

Temperature dependence of the autoxidation and antioxidants of soybean, sunflower, and olive oil

Jiyeun Lee · Yoosung Lee · Eunok Choe

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Abstract Effects of temperature on the autoxidation and antioxidants changes of soybean, sunflower, and olive oils were studied. The oils were oxidized in the dark at 25, 40, 60, and 80 °C. The oil oxidation was determined by peroxide (POV) and *p*-anisidine values (PAV). Polyphenols and tocopherols in the oils were also monitored. The oxidation of oils increased with the oxidation time and temperature. Induction period decreased with the oxidation temperature; 87 and 3.6 days at 25 and 60 °C, respectively, for sunflower oil. The activation energies for the autoxidation of soybean, sunflower, and olive oils were 17.6, 19.0, and 12.5 kcal/mol, respectively. Olive oil contained polyphenols at 180.8 ppm, and tocopherols were present at 687, 290, and 104 ppm in soybean, sunflower, and olive oils, respectively. Antioxidants were degraded during the oil autoxidation and the degradation rates increased with the oxidation temperature of oils; for tocopherols, 2.1×10^{-3} and $8.9 \times 10^{-2}\%$ /day at 25 and 60 °C, respectively, in soybean oil.

Keywords Oil autoxidation · Temperature dependence · Activation energy · Tocopherols · Polyphenols

Introduction

Autoxidation of oil is an autocatalytic reaction, in which hydroperoxides of acylglycerols are produced and decomposed to lower molecular weight compounds [1]. Low molecular weight compounds contribute to the off-flavor of oil and make the oil less acceptable or unacceptable to consumers.

The oxidation of oil also destroys essential fatty acids and produces oxidized polymers, some of which are detrimental to the health [2].

Autoxidation of oil is affected by many factors; temperature, light, fatty acid composition, antioxidants, and prooxidants [3]. The autoxidation proceeds slowly at low temperature, and the rate increases as the temperature increases [4, 5]. Higher temperature results in higher decomposition of primary oxidation products and formation of dimers or oxidized compounds, in addition to the production of hydroperoxides. Light accelerates the oil oxidation, especially in the presence of sensitizers such as chlorophylls, mainly by producing singlet oxygen [6]. Unsaturated fatty acids are more susceptible to the oxidation than saturated ones, primarily due to their low activation energy for the formation of fatty acid radicals [7]. Natural and synthetic antioxidants decrease the oil oxidation by scavenging free radicals and oxygen and chelating the metals [8]. Antioxidants also decrease the activation energy of oil oxidation [9].

Tocopherols are the most common antioxidants found in vegetable oils, and polyphenols are also present in some oils. Tyrosol and hydroxytyrosol are examples of polyphenols present in olive oil [10]. Tocopherols and polyphenols donate hydrogen to peroxy and alkyl radicals of lipids, and convert them to more stable non-radical species [11]. Metal chelators such as phosphoric acid and EDTA can convert iron or copper ions into insoluble complexes or sterically hinder the formation of the complexes between metals and lipid hydroperoxides, resulting in decrease in the oil oxidation [12]. Ascorbic acid, erythorbic acid, sodium erythorbate, and sulfite can scavenge the oxygen; however, their hydrophilic character limits their usefulness in the oil system.

Since oils have different fatty acid compositions and minor components and are under different processing

J. Lee · Y. Lee · E. Choe (✉)
Department of Food and Nutrition, Inha University,
253 Younghyundong, Namku, Incheon, 402-751 Korea
e-mail: eochoe@inha.ac.kr

conditions, they could show different behaviors in the oxidation. In addition, the oils are exposed to various environments at different temperatures. In order to monitor and control the oil quality, it is important to pile up the data on the oil oxidation and minor compounds at various temperatures for different oils. This research, as a preliminary study, was performed to study the autoxidation of soybean, sunflower, and olive oils at various temperatures along with antioxidants changes to give the information on their temperature dependence, and this is the first report on the temperature dependence of the oil oxidation correlated with the antioxidants degradation.

