

Oxidation-Derived Flavor Compounds as Quality Indicators for Packaged Olive Oil

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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 conditions of temperature, light, and oxygen availability. In this study, the identity and quantity of flavor compounds were determined for extra virgin olive oil packaged in 0.5-L glass, poly(ethylene terephthalate), and poly(vinyl chloride) bottles and stored at 15, 30, and 40°C under fluorescent light or in the dark for 1 yr. A set of mathematical equations concerning the rates of the most fundamental oxidation reactions 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 elevated temperature, stimulated oxidative alterations in the 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, those most clearly describing oxidation were hexanal, nonanal, (*E*)-2-decenal, (*E*)-2-heptenal, and 2-pentyl furan. These compounds could be used as markers of the oxidation process to monitor and describe the quality of packaged olive oil quantitatively.

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KEY WORDS: Auto-oxidation, flavor compounds, oil quality, olive oil, oxidation model, packaging, photo-oxidation, storage conditions.

The availability of oxygen, elevated temperatures of storage, and the action of light can create the conditions for some decomposition of olive oil TAG. The initial monohydroperoxides 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, the production of carbonyl compounds, a decrease of the α -tocopherol concentration, and the 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 follows: 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-nonanal,

and hexanal from arachidonic acid. Their presence depends on the relative amount of FA on the TAG molecules in each oil.

When vegetable oils are stored commercially under light, their natural photosensitizers (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 a 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 the substrate or photosensitizers 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. The conjugated and nonconjugated 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 oil quality (11). Oil in bottles with high air permeability (polyethylene, polypropylene) should be sold within 4 wk, in contrast to poly(vinyl chloride) (PVC) bottles, which can hold olive oil for 3 mon without appreciable quality loss. Significant changes have been observed in the quality of oil stored in transparent glass bottles and exposed to light (12), whereas oil samples in PE 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 that of oil stored in plastic bottles in the dark; in any case, samples stored in light showed higher peroxide concentrations than those in the dark (13). Olive oil stored in polyethylene bottles and exposed to diffused light for 3 mon developed an off-taste and lost most of its original color (14). In contrast, samples stored in glass or PVC bottles under light experienced greater changes in sensory characteristics than those stored in the dark (10).

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

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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 packages during storage at various temperature conditions with varying packaging materials. Their model was based on the reaction kinetics of the food and its active ingredients, the permeability of the film, and the mass transfer rate within the product. Using the modeling approach, a good estimation of 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 or plastic containers and stored in light or in the dark by observing 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), and in 500-mL glass bottles (Fisher Scientific Co., Fairlawn, NJ). The oxygen transmission rates for PET and PVC were to be approximately 8 and 9.8 cc/m²/d, respectively, at 0.21 atm driving force. Both materials seemed to be effective barriers to wavelengths shorter than 340 nm, whereas visible light was highly transmitted almost equally 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 of the PET bottles was 400 μ m, and that of the PVC bottles was 640 μ m (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°C and 60% RH. During the experiment, four 40-W fluorescent light bulbs were placed 30 cm above the bottles. The bottles were rearranged weekly to ensure uniform exposure to light. Two bottles per treatment were analyzed in triplicate monthly for up to 12 mon. Peroxide concentration values, namely, PV, were collected according to IUPAC Method 2-501 (18). The concentrations of the conjugated dienes derived 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, Darmstadt, Germany) and analyzed at 232 nm using a PerkinElmer (Norwalk, CT) Lambda 25 UV-vis spectrophotometer. Data were recorded by UVWin-Lab software (Perkin-Elmer), and K_{232} values were calculated from absorbency readings. An automatic stripping apparatus (Dynatherm 1000; Dynatherm Analytical Instruments Inc., Kelton, PA) was used to strip volatile

compounds out of the oil (kept at 37°C) and into a Tenax-TA trap (Supelco, Bellefonte, PA). Compounds were desorbed using a desorption unit (Model 890; Dynatherm Analytical Instruments Inc., Kelton, PA) connected to a GC apparatus (Hewlett-Packard 5890 Series II; Hewlett-Packard, Philadelphia, PA) with a 30 m \times 0.32 mm i.d. \times 0.25 μ m film-thickness fused-silica capillary column (SPB-5; Supelco). The temperature program was as follows: initial temperature, 35°C for 5 min, 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, Walnut Creek, CA) interfaced with the Dynatherm desorption unit. The tuning value for the ion trap MS was 100, with cedrol as the tuning standard. Other parameters were as follows: tune sensitivity, 9000; acquisition parameters: full scan; scan range, 41–300 amu; scan time, 1.0 s, threshold, 1 count; multiplier from 1500 to 2300 V, depending on multiplier conditions; transfer-line temperature, 240°C; exit nozzle, 240°C; manifold, 240°C. In addition, the following standard compounds were injected into the gas chromatograph to be analyzed for their retention times: pentane, 1-hexene, ethyl acetate, 1-penten-3-ol, 2-propanol, 1-penten-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-hepten-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 (SASTM Proprietary Software, Release 8.2, TS2M0; SAS Institute Inc., Cary, NC) to determine differences between treatments for the rate of evolution for each flavor compound. A general linear model analysis was applied, and the Tukey and Duncan tests were implemented to separate the means of GC area changes among the compounds, with a confidence level of $\alpha = 0.05$.

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 oxidative degradation inside the oil phase, was also applied. This model can be summarized as follows:



with RH being any FA serving as the oxidation substrate, ROOH the derived hydroperoxide, and k_a , k_b , and k_c the reaction constants influenced only by temperature. Simultaneous reactions (Eqs. 1 and 2) take place only in the presence of light.

By assuming a pseudo-steady state for the intermediate product (19), namely, the O_3^- , the concentration of ROOH increases according to the following relationship:

$$\frac{dC_{ROOH}(t)}{dt} = k_a(T)C_{O_2}(t) + k_c(T)C_{RH}(t)C_{O_2}(t) \quad [4]$$

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

$$\text{PET, dark: } \frac{dC_{ROOH,PET,d}(t)}{dt} = k_c(T_1)C_{RH,PET,d}(t)C_{O_2,PET,d}(t) \quad [5]$$

$$\text{PVC, dark: } \frac{dC_{ROOH,PVC,d}(t)}{dt} = k_c(T_1)C_{RH,PVC,d}(t)C_{O_2,PVC,d}(t) \quad [6]$$

$$\text{glass, light: } \frac{dC_{ROOH,G,l}(t)}{dt} = k_a(T_1)C_{O_2,G,l}(t) + k_c(T_1)C_{RH,G,l}(t)C_{O_2,G,l}(t) \quad [7]$$

$$\text{PET, light: } \frac{dC_{ROOH,PET,l}(t)}{dt} = k_a(T_1)[C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)] + k_c(T_1)[C_{RH,PET,d}(t) + C_{RH,G,l}(t)][C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)] \quad [8]$$

$$\text{PVC, light: } \frac{dC_{ROOH,PVC,l}(t)}{dt} = k_a(T_1)[C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)] + k_c(T_1)[C_{RH,PVC,d}(t) + C_{RH,G,l}(t)][C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)] \quad [9]$$

where $C_{X,Y,Z}(t)$ denotes the concentration of substance X (O_2 or RH) stored in material Y [glass (G), PET, or PVC] at Z luminosity conditions (d or l).

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

$$\text{PET, dark: } \frac{dC_{ROOH,PET,d}(t)}{dt} = k_c(T_2)C_{RH,PET,d}(t)C_{O_2,PET,d}(t) \quad [10]$$

$$\text{PVC, dark: } \frac{dC_{ROOH,PVC,d}(t)}{dt} = k_c(T_2)C_{RH,PVC,d}(t)C_{O_2,PVC,d}(t) \quad [11]$$

$$\text{glass, light: } \frac{dC_{ROOH,G,l}(t)}{dt} = k_a(T_2)C_{O_2,G,l}(t) + k_c(T_2)C_{RH,G,d}(t)C_{O_2,G,d}(t) \quad [12]$$

$$\text{PET, light: } \frac{dC_{ROOH,PET,l}(t)}{dt} = k_a(T_2)[C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)] + k_c(T_2)[C_{RH,PET,d}(t) + C_{RH,G,l}(t)][C_{O_2,PET,d}(t) + C_{O_2,G,l}(t)] \quad [13]$$

$$\text{PVC, light: } \frac{dC_{ROOH,PVC,l}(t)}{dt} = k_a(T_2)[C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)] + k_c(T_2)[C_{RH,PVC,d}(t) + C_{RH,G,l}(t)][C_{O_2,PVC,d}(t) + C_{O_2,G,l}(t)] \quad [14]$$

The overall set of 10 differential equations above (Eqs. 5–9, 10–14) was solved by using a modified numerical algorithm that involved a typical Newtonian method for nonlinear systems in conjunction with a fourth-order Runge–Kutta method for ordinary differential equations (20). The concentrations $C_{O_2,PET,d}(t)$, $C_{O_2,PVC,d}(t)$, $C_{RH,PVC,d}(t)$, $C_{RH,PET,d}(t)$, $C_{O_2,G,l}(t)$, $C_{RH,G,l}(t)$, as well as the reaction rate values $k_a(T_1)$, $k_a(T_2)$, $k_c(T_1)$, and $k_c(T_2)$, were calculated.

RESULTS AND DISCUSSION

Only conjugated dienes are formed in free-radical auto-oxidation, whereas nonconjugated dienes, such as linoleic acid, can be found in photo-oxidation (7). Hence, the K_{232} values should represent only part of the dienes (the conjugated ones) formed from the substrate, and a relatively higher ratio of PV/K_{232} for oil stored in light and subjected to photo-oxidation should be expected compared with that stored in the dark (free-radical auto-oxidation only). The ratio of PV/K_{232} values for every treatment vs. storage time showed that olive oil stored in PET containers in the light had lower PV/K_{232} values compared with olive oil stored in glass in the light, most probably indicating the protective role of PET in olive oil oxidation, as also concluded by Kaya *et al.* (21). For olive oil in glass containers in the light, the PV/K_{232} ratio increased sharply after 6 mon when stored at 40 and 30°C, but not at 15°C. For most of the storage period, PV/K_{232} values for olive oil stored in the light in PVC bottles showed slightly higher values than oil stored in PET and much higher values than oil stored in glass (Fig. 1). Volatile compounds, roughly appearing at the reported corresponding retention times (average of six replicates), were identified (see Table 1).

The increases in the amounts of various volatile flavor compounds over time for every treatment were statistically analyzed using the SASTM 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, $\alpha < 0.05$, for the aforementioned compounds over time).

The compounds most influenced by storage conditions were hexanal, (*E*)-2-octenol, (*Z*)-2-nonenol, (*E,E*)-2,4-heptadienal,

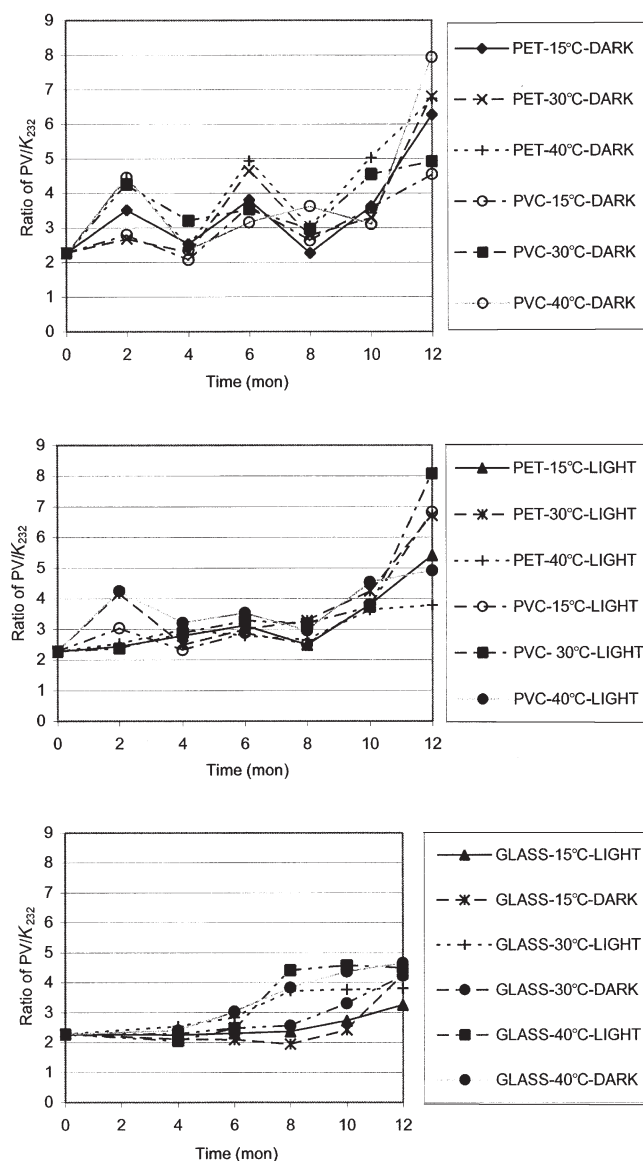


FIG. 1. PV/K₂₃₂ values for olive oil placed in poly(ethylene terephthalate) (PET), poly(vinylchloride) (PVC), or glass bottles and stored in the light at various temperatures.

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, and 2-pentyl furan in olive oil showed that these compounds can 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°C contained the highest amounts of hexanal, followed by the oil stored in glass at 40°C, whereas the oil stored in PVC containers had a lower hexanal content at 12 mon (Fig. 2). Oil stored in the same bottles but at lower temperatures under light had lower amounts of hexanal.

TABLE 1
Selected Flavor Compounds Isolated from Olive Oil and Their Kovats Indexes

Compound	Kovats index	Compound	Kovats index
Hexanal	622	Nonanal	932
(<i>E</i>)-2-Heptenal	790	(<i>E</i>)-2-Decenal	1093
2-Pentyl furan	909		

Statistical analysis of the data showed that the hexanal content of olive oil in glass containers kept at 15°C was not significantly different from that of oil kept in PVC at the same temperature after 12 mon of storage ($P = 0.08$), whereas at 30 and 40°C, the differences were highly significant ($P = 0.001315$ and $P = 5.28 \times 10^{-16}$, respectively). The hexanal content of oil in glass at 15°C was significantly different from that of oil in glass at 30°C ($P = 0.04027$) and at 40°C ($P = 3.02 \times 10^{-34}$). The same was the case for the hexanal content of oil in PET (15 and 30°C, $P = 4.16 \times 10^{-07}$; 15 and 40°C, $P = 4.46 \times 10^{-31}$; and 30 and 40°C, $P = 3.54 \times 10^{-18}$) and in PVC ($P = 0.00015$, $P = 3.54 \times 10^{-16}$, and $P = 2.33 \times 10^{-07}$, respectively). For any temperature, the hexanal content of oil stored in PET was always statistically different from that of oil stored in glass (e.g., glass at 15°C and PET at 15°C, $P = 0.00021$; glass at 30°C and PET at

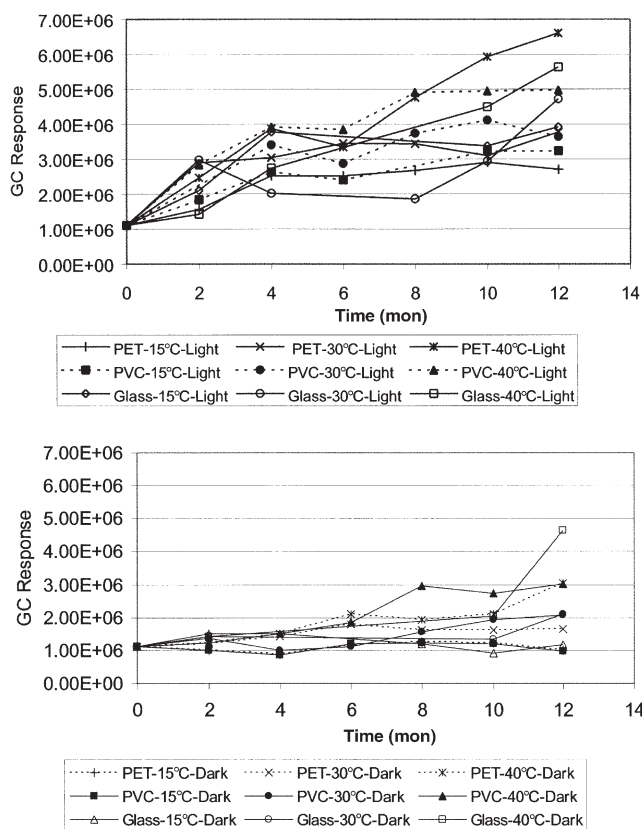


FIG. 2. Hexanal production in olive oil kept in PET, PVC, and glass containers at 15, 30, and 40°C in the light and in the dark for 12 mon. For abbreviations, see Figure 1.

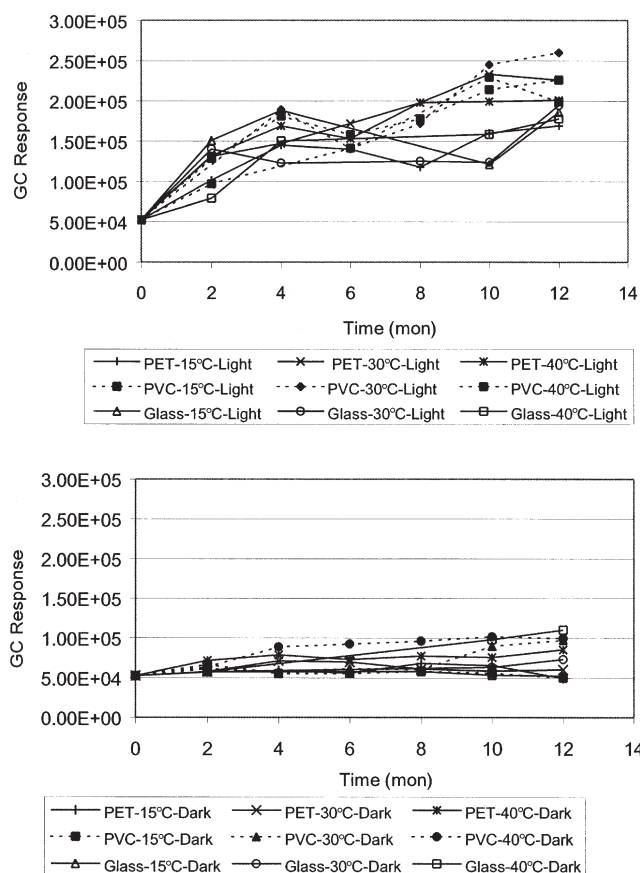


FIG. 3. Nonanal production in olive oil kept in PET, PVC, and glass containers at 15, 30, and 40°C in the light or in the dark for 12 mon. For abbreviations, see Figure 1.

15°C, $P = 7.2 \times 10^{-16}$). Among the oil samples in PET and PVC, the amount of hexanal was significantly different at 15°C ($P = 0.041921$) and at 40°C ($P = 7.17 \times 10^{-05}$), but not at 30°C ($P = 0.534109$). Oil placed in PET, PVC, or glass containers and stored in the dark at any temperature did not contain significantly different amounts of hexanal over time. For the samples stored in the light, since the hexanal reached almost twice the value of samples stored in the dark, we concluded that fluorescent light significantly influenced the evolution of hexanal, whereas the availability of oxygen passing through the plastic containers was less influential, especially at lower storage temperatures (Fig. 2).

The evolution of nonanal was similar for all the oil samples stored in either PET, PVC, or glass containers in the light at any temperature, and for oil in these containers stored in the dark at any temperature (Fig. 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 among containers at any temperature. Samples stored in the dark were significantly altered after 12 mon compared with the original oil. The influence of light was significant even after 2 mon of storage at 40°C ($P = 0.000846$). The significance increased with time and increasing temperature of storage.

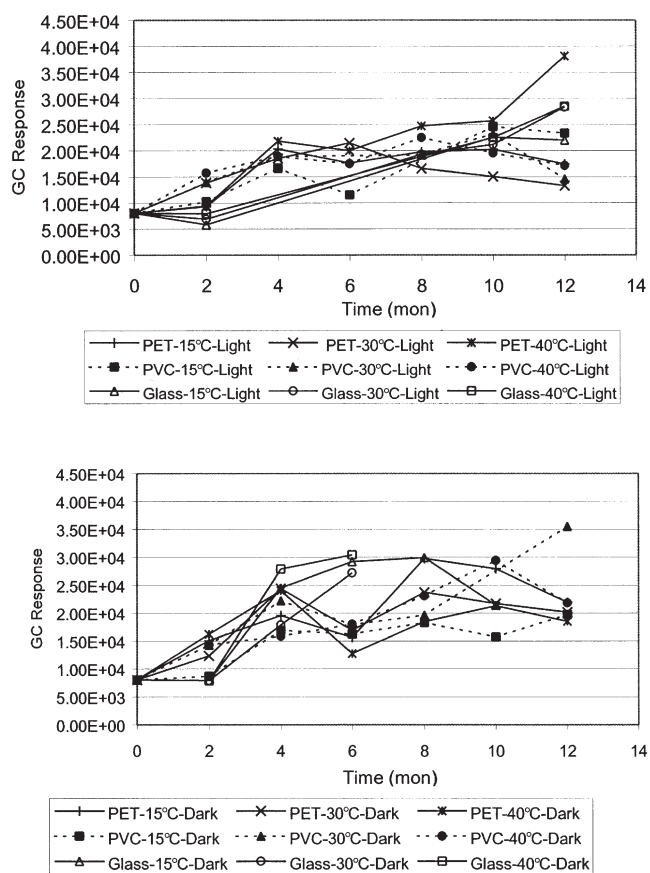


FIG. 4. (*E*)-2-Decenal production in olive oil kept in PET, PVC, and glass containers at 15, 30, and 40°C in the light or in the dark for 12 mon. For abbreviations, see Figure 1.

Figure 4 shows that the amounts of (*E*)-2-decenal present in the oil after 2 mon of storage were significantly greater than the amount originally present for all treatments in the dark ($P = 0.01055$); when stored in the light, (*E*)-2-decenal increased significantly after 4 mon of storage compared with the amounts originally present in the oil ($P = 0.001164$). It could be that (*E*)-2-decenal was influenced more by the triplet 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 the light at 40°C, whereas the amounts detected were lower for oil stored in glass containers. For all conditions, oil stored in the dark had lower amounts of (*E*)-2-heptenal compared with oil stored in the light (Fig. 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 sixth month of storage compared with oil stored in glass or PET at any temperature. Among the different materials, there was no significant difference in the amount of (*E*)-2-heptenal at the same time intervals and temperatures. However, light had a significant influence even after 2 mon. Samples stored in the dark did not differ significantly for any temperature or material. Oil kept in the light after 10 and 12 mon had a significantly different amount of (*E*)-2-heptenal compared with oil stored in the dark for any time period up to 12 mon.

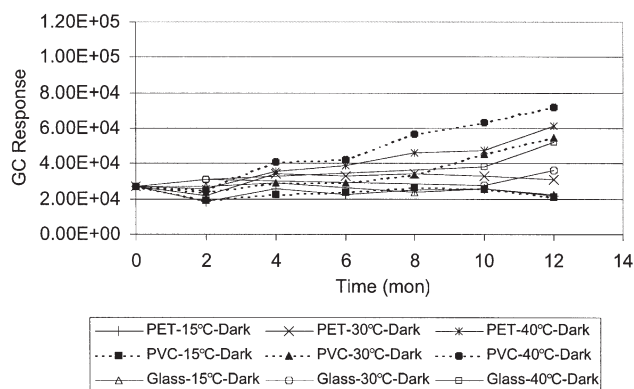
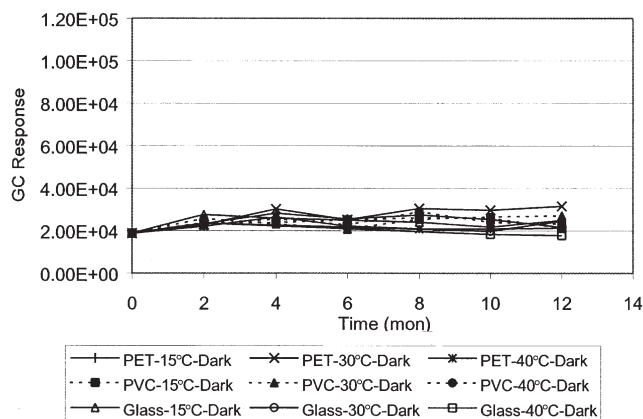
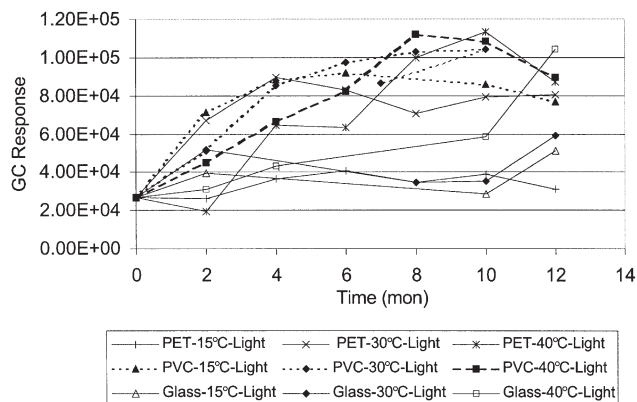
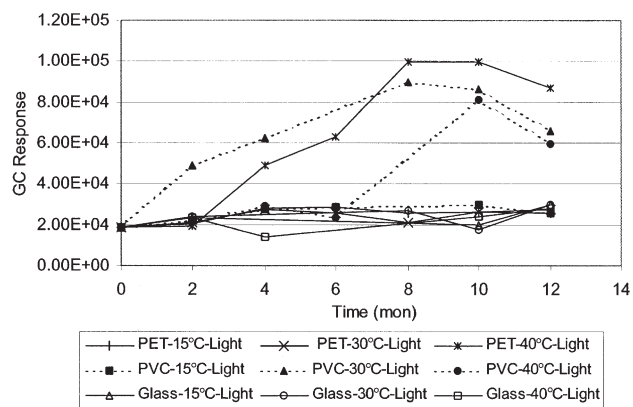


FIG. 5. (*E*)-2-Heptenal production in olive oil kept in PET, PVC, and glass containers at 15, 30, and 40°C in the light or in the dark for 12 mon. For abbreviations, see Figure 1.

FIG. 6. 2-Pentyl furan production in olive oil kept in PET, PVC, and glass containers at 15, 30, and 40°C in the light or in the dark for 12 mon. For abbreviations, see Figure 1.

The formation of 2-pentyl furan is proposed to result from 4-ketononanal, an oxidized linoleic acid 10-OOH derivative. Although not a typical hydroperoxide, 10-OOH can derive from singlet oxidation of linoleic acid. As another possible pathway, it may derive from the 9-OOH of linoleic acid in the presence of singlet oxygen combined with a liberation of formaldehyde, although its formation from linolenic acid also has been suggested (2). Because of the demand for singlet oxygen, the presence of 2-pentyl furan should be closely related to photo-oxidation and the availability of oxygen. For olive oil stored in PVC, PET, or glass at 40°C in the light, the amounts of 2-pentyl furan were comparable, but all were higher than the amounts isolated from oil stored at 15°C in any of the packaging materials. In dark conditions, the oil stored in PVC at 40°C had the highest amount of 2-pentyl furan, followed by the oil in PET, whereas the oil in glass had the lowest amount except when stored at 40°C. For any other temperature or light vs. dark condition, the amount of 2-pentyl furan was clearly lower. For the same temperature and material, the amount of 2-pentyl furan was always higher in the oil kept in the light compared with the oil kept in the dark (Fig. 6). The differences seen in the two panels of Figure 6 were not 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 mon of storage. On the other hand, the amounts 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 Eqs. 5–9 and 10–14) was derived from 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 lower 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 $k_c(T)$ values for 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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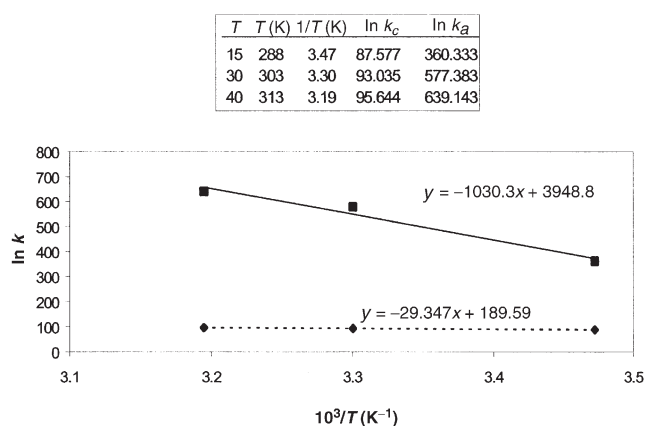


FIG. 7. Plot of $\ln k_a$ (■) and $\ln k_c$ (◆) as a function of $1/T$ (K).

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