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Evaluation the kinetic of peroxide and hexanal formation in ascorbyl palmitate incorporated sunflower oil during accelerated oxidation

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SUMMARY: The effects of temperature (40-80 °C), time (0-28 days), and different concentrations (0-1000 mg/kg) of ascorbyl palmitate (AP) on peroxide value, conjugated diene, triene acids and hexanal contents in sunflower oil kept under accelerated oxidation conditions have been evaluated. Samples with added AP showed lower peroxide values and hexanal contents than their counterparts without AP. While with increasing temperature, the reaction orders for peroxide formation reduced from first to zero order, those for hexanal formation were found to be first order under different experimental conditions. AP reduced the reaction rate constant for peroxide and hexanal formation. The activation energy required for peroxide and hexanal formation ranged from 14.64–89.40 and 1.62–12.14 kJ/mol K, respectively. 400 mg/kg AP, providing the highest activation energies for peroxide and hexanal formation, was found to be the best concentration to enhance the oxidative stability of sunflower oil under defined conditions.

KEYWORDS: *Activation energy; Ascorbyl palmitate; Hexanal; Kinetic parameters; Oxidative stability; Peroxide value.*

RESUMEN: ***Evaluación de la cinética de formación de peróxido y hexanal en aceite de girasol con palmitato de ascorbilo incorporado durante oxidación acelerada.*** Se ha determinado los efectos de la temperatura (40-80°C), el tiempo (0-28 días) y diferentes concentraciones (0-1000 mg/kg) de palmitato de ascorbilo (AP) sobre el índice de peróxidos, dienos conjugados, ácidos trieno y hexanal, en aceites de girasol sometidos a condiciones de oxidación acelerada. Las muestras con AP agregado mostraron valores de peróxido y contenidos de hexanal más bajos que sus correspondientes sin AP, mientras que al aumentar la temperatura los órdenes de reacción para la formación de peróxido se redujeron del primer orden a orden cero. Se encontró que la formación de hexanal era de primer orden para las diferentes condiciones experimentales. AP redujo la constante de velocidad de reacción para la formación de peróxido y hexanal. La energía de activación requerida para la formación de peróxidos y hexanal osciló entre 14,64–89,40 y 1,62–12,14 kJ/molK, respectivamente. Se encontró que la concentración de AP de 400 mg/kg, que proporciona las energías de activación más altas para la formación de peróxido y hexanal, era la mejor concentración para mejorar la estabilidad oxidativa del aceite de girasol en las condiciones definidas.

PALABRAS CLAVE: *Energía de activación; Estabilidad oxidativa; Hexanal; Índice de peróxidos; Palmitato de ascorbilo; Parámetros cinéticos.*

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1. INTRODUCTION

As an important food ingredient, the production and consumption of vegetable oils shows an increasing trend all over the world. Vegetable oils attract the intention of health-conscious consumers due to their high unsaturated fatty acids (UFAs) contents. A higher consumption of UFA reduces blood pressure, total and low-density lipoprotein (LDL) cholesterol. Consequently, it is considered to decrease the risk of coronary heart disease (Iso *et al.*, 2002). However, high UFAs lead to a high oxidation rate and short shelf-life owing to their susceptibility to oxidation. Oxidation consists of a series of chain reactions, resulting in quality loss, including the formation of primary and secondary oxidation products and undesirable rancid taste and flavor in oils (Shahidi and Wandanasundara, 2002). Recently, extracts from natural sources have been used as alternatives to synthetic antioxidants such as butylated hydroxyanisole, butylated hydroxytoluene, and tert-butylhydroquinone because of their possible adverse effects on health (Yanishlieva and Marinova, 2001). Extracts from nettle, flax seed, sage, mint, thyme and walnut press-cake have been investigated for their antioxidative activity in different oils (Martínez *et al.*, 2013, Baştürk *et al.*, 2018, Bakkalbaşı, 2019). However, these applications are still far from being widely used in the oil industry due to their high cost.

Another alternative is to use derivatives of natural antioxidants. Ascorbic acid is an excellent antioxidant in a hydrophilic medium and can be produced synthetically. AP is a fat-soluble synthetic ester of ascorbic and palmitic acids. It has a “generally recognized as safe” (GRAS) status with no limitation for use in the food, pharmaceutical, or cosmetic industries (Perricone *et al.*, 1999, Špiclin *et al.*, 2001).