Materials and methods

Materials and chemicals

Soybean, sunflower, and olive oils were products of Cheiljedang Co. Ltd. (Seoul, Korea). Soybean and sunflower oils were refined oils and olive oil was a virgin olive oil. Physical and chemical characteristics of the oils are shown in Table 1. Isooctane was purchased from Junsei Chemical Co. Ltd. (Tokyo, Japan). BF₃ in methanol, *p*-anisidine, caffeic acid, Folin-Ciocalteu reagent, and the standard fatty acid (palmitic, stearic, oleic, linoleic, and linolenic acids) methyl esters were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Standard α -, β -, γ -, and δ -tocopherols were products of EMD Bioscience Inc.

(La Jolla, CA, USA). *n*-Hexane and isopropanol in HPLC grade were purchased from J.T. Baker (Philipsburg, NJ, USA).

Preparation and oxidation of oils

Fifteen grams of soybean, sunflower, or olive oil was poured into a 50 mL serum vial (Supelco Inc., Bellefonte, PA, USA), and the vials were capped with paper and aluminum crimp seals with an open center to allow the air pass through the vials. The vials containing oils were stored in the dark for 180, 42, 18, and 6 days at the respective temperatures of 25, 40, 60, and 80 °C, representing ambient and accelerating temperatures. All samples were prepared in triplicate.

Analysis of oil

Free fatty acid values of oils were determined by AOCS Cd 3a-63 method [13]. Color of the oils was determined by measuring tristimulus *L*, *a*, and *b* values using a Hunter Lab colorimeter (Σ 90 Nippon Denshoku, Tokyo, Japan): *L*, lightness from 0 (dark) to 100 (light); *a*, redness from $-a$ (green) to $+a$ (red); and *b*, yellowness from $-b$ (blue) to $+b$ (yellow). The oxidizability of oils was determined by Rancimat at 100 °C. The instrument was 743 Rancimat (Metrohm Ltd., Herisau, Switzerland). Degree of oil oxidation at different temperatures was evaluated by measuring peroxide values (POV) and *p*-anisidine values (PAV) by AOCS Cd 8–83 and

Table 1 Physical and chemical characteristics of soybean, sunflower, and olive oils

| | | Soybean oil | Sunflower oil | Olive oil |
|---|---|-------------|---------------|--------------|
| Fatty acid composition (relative %) | 16:0 | 11.1 ± 0.76 | 5.3 ± 0.28 | 10.2 ± 0.28 |
| | 16:1 | 0.3 ± 0.01 | 0.2 ± 0.02 | 1.3 ± 0.07 |
| | 18:0 | 4.1 ± 0.39 | 3.3 ± 0.09 | 3.6 ± 0.07 |
| | 18:1 | 24.7 ± 0.71 | 40.9 ± 0.18 | 75.8 ± 0.41 |
| | 18:2 | 53.7 ± 0.94 | 49.7 ± 0.23 | 7.9 ± 0.21 |
| | 18:3 | 6.0 ± 1.16 | 0.2 ± 0.02 | 0.7 ± 0.04 |
| | MUFA/S ^a | 1.64 | 4.78 | 5.59 |
| | PUFA/S ^b | 3.93 | 5.80 | 0.62 |
| | Free fatty acid value (as oleic acid %) | 0.5 ± 0.02 | 0.6 ± 0.03 | 1.4 ± 0.12 |
| | Peroxide value, POV (meq/kg oil) | 0.6 ± 0.30 | 1.7 ± 0.14 | 10.4 ± 0.64 |
| <i>p</i> -Anisidine value, PAV | 0.8 ± 0.19 | 6.9 ± 0.34 | 5.8 ± 0.53 | |
| Induction period (h) by Rancimat (100 °C) | 13.9 ± 0.17 | 11.6 ± 0.04 | 48.3 ± 0.72 | |
| Polyphenols (ppm) | nd ^c | nd | 180.8 | |
| Tocopherols (ppm) | α | 143 ± 2.42 | 266 ± 14.26 | 104 ± 4.07 |
| | β | 0.3 ± 0.05 | 19 ± 3.26 | nd |
| | γ | 425 ± 14.67 | 4.9 ± 7.37 | nd |
| | δ | 116 ± 8.3 | nd | nd |
| | Total | 684 | 290 | 104 |
| Hunter's Color ^d | <i>L</i> | 97.4 ± 0.02 | 97.1 ± 0.03 | 88.7 ± 0.00 |
| | <i>a</i> | -3.6 ± 0.00 | -2.7 ± 0.01 | -13.2 ± 0.00 |
| | <i>b</i> | 8.5 ± 0.02 | 6.5 ± 0.02 | 92.7 ± 0.25 |

^aContent ratio of monounsaturated fatty acids to saturated fatty acids.

