and Duncan tests were implemented for separating the means of GC area changes among the compounds with confidence level $\alpha = 0.05$.

To further explain the mechanisms of the chemical phenomena, a representative model for the evolution of off-flavor compounds in the packaged oil, based on the main chemical reactions related to the oxidative degradation inside the oil phase, was also applied. It can be summarized as follows:

$$O_2 \xrightarrow[hv]{k_a} O_3^- \tag{1a}$$

$$RH + O_3^- \xrightarrow{k_b} ROOH \tag{1b}$$

$$RH + O_2 \xrightarrow{k_c} ROOH \tag{2}$$

with RH being any fatty acid serving as the oxidation substrate, ROOH the derived hydroperoxide, and k_a, k_b and k_c the reaction constants influenced only by temperature. The simultaneously occurring reactions (1a) and (1b) take place only in the presence of light. By assuming pseudo-steady state for the intermediate product (18), namely the O_3^-, the concentration of the ROOH increases according to the following relationship:

$$\frac{dC_{ROOH}(t)}{dt} = k_a(T)C_{O_2}(t) + k_c(T)C_{RH}(t)C_{O_2}(t) \tag{3}$$

By assuming that the time variation of the amount of ROOH in olive oil packaged in glass and stored in darkness is a negligible background noise, the above rate can be described for a standard storage temperature, T_1, and for different packaging materials (glass, PET, PVC) and storage conditions (light, darkness) using the following set of equations, each one referring to a specific set of experimental conditions:

PET, dark:

$$\frac{dC_{ROOH,PET,d}(t)}{dt} = k_c(T_1)C_{RH,PET,d}(t)C_{O_2,PET,d}(t) \tag{4a}$$

PVC, dark:

$$\frac{dC_{ROOH,PVC,d}(t)}{dt} = k_c(T_1)C_{RH,PVC,d}(t)C_{O_2,PVC,d}(t) \tag{4b}$$

glass, light:

$$\frac{dC_{ROOH,G,l}(t)}{dt} = k_a(T_1)C_{O_2,G,l}(t) + k_c(T_1)C_{RH,G,l}(t)C_{O_2,G,l}(t) \tag{4c}$$

PET, light:

$$\frac{dC_{ROOH,PET,l}(t)}{dt} = k_a(T_1)\left[C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)\right] + k_c(T_1)\left[C_{RH,PET,d}(t)+C_{RH,G,l}(t)\right]\left[C_{O_2,PET,d}(t)+C_{O_2,G,l}(t)\right] \tag{4d}$$

PVC, light:

$$\frac{dC_{ROOH,PVC,l}(t)}{dt} = k_a(T_1)\left[C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)\right] + k_c(T_1)\left[C_{RH,PVC,d}(t)+C_{RH,G,l}(t)\right]\left[C_{O_2,PVC,d}(t)+C_{O_2,G,l}(t)\right] \tag{4e}$$

where $C_{X,Y,Z}(t)$ denotes the concentration of substance X (O_2 and RH) stored in the material Y (glass, PET and PVC) at Z luminosity conditions (dark and light).

In order to evaluate the influence of the temperature on the reaction constants k_a and k_c, we can apply the above set of equations to a new temperature. Because of the change in the physicochemical properties of the packaging materials at elevated temperatures, the new temperature T_2 should be close enough to the temperature T_1 to avoid major changes. The new set of equations becomes:

PET, dark: $$\frac{dC_{ROOH,PET,d}(t)}{dt} = k_c(T_2)C_{RH,PET,d}(t)C_{O_2,PET,d}(t) \quad (5a)$$

PVC, dark: $$\frac{dC_{ROOH,PVC,d}(t)}{dt} = k_c(T_2)C_{RH,PVC,d}(t)C_{O_2,PVC,d}(t) \quad (5b)$$

glass, light: $$\frac{dC_{ROOH,G,l}(t)}{dt} = k_a(T_2)C_{O_2,G,l}(t) + k_c(T_2)C_{RH,G,d}(t)C_{O_2,G,d}(t) \quad (5c)$$

PET, light: $$\frac{dC_{ROOH,PET,l}(t)}{dt} = k_a(T_2)\left[C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)\right] + k_c(T_2)\left[C_{RH,PET,d}(t)+C_{RH,G,l}(t)\right]\left[C_{O_2,PET,d}(t)+C_{O_2,G,l}(t)\right] \quad (5d)$$

PVC, light: $$\frac{dC_{ROOH,PVC,l}(t)}{dt} = k_a(T_2)\left[C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)\right] + k_c(T_2)\left[C_{RH,PVC,d}(t)+C_{RH,G,l}(t)\right]\left[C_{O_2,PVC,d}(t)+C_{O_2,G,l}(t)\right] \quad (5e)$$

The overall set of the above 10 differential equations (4a-e, 5a-e) was numerically solved using a modified numerical algorithm that involves a typical Newton method for non-linear systems in conjunction with a 4th order Runge-Kutta method for the ordinary differential equations (19). The concentrations $C_{O2,PET,d}$(t), $C_{O2,PVC,d}$(t), $C_{RH,PVC,d}$(t), $C_{RH,PET,d}$(t), $C_{O2,G,l}$(t), $C_{RH,G,l}$(t), as well as the reaction rate~~s~~ values $k_a(T_1)$, $k_a(T_2)$, $k_c(T_1)$ and $k_c(T_2)$, were calculated.

RESULTS AND DISCUSSION

Since only conjugated dienes are formed in free radical auto-oxidation while non-conjugated dienes, such as linoleic acid, can be found in photo-oxidation (7), the K_{232} values should represent only part of the dienes (the conjugated ones) formed from the substrate. Thus, a relatively higher ratio of PV/K_{232} for oil stored in light and subjected to photo-oxidation should be expected compared to that stored in the dark (free radical auto-oxidation only). The ratio of PV/K_{232} values for every treatment versus storage time showed that olive oil in PET containers, in light, had lower values of PV/K_{232} compared to olive oil stored in glass in light, most probably indicating the protective role of PET in olive oil oxidation, as also concluded by Kaya et al. (20). For olive oil in glass containers in light, the PV/K_{232} ratio increased sharply after 6 months when stored at 40 and 30^{o}C, but not at 15^{o}C. For most of the storage period, PV/K_{232} values for olive oil stored in light in PVC bottles showed slightly higher values than oil stored in PET and much higher than oil stored in glass, (Figures 1). Volatile compounds, roughly appearing at the reported corresponding retention times (average of 6 replicates), were identified as shown in Table 1.

The increases in the amounts of various flavor volatile compounds over time for every treatment were statistically analyzed using the SAS^{TM} program. Compounds with insignificant differences in their evolution over time were grouped together using the Duncan test (different letters indicate significant differences among the mean GC area values, $\alpha<0.05$, between the aforementioned compounds during time).

The compounds most influenced by the storage conditions were: hexanal, (E)-2-octenol, (Z)-2-nonenol, (E,E)-2,4-heptadienal, 1-heptanone, 2,4-hexadienal, hexanoic acid, 3-hexyl acetate, (E)-2-heptenal, (Z)-2-hexenol, 2-pentyl furan, octanal, pentanal, heptanal, and (Z)-1,5-octadien-3-one. Statistical analysis of the evolution and relative amounts of hexanal, nonanal, (E)-2-decenal, (E)-2-heptenal, 2-pentyl furan in olive oil, recognized that these compounds may be used as indicators to distinguish among samples stored under dark or light conditions, in oxygen permeable or impermeable materials, or at elevated temperatures.

Olive oil stored in PET at 40^{o}C contained the highest amounts of hexanal, followed by the oil stored in glass at 40^{o}C, while the oil stored in PVC containers had a lower hexanal content at 12 months (Figure 2). Oil stored in the same bottles but at lower temperatures under light had lower amounts of hexanal. Statistical analysis showed that hexanal content in olive oil in glass containers kept at 15^{o}C was not significantly different from that in oil kept in PVC at the same temperature after 12 months of storage (P=0.08), while at 30^{o}C and at 40^{o}C the differences were highly significant (P=0.001315 and P=5.28x10^{-16}, respectively). Hexanal content in oil in glass at 15^{o}C was significantly different from that in oil in glass at 30^{o}C (P= 0.04027) at 40^{o}C (P= 3.02x10^{-34}). The same was the case for hexenal content in oil in PET (15^{o}C and 30^{o}C, P= 4.16x10^{-07}~~,~~ 15^{o}C and 40^{o}C, P= 4.46x10^{-31}; and 30^{o}C and 40^{o}C, P= 3.54x10^{-18}), and in PVC (P= 0.00015, P= 3.54x10^{-16}, and P= 2.33x10^{-07}, respectively). For any temperature, hexanal content in PET was always statistically different from that in oil stored in glass (e.g. glass 15^{o}C and PET 15^{o}C, P=0.00021, glass 30^{o}C and PET at 15^{o}C, P=7.2x10^{-16}). Among oil samples in PET and PVC, the amount of hexanal was significantly different at 15^{o}C (P=0.041921) and 40^{o}C (P= 7.17x10^{-05}), but not at 30^{o}C (P=0.534109). Oil placed in PET, PVC and glass containers and stored in the dark at any temperature-did not contain significantly different amounts of hexanal over time. Since for the samples stored in light, hexanal reached almost twice the value compared to samples stored in the dark, it can be concluded that fluorescent light significantly influences the evolution of hexanal, while the availability of oxygen passing through the plastic containers was less influential, especially at lower temperatures of storage (Figure 2).

The evolution of nonanal was similar for all the oil samples stored in either PET, PVC or glass containers in light at any temperature, and for oil in these containers stored in the dark at any temperature (Figure 3). Statistical treatment of the data showed no significant changes in the production of nonanal for any of the materials as a function of temperature. Also no differences were found between containers at any temperature. Samples stored in the dark were significantly altered after 12 months compared to original oil. The influence in light was significant even after 2 months of storage at 40^{o}C (P=0.000846). The significance increased with time and increasing temperature of storage.

Figure 4 shows that the amounts of (E)-2-decenal present in the oil after 2 months of storage were significantly greater than the amount originally present for all treatments in the dark (P=0.01055); when stored in light, (E)-2-decanal significantly increased after 4 months of storage compared to the amounts originally present in the oil (P=0.001164). It could be that (E)-2-decenal is more influenced by the triplet rather than the singlet form of oxygen present in the oil.

(E)-2-heptenal was more abundant in olive oil stored in PET and PVC in light and 40°C, while the amounts detected were lower for the oil stored in glass containers. For all conditions, the oil stored in the dark had lower amounts of (E)-2-heptenal compared to the oil stored in light (Figure 5). Statistical analysis of the data showed that (E)-2-heptenal was significantly different for oil samples stored in PVC bottles at 40°C after the 6th month of storage compared to oil stored in glass or PET at any temperature. Between the different materials, there was no significant difference in the amount of (E)-2-heptenal at the same time intervals and temperatures. Light had a significant influence even after 2 months. Samples stored in the dark did not differ significantly for any temperature or material. Oil kept in light after 10 and 12 months had a significantly different amount of (E)-2-heptenal compared to oil stored in the dark for any time period up to 12 months.

The formation of 2-pentyl furan is proposed to result from 4-ketononanal, an oxidized linoleic acid 10-OOH derivative. Though not a typical hydroperoxide, 10-OOH can derive from singlet oxidation of linoleic acid. Another possible pathway suggests that it may derive from 9-OOH of linoleic acid in the presence of singlet oxygen combined with a liberation of formaldehyde, while its formation from linolenic acid has also been suggested (2). Due to the demand for singlet oxygen, the presence of 2-pentyl furan should be closely related to photo-oxidation and the available oxygen. Olive oil stored in PVC, PET and glass at 40^{o}C in light indicated that the amounts of 2-pentyl furan were comparable but all were higher than the amounts isolated from oil stored at 15^{o}C at any of the packaging materials. In dark conditions, the oil stored in PVC at 40^{o}C had the highest amount, followed by the oil in PET, while the oil in glass had the lowest amount of 2-pentyl furan, except when stored at 40°C. For any other temperature or light and dark conditions, the amounts of 2-pentyl furan were clearly lower. For the same temperature and material, the amount of 2-pentyl furan was always higher in the oil kept in light compared to the oil kept in the dark (Figure 6). The differences seen in two parts of Figure 6 were not found to be statistically significant. There was no dependence on the material or temperature of storage. Samples stored in the light were significantly different from the original after only 4 months of storage. On the other hand, the amount of 2-pentyl furan in oil samples stored in the dark did not differ significantly over time.

Applying the experimental results for the flavor compound hexanal to the model, the reaction constants $k_a(T)$ and $k_c(T)$ were calculated for the three temperatures. The growth rate of hexanal in packaged olive oil (left-hand-side of eq. 4a-e and 5a-e) was derived from the experimental data for all the combinations of materials and storage conditions and was used as input for the results presented in Figure 7. The growth rate constants clearly increased with temperature. This influence was much less for $k_c(T)$, as the auto-oxidation reactions appeared to be less sensitive to the temperature variance. Additionally, $k_a(T)$ values were 2.5-4 times higher than the $k_c(T)$ values at the same conditions, underlining the significance of light exposure that has already been discussed based on the results of Figures 2-6.

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Table 1. Selected olive oil flavor compounds isolated from olive oil and their Kovats indexes.

Figure 1. Peroxide Value/K_{232} values for olive oil placed in PET, PVC or glass bottles and stored in the light at various temperatures.

Figure 2. Hexanal production in olive oil kept in PET, PVC and glass containers at 15, 30 and 40^{o}C in the light and dark for 12 months.

Figure 3. Nonanal production in olive oil kept in PET, PVC and glass containers at 15, 30 and 40^{o}C in the light or dark for 12 months.

Figure 4. (E)-2-decenal production in olive oil kept in PET, PVC and glass containers at 15, 30 and 40^{o}C in the light or dark for 12 months.

Figure 5. (E)-2-heptenal production in olive oil kept in PET, PVC and glass containers at 15, 30 and 40^{o}C in the light or dark for 12 months.

Figure 6. 2-pentyl furan production in olive oil kept in PET, PVC and glass containers at 15, 30 and 40^{o}C in the light or dark for 12 months.

Figure 7. Plot of the $\ln k_a$ and $\ln k_c$ as a function of 1/T (^{o}K).