According to Lee *et al.* (1997) AP leads to the retarding of oxidative rancidity by quenching singlet oxygen. Coppen (1994) noted the ability of AP to remove or sequester trace metals that catalyze peroxide formation. There are several studies regarding the antioxidative effect of AP in different oils. Bartee *et al.* (2007) indicated that different concentrations of AP (300-1200 mg/kg) significantly affected the oxidative stability of oils with different ratios of arachidonic, docosapentaenoic, and docosahexaenoic acids. Baştürk *et al.* (2017) investigated the effects of AP (0, 200, and 400 mg/kg), Cu^{+2} and Fe^{+2} ions (0, 0.15, and 0.3 mg/kg) on the oxidative stability of sunflower oil during accelerated oxidation. They reported that the addition of 400 mg/kg AP limited the formation of peroxides in both Fe^{2+} and Cu^{2+} added samples. Javidipour *et al.* (2015) reported that cottonseed and olive oils containing 400 mg/kg AP showed higher tocopherol, and lower peroxide value (PV) and malondialdehyde contents than those without AP during chemical interesterification, and storage at 60 °C.

The objective of this study was to determine the effects of AP on the levels of oxidation of sunflower oil by evaluating PV, conjugated dienes and trienes, and hexanal contents and some kinetic parameters in terms of the formation of peroxide and hexanal under accelerated oxidation conditions. Unlike previous studies, a wide range of AP concentrations (0, 200, 400, 600, 800, and 1000 mg/kg), including higher levels wase evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Sunflower oil (Komili, Türkiye) was obtained from a local market in the Van province of Turkey. Ethanol, diethyl ether, n-hexane, isooctane, potassium hydroxide (KOH), and acetic acid were obtained from Merck (Darmstadt, Germany). AP, 2-methyl-3-heptanone, and hexanal were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA).

2.2. Methods

2.2.1. Experimental design for accelerated oxidation

AP was added in concentrations of 200, 400, 600, 800, and 1000 mg/kg to sunflower oil as antioxidant preparate. Sunflower oil without AP was used as a control. The AP was added to the sunflower oil (50 g) in a glass bottle (100 mL) and mixed for 60 s using a magnetic stirrer (MR Hei-Tec, Heidolph, Germany). Accelerated oxidation in the dark (at 40, 60, and 80 °C for 28 days) was applied in a thermostated oven (EN 400 Y, Nuve, Istanbul, Turkey) to the un-sealed antioxidant-added oil and control samples. Samples were withdrawn from each treatment at 0, 7, 14, 21, and 28 days of storage for chemical analysis (Javidipour *et al.*, 2015). Three independent series of experiments were carried out under the same conditions and the analysis was made in triplicate.

2.2.2. PV analysis

The PVs of the oil samples were determined using a titration method according to the AOCS (1998) Official Method Cd 8– 53 and was expressed as milliequivalents of active oxygen per kilogram of oil (meq O_2/kg oil).

2.2.3. Analysis of conjugated dienes (k_{232}) and trienes (k_{270})

The k_{232} and k_{270} values were determined according to the AOCS (2003) Official Method Ch 5-91. Samples were diluted with isooctane and specific extinctions at 232 nm for conjugated dienes and 270 nm for conjugated trienes were determined by using a spectrophotometer (Agilent 8453, CA, USA).

2.2.4. Hexanal analysis

The Solid-Phase Micro-Extraction (SMPE) method proposed by Javidipour and Qian (2008) with slight modifications was applied to analyze the hexanal contents in the samples. Hexanal was extracted by a 1-cm (65 µm polydimethylsiloxane/divinylbenzene) SPME fiber (Supelco Co., Bellefonte, PA, USA). 2.0 g of sunflower oil was weighed into 20-mL glass vials and as an internal standard 0.1 g 2-methyl-3-heptanone (100 mg/kg, w/w) was added. The vials were capped with teflon-lined septa, crimped, and then placed in a magnetic stirrer (MR Hei-Tec, Heidolph, Germany). The pre-conditioned fiber (at 250 for 10 min) was applied to the vial in the injection port of an Agilent 6890 N (USA) gas chromatography (GC) for the extraction of hexanal (30 minutes) after 5 minutes equilibration. The desorption, separation and identification of hexanal were carried out in a flame ionization detector (FID) donated (270 °C) GC equipped with a HP- Innowax column (30 m × 0.25 mm id × 0.25 mm film thickness, J&W Scientific, Folsom, CA, USA). The splitless injection mode was used for 3 min (250 °C) with nitrogen as carrier gas (0.5 mL/min). The oven temperature was initially adjusted at 37 °C, held for 5 min, then increased to 75 °C (8 °C/min) and 220 °C (40 °C/min) and finally held at 220 °C for 1 min. All measurements were carried out in triplicate using the same SPME fiber.

2.2.5. Kinetic calculations

The experimental results were analyzed according to Baştürk *et al.* (2007) to estimate the kinetic parameters. Lipid oxidation reactions are defined as an autocatalyzed reaction by hydroperoxides. Ozilgen and Ozilgen (1990) provided Equation (1), according to PV determination:

$$\frac{dC}{dt} = k\left(\frac{C}{1-\frac{C}{Cmax}}\right) \quad (1)$$

where C is the concentration of the total oxidation products, Cmax is the maximum attainable concentration of the oxidation product (in this case, hydroperoxides), k is the rate constant and t is time. In the early stages of the lipid oxidation process when C << C max, the term 1–C/Cmax = 1, and Equation (2) were obtained (Kamal-Eldin and Yanishlieva, 2005).

$$\frac{dC}{dt} = kC \quad (2)$$

A kinetic model (Equation 3) was derived from a first-order autocatalytic reaction and a second-order decomposition reaction (Crapiste *et al*., 1999):

$$\frac{\mathrm{dPV}}{\mathrm{dt}} = \mathrm{k_1PV} - \mathrm{k_2PV^2} \quad (3)$$

where PV is the peroxide value, and k_1 and k_2 are the autocatalytic formation and decomposition rate constants, respectively. The orders and the rate constants of the reactions were determined according to Equations (4) and (5). The kinetic model of autoxidation reaction is written as Equation (4):

$$\frac{\mathrm{dPV}}{\mathrm{dt}} = \mathrm{k_1PV^{\alpha}} - \mathrm{k_2PV^{\beta}} \quad (4)$$

where α and β are the orders of the oxidation and decomposition reactions, respectively.

The decomposition reaction rate of PV is equal to the production reaction rate of hexanal (HC) (Equation 5):

$$\left(\frac{-\mathrm{dPV}}{\mathrm{dt}}\right)_{\mathrm{decomposition}} = \frac{\mathrm{dHC}}{\mathrm{dt}} = \mathrm{k_2PV^{\beta}} \quad (5)$$

The increasing rates of hexanal were determined using the measured hexanal content during oxidation periods. Equation (5) was linearized and Equation (6) was obtained:

$$\ln\left(\frac{dHC}{dt}\right) = \ln(k_2) + \beta \ln PV \qquad (6)$$

ln(dHC/dt) versus ln(PV) was plotted for each sample, and the slope and intercept of the lines were determined as β and $\ln(k_2)$, respectively.

Thereafter, Equation (4) was rewritten as Equation (7)

$$\frac{dPV}{dt} + k_2 PV^{\beta} = k_1 PV^{\alpha} \qquad (7)$$

and then linearized, and Equation (8) was obtained:

$$\ln(dPV/dt + k_2 PV^{\beta}) = \ln(k_1) + \alpha \ln(PV) \qquad (8)$$

$\ln(dPV/dt + k_2PV^{\beta})$ versus ln(PV) was plotted for each sample, and the slope and intercept of the lines were determined as α and ln(k1), respectively.

Secondly, the temperature dependence of a reaction rate constant was described by the Arrhenius equation:

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (9)$$

where k is the reaction rate constant, A is the frequency factor, E_a is the activation energy, R is the universal gas constant (8.314 J/molK), and T is the absolute temperature (K).

2.3. Statistical analysis

All values were reported as mean ± standard deviation. The data from three independent series of experiments were analyzed using the Minitab 14 program for two-way ANOVA. Duncan's multiple comparison test was applied to identify the significantly different groups ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. PV

PV represents the concentration of peroxides and hydroperoxides known as primary oxidation products formed in the initial stage of lipid oxidation. The PVs of samples with different AP concentrations kept under different temperatures are given in Figure 1. Storage time and temperature and AP concentration significantly ($p < 0.05$) affected the PV of the samples. The PV of all samples continuously increased during storage and considerably decreased as their AP concentrations increased. Javidipour *et al*. (2015) reported that olive and cottonseed oils with added AP (400 mg/kg) showed lower PV than their counterparts without AP during accelerated oxidation. Baştürk *et al*. (2017) noted that the addition of 400 mg/kg AP restricted the increase in peroxide value in both Fe^{2+} and Cu^{2+} added samples.

3.2. Conjugated acids

Conjugated diene (k_{232}) and triene (k_{270}) acids are characteristic intermediate products of lipid oxidation. The conjugated diene acid contents of the samples showed an increasing trend as the storage time and temperature increased (Figure 2). The conjugated triene acid contents in the samples showed a lower value than their conjugated diene acid contents. This is due to the low linolenic acid content in sunflower oil. While the conjugated triene acid contents in the samples did not show a significant change during storage at 40 or 60 °C, they showed an increasing trend at 80 °C (Figure 3). The results showed that AP did not significantly ($p > 0.05$) affect the formation of conjugated diene acids. However, the presence of AP significantly ($p < 0.05$) reduced the formation of triene acids. Günal and Turan (2017) noted that AP (200 mg/kg) effectively decreased the k_{232} and k_{270} values of sunflower oil during accelerated oxidation.

3.3. Hexanal

Hexanal is a secondary metabolite formed during the oxidation of linoleic acid, which is the major fatty acid in sunflower oil. The changes in the hexanal contents in the sunflower oil samples during accelerated oxidation are shown in Figure 4. The hexanal content in the samples started to rise at the beginning of storage and reached a maximum value after 28 days of accelerated oxidation. All AP levels significantly reduced the formation of hexanal during accelerated oxidation compared to the control ($p < 0.05$). Samples with 400 mg/kg AP, stored at 40 and 60 °C, had lower hexanal contents than those in the other samples. Kim *et*

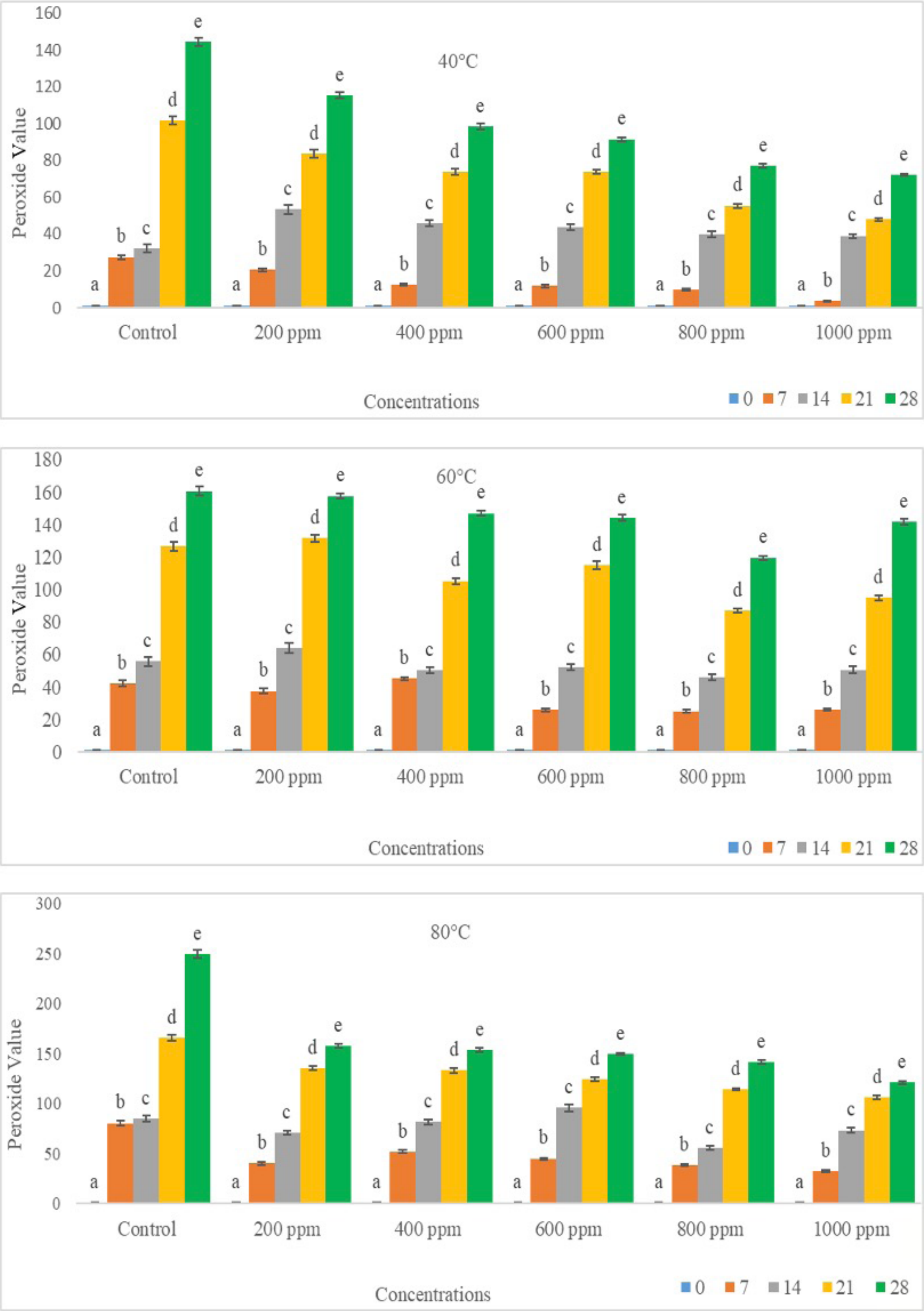

FIGURE 1. The effect of AP on peroxide values (meq O_2/kg oil) for sunflower oil samples stored at 40, 60, 80 °C for 28 days

Data are expressed as mean±standard deviation. Duncan's multiple range test procedure was used to identify significant differences ($p < 0.05$). Different letters in each column show differences among storage days at the same concentration. All treatments were performed in three replicates.

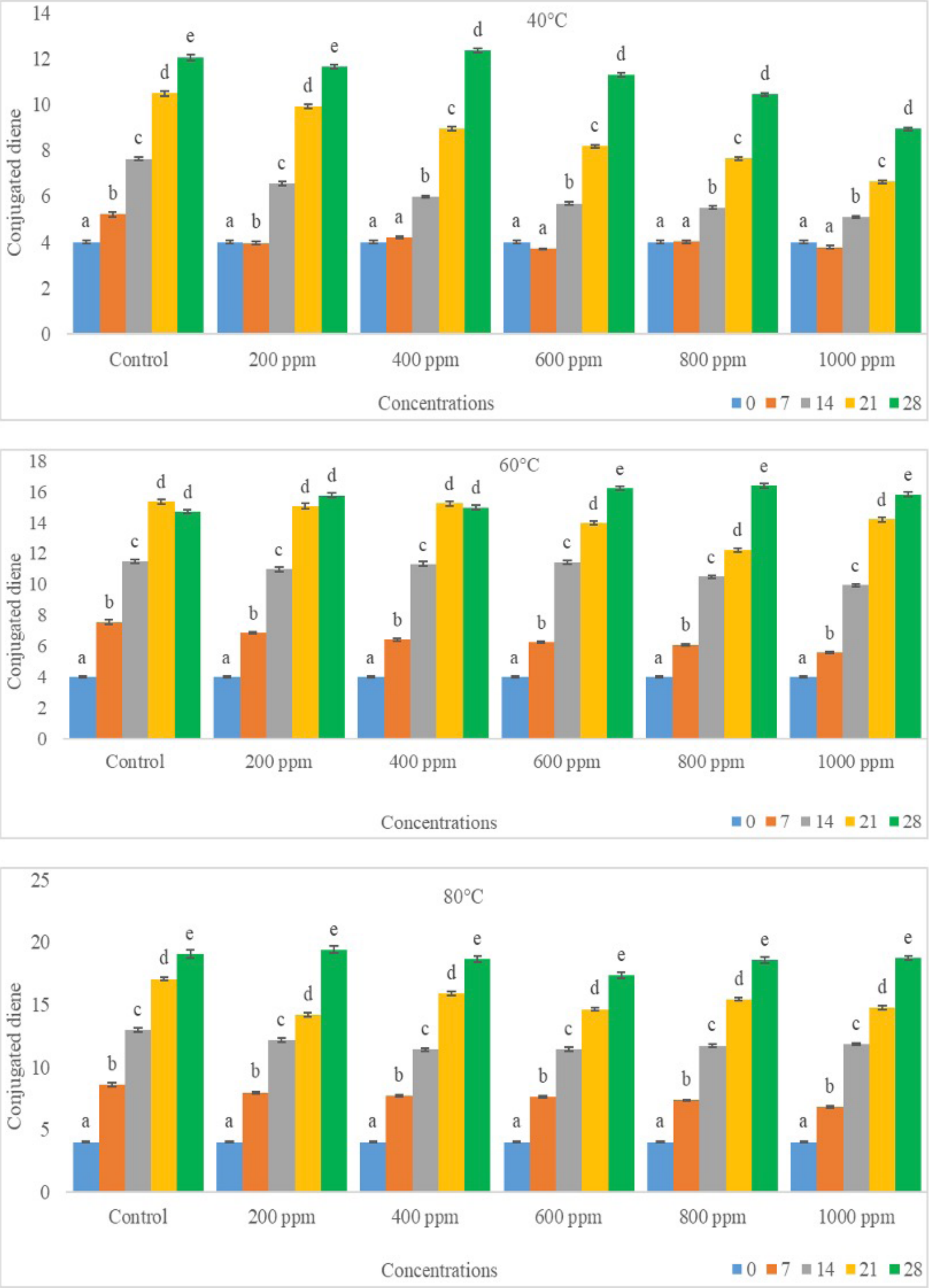

FIGURE 2. The effect of AP on conjugated diene acid contents in sunflower oil samples stored at 40, 60, 80 °C for 28 days

Data are expressed as mean±standard deviation. Duncan's multiple range test procedure was used to identify significant differences ($p < 0.05$). Different letters in each column show differences among storage days at the same concentration. All treatments were performed in three replicates.

FIGURE 3. The effect of AP on conjugated triene acid contents in sunflower oil samples stored at 40, 60, 80 °C for 28 days

Data are expressed as mean±standard deviation. Duncan's multiple range test procedure was used to identify significant differences ($p < 0.05$). Different letters in each column show differences among storage days at the same concentration. All treatments were performed in three replicates.

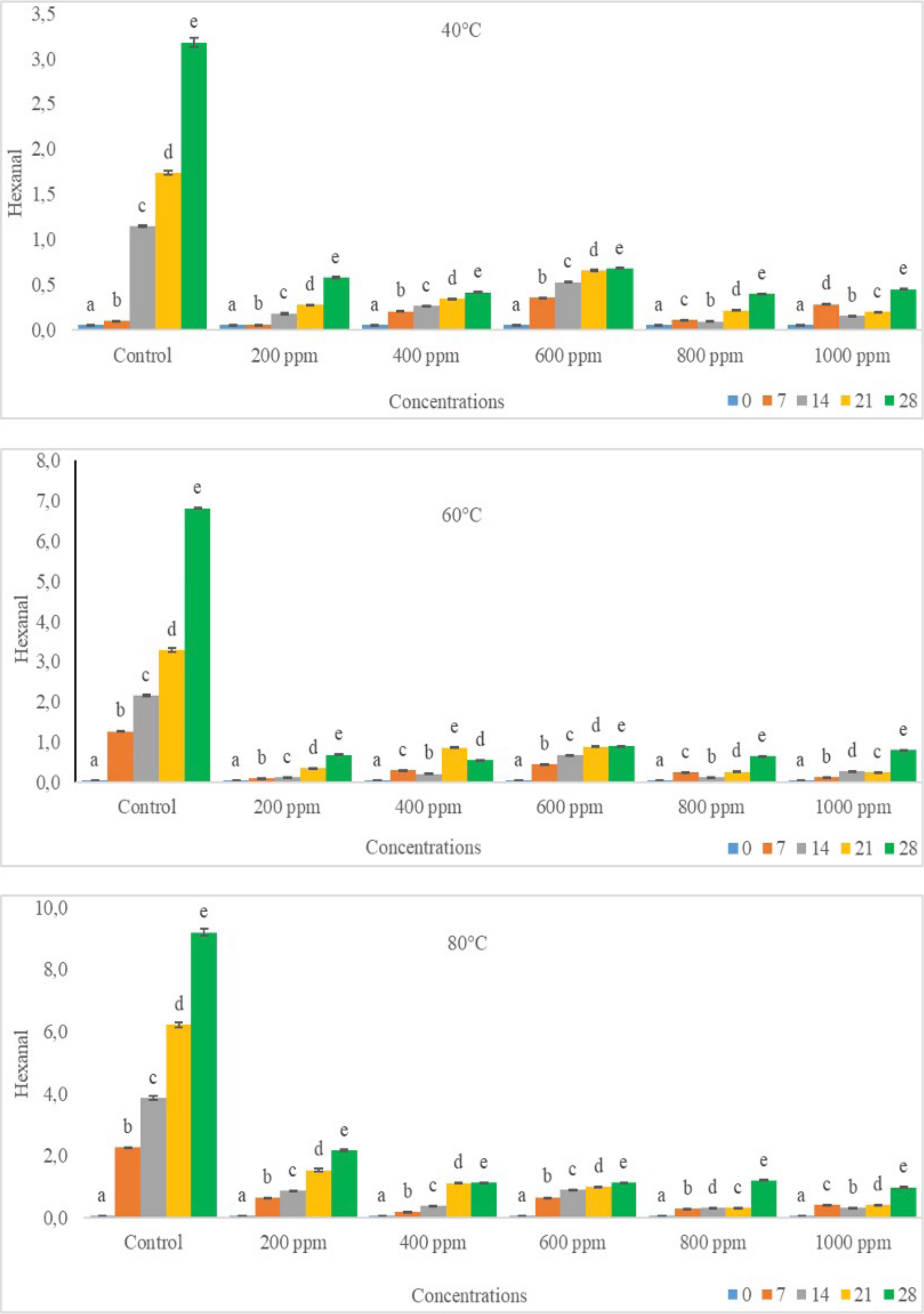

Figure 4. The effect of AP on hexanal contents in sunflower oil samples stored at 40, 60, 80 °C for 28 days

Data are expressed as mean±standard deviation. Duncan's multiple range test procedure was used to identify significant differences ($p < 0.05$). Different letters in each column show differences among storage days at the same concentration. All treatments were performed in three replicates.

al. (2012) indicated that hexanal concentrations were the lowest in samples with 1.0 mM AP in riboflavin photosensitized oil in water emulsions. However, the addition of AP (250 µmol/L oil) had little influence on the hexanal formation in vegetable oil kept at 60 °C for 16 days (van Ruth *et al*., 1999).

3.4. Kinetic analysis

Oxidation is a highly complex process because of the effects of various internal and external parameters. Oxidation is a mixed reaction which involves series and parallel reactions. The oxidative stability of an oil is generally evaluated based on parameters such as PV, AV, thiobarbituric acid reactive substances (TBARS), and recently, the hexanal content in the sample during the oxidation process. By kinetic analysis of the data, it is possible to evaluate the oxidation levels based on simplified data which represent the whole process, and is easier to understand. To evaluate the oxidation reactions, Baştürk *et al*. (2007) investigated the kinetic analysis of oxidized oils based on the changes in primary and secondary oxidation products. In this study, the kinetic analysis was applied to PVs and hexanal contents obtained during accelerated oxidation in the sunflower oil samples with and without the AP addition. The orders and rate constants of the reactions for oxidation are given in Table 1. The results showed that the reaction rate constants regarding peroxide and hexanal forma-

Table 1. Kinetic parameters of peroxide and hexanal formation in sunflower oil with ascorbyl palmitate

	Peroxide Formation		**Hexanal Formation**		**Peroxide Formation**	**Hexanal Formation**
Control	**k_1**	**α**	**k_2**	**β**	**Ea (kJ/molK)**	**Ea (kJ/molK)**
313.15 K	4.03±0.04	0.3±0.005	0.151±0.001	1.10±0.05	28.71±2.32	1.62±0.08
333.15 K	6.67±0.08	0.2±0.004	0.154±0.001	0.98±0.03		
353.15 K	14.12±0.20	0.2±0.004	0.162±0.002	1.08±0.06		
200 mg/kg						
313.15 K	1.68±0.02	0.4±0.004	0.090±0.000	0.99±0.02	28.23±2.89	6.26±1.01
333.15 K	5.26±0.06	0.2±0.003	0.093±0.001	1.12±0.03		
353.15 K	5.61±0.07	0.2±0.004	0.118±0.003	1.06±0.04		
400 mg/kg						
313.15 K	0.18±0.004	0.9±0.006	0.066±0.000	1.10±0.04	89.40±4.65	12.14±0.23
333.15 K	7.70±0.08	0.1±0.001	0.089±0.001	1.02±0.03		
353.15 K	8.21±0.10	0.2±0.002	0.112±0.002	1.07±0.05		
600 mg/kg						
313.15 K	0.14±0.003	1.0±0.005	0.082±0.000	1.04±0.05	85.33±1.02	3.12±0.02
333.15 K	2.98±0.04	0.3±0.003	0.091±0.002	0.99±0.04		
353.15 K	5.47±0.06	0.2±0.002	0.093±0.001	1.00±0.03		
800 mg/kg						
313.15 K	0.43±0.005	0.7±0.004	0.067±0.000	1.02±0.04	61.48±1.29	6.99±0.65
333.15 K	3.08±0.03	0.3±0.003	0.088±0.000	0.99±0.05		
353.15 K	6.08±0.07	0.2±0.001	0.091±0.002	0.96±0.02		
1000 mg/kg						
313.15 K	1.92±0.02	0.3±0.003	0.073±0.000	1.01±0.02	14.64±0.80	7.78±1.02
333.15 K	2.97±0.03	0.3±0.002	0.088±0.001	0.99±0.08		
353.15 K	3.61±0.05	0.3±0.002	0.103±0.003	0.98±0.04		

Data are expressed as mean±standard deviation. k_1: peroxide formation rate constant, α: reaction order for peroxide formation, k_2: hexanal formation rate constant, β: reaction order for hexanal formation, Ea: activation energy. All treatments were performed in three replicates.

tion increased depending on the reaction temperature. The AP-incorporated samples showed lower rate constants than their counterparts without AP. For hexanal formation, samples with 400 mg/kg AP stored at 40 and 60 °C had the lowest reaction rate constant. Crapiste *et al.* (1999) indicated that in an autocatalyzed lipid oxidation the decomposition reactions followed second-order kinetics. We found that the reaction order for peroxide formation was generally lower than first-order which decreased with increasing reaction temperature. Decreasing the reaction order shows that the reaction rate becomes independent of the reactant concentration. In zero-order reactions, the reaction rate is controlled by the reaction rate constant. Baştürk *et al.* (2007) reported that under accelerated oxidation the orders of formation and decomposition reactions in cottonseed, palm and soybean oils varied from first-order to zero-order with increasing temperature. Similar results were reported by Ozdemir *et al.* (2021). Our results showed that the reaction orders for hexanal, as a secondary oxidation product, were found as first-order in all treatments. The hexanal formation in sunflower oil depended on lipid peroxide concentration as reactant. Bakkalbaşı *et al.* (2012) reported that the reaction order for hexanal formation in walnut was first-order.

E_a is a temperature dependent parameter, defined as the energy barrier which must be overcome for a reaction to occur. The E_a for both peroxide and hexanal formation summarized the whole process in a single data which led to an easier understanding of the changes in peroxide and hexanal contents during the oxidation process. To evaluate the effect of AP on changes in peroxide and hexanal concentrations during the accelerated oxidation, the related E_a values were calculated. The activation energy required for peroxide and hexanal formation at different AP concentrations ranged from 14.64 to 89.40 and 1.62 to 12.14 kJ/molK, respectively. The E_a for peroxide formation was higher than that of hexanal formation. Higher E_a for peroxide formation showed that there was a high energy requirement at the first stage of oxidation. After overcoming this initial energy barrier which resulted in the formation of primary oxidation products (i.e. peroxides), the formation of secondary oxidation products such as hexanal could have happened with less energy requirements. The highest activation energies for peroxide and hexanal formation were 89.40 and 12.14 kJ/molK in samples with 400 mg/kg AP, respectively. By taking into account the E_a values, we observed that the 400 mg/kg AP showed the highest energy barrier to be overcome for peroxide and hexanal formation. Ixtaina *et al.* (2012) reported that AP addition increased the E_a of chia oil thermal oxidation from 71.9 to 87.5 kJ/molK. Bakkalbaşı *et al.* (2012) noted that E_a for hexanal formation in oil from wrapped walnut samples with different oxygen permeabilities varied between 54.79 and 146.78 kJ/molK.

4. CONCLUSIONS

Ascorbyl palmitate is a lipophilic derivative of ascorbic acid, which is widely used in oil and emulsions as an antioxidant. In this study the effects of AP concentration and temperature on oil oxidation were investigated. The reaction rate constants for both peroxide and hexanal formation rose with increasing temperature. Particularly, the addition of different levels of the AP reduced the reaction rate constants of peroxides. Furthermore, according to E_a values for peroxide and hexanal formation, increasing the AP concentration increased the oxidative stability of the sunflower oil. While the reaction order for peroxide formation was generally lower than first-order and decreased with increasing reaction temperature, hexanal showed the first reaction order in all applied temperatures. The addition of 400 mg/kg AP increased the E_a to the highest level for peroxide and hexanal formation. It can be concluded that 400 mg/kg AP was the most effective concentration to increase the oxidative stability of sunflower oil under accelerated oxidation based on PV and hexanal contents.

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6. DECLARATION OF COMPETING INTEREST

The authors of this article declare that they have no financial, professional or personal conflicts of interest that could have inappropriately influenced this work.

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