^bContent ratio of polyunsaturated fatty acids to saturated fatty acids.

^cnd: not detected.

^d*L* (lightness; 0, dark ~ 100, light); *a* (redness; -, green ~ +, red); *b* (yellowness; -, blue ~ +, yellow).

AOCS Cd 18–90 methods [13], respectively, and the analysis of fatty acid composition by gas chromatography after esterification with 14% BF₃ in methanol. A gas chromatograph was a Younglin M600D gas chromatograph (Younglin Co. Ltd., Anyang, Korea) equipped with a Supelcowax capillary column (30 m × 0.53 mm, 1.0 μm thick; Supelco Inc.) and a flame ionization detector. Temperatures of the oven, the injector, and the detector were 200, 270, and 280 °C, respectively. The nitrogen flow rate was 5 mL/min, and the split ratio was 33:1. Each fatty acid in the chromatogram was identified by comparing the retention times of standard fatty acid methyl esters, and quantified by the peak areas.

Determination of polyphenols and tocopherols in oils

Polyphenols in oils were determined by spectrophotometry using a Folin-Ciocalteu reagent [14]. The oil (10 g) was dissolved in 50 mL *n*-hexane, and the solution was extracted with 20 mL of methanol–water mixture (60:40, v/v) three times. After the evaporation of combined extracts at 40 °C, the residue was redissolved in 5 mL methanol. The aliquot was diluted with distilled water and 0.5 mL Folin-Ciocalteu reagent was added. After 3 min, 1 mL saturated Na₂CO₃ solution was added. The solution was diluted to the volume with distilled water. The absorbance of the solution was measured at 725 nm after 1 h standing at room temperature. Contents of polyphenols in oils were expressed as caffeic acid.

Contents of tocopherols in soybean, sunflower, and olive oils were determined by high performance liquid chromatography (HPLC). The oils were mixed with 5 mL *n*-hexane and filtered through a 0.2 μm PTFE membrane (Millipore, Molsheim, France). The filtrate (20 μL) was injected into a Younglin SP 930D HPLC (Younglin Co. Ltd.). A μ-Porasil column (330 mm × 3.9 mm, 10 μm size; Waters Co., Milford, MA, USA) and a fluorescence detector with an excitation wavelength of 290 nm and emission of 330 nm were used. The mobile phase was 0.2% isopropanol in *n*-hexane (v/v) with a flow rate of 2.0 mL/min. Each tocopherol was identified by comparing with retention times of standard tocopherols, quantified by the calibration curve, and reported as total tocopherols by summing up each tocopherol content.

Data analysis

A Microsoft Excel 2003 (Microsoft Corporation, Seoul, Korea) was used for the statistical treatment of the data. Statistical treatment included the linear regression analysis as well as determination of means and standard deviations.

Results and discussion

Characteristics of soybean, sunflower, and olive oils

Physical and chemical characteristics of soybean, sunflower, and olive oils used in the experiments are shown in Table 1. Soybean, sunflower, and olive oils contained palmitic, palmitoleic, stearic, oleic, linoleic, and linolenic acids. Soybean oil contained higher amount of polyunsaturated fatty acids (PUFA; 59.7%) than sunflower oil (49.9%). Sunflower oil showed higher content ratio of monounsaturated fatty acids to saturated fatty acids (MUFA/S) and polyunsaturated fatty acids to saturated fatty acids (PUFA/S) than soybean oil. The ratios of MUFA/S and PUFA/S of sunflower oil were 4.78 and 5.80, respectively. Olive oil contained low amount of PUFA (8.6%) with oleic acid as a major fatty acid (75.8%), and its MUFA/S and PUFA/S ratios were 5.59 and 0.62, respectively.

Soybean, sunflower, and olive oil contained free fatty acids at 0.5, 0.6, and 1.4%, respectively. Olive oil, which did not go through a refining process, contained higher amount of free fatty acids than soybean and sunflower oils.

POV of soybean, sunflower, and olive oils before oxidation was 0.6, 1.7, and 10.4 meq/kg oil, respectively, which was within the ranges reported by others; POV of sunflower and olive oils were reported as 1.0–2.0 meq/kg [15] and 6.0–14.8 meq/kg [16], respectively. Higher POV of olive oil than those of soybean and sunflower oils could be due to the absence of refining in olive oil processing. List and others reported that 67% of peroxides in soybean oil were removed during the oil refining such as bleaching [17]. PAV of soybean oil was 0.8 and those of olive and sunflower oils were higher, 6.9 and 5.8, respectively.

Induction period determined by Rancimat at 100 °C was 11.6 h in sunflower oil, followed by soybean (13.9 h) and olive oil (48.3 h).

Polyphenols were present only in olive oil at 180.8 ppm. Reported values of total polyphenols in olive oil are widely ranged, 104–516 ppm [15, 18]. Contents of total tocopherols in soybean, sunflower, and olive oils were 684, 290, and 104 ppm, respectively, which were lower than reported values. Soybean and sunflower oils were reported to contain total tocopherols at 950 and 681 ppm, respectively [16]. Refined olive oil contained α-tocopherol at 105 ppm [19]. The difference in the antioxidant contents between our study and others' is thought to be due to differences in species of oilseeds and extraction methods. A major tocopherol in soybean oil was γ-tocopherol (62%) followed by α-tocopherol (21%) and δ-tocopherol (17%), while α-tocopherol was a major form in sunflower oil (92%) and olive oil (100%).

Lightness in color of soybean and sunflower oils was very similar, and olive oil was darker-colored due to the lack of refining. Olive oil showed more greenish and yellowish tint than soybean or sunflower oil. This could be due to chlorophyll and carotenoids in olive oil. Chlorophyll and carotene contents in olive oil were reported as 0.7–27.5 and 1.6–18.1 ppm [20], respectively. Chlorophylls are well-known antioxidants in the oxidation in the dark [21, 22].

Effects of temperature on the autoxidation of soybean, sunflower, and olive oils

POV of soybean, sunflower, and olive oils during autoxidation at 25, 40, 60, and 80 °C in the dark is shown in Figs. 1, 2, and 3, respectively. As the oxidation time and temperature increased, POV of the oils increased. POV increase with the oxidation time in oils showed two distinct

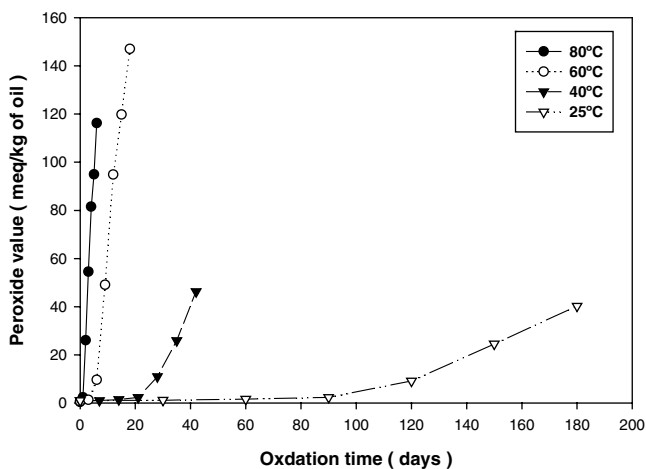


Fig. 1 Effects of oxidation temperature on the peroxide values of soybean oil during oxidation in the dark

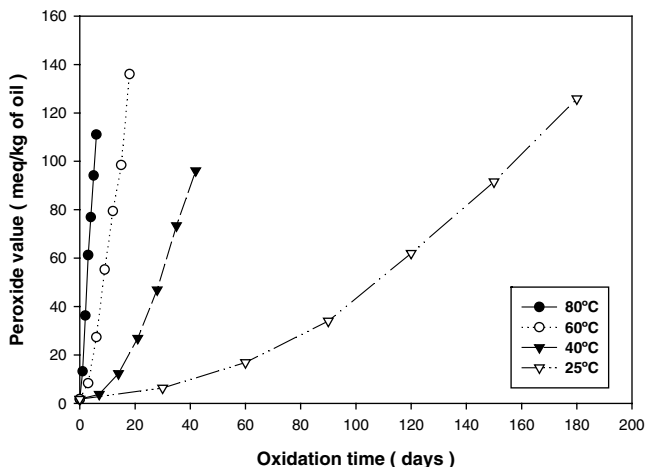


Fig. 2 Effects of oxidation temperature on the peroxide values of sunflower oil during oxidation in the dark

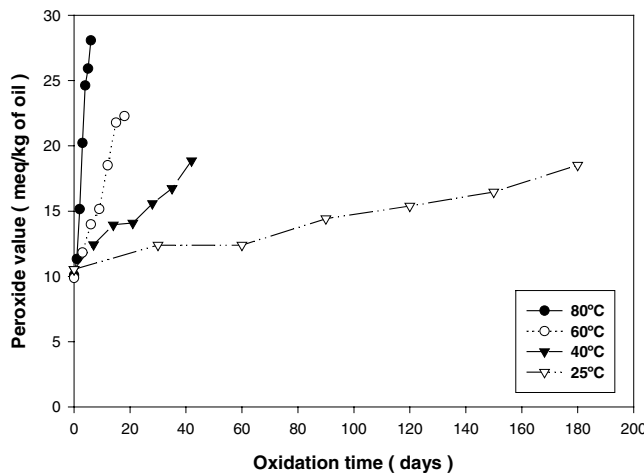


Fig. 3 Effects of oxidation temperature on the peroxide values of olive oil during oxidation in the dark

phases; a phase with a relatively low rate and one having a high rate. A phase having a low rate can be regarded as an induction period, IP [1, 23], and Table 2 shows the IP estimated based on the POV of the oils. IP of soybean, sunflower, and olive oils was 5.3, 3.6, and 7.5 days, respectively, in the oxidation at 60 °C, and was 22.4, 15.3, and 35.3 days at 40 °C. This trend coincides with the result of induction period obtained by Rancimat in Table 1. IP of the oils decreased with oxidation temperature. Sunflower oil showed short IP, and IP of the olive oil was long. This indicates that sunflower oil was more sensitive to the autoxidation than soybean oil, and the olive oil was the most stable in spite of its higher initial amount of free fatty acids and peroxides than sunflower or soybean oil. It was reported that peroxides accelerated the oxidation of soybean oil as determined by volatile compounds formation during storage in the dark [24]. Higher autoxidation stability of olive oil and soybean oil was reported by others [16, 25]. Guillen and Cabo reported lower POV in olive oil than in sunflower oil during storage at 70 °C [25]. Induction periods of tocopherol-stripped soybean and sunflower oil were reported as 0.6 and 0.35 h, respectively, at 100 °C [16].

Temperature dependence of the oil autoxidation can be expressed by the Arrhenius equation [26],

Table 2 Induction periods (days) in the autoxidation of soybean, sunflower, and olive oils

| Oxidation temperature (°C) | Soybean oil | Sunflower oil | Olive oil |
|----------------------------|-------------|---------------|------------------|
| 25 | 96.0 | 87.3 | und ^a |
| 40 | 22.4 | 15.3 | 35.3 |
| 60 | 5.3 | 3.6 | 7.5 |
| 80 | 0.9 | 0.5 | 3.7 |

^aCould not be determined due to the undistinguishable phases.

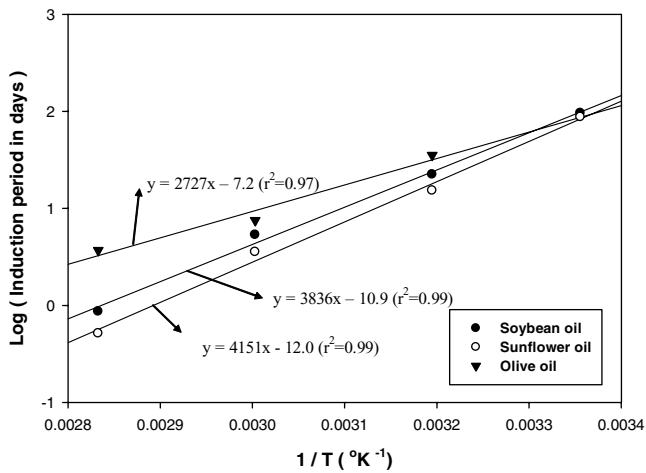


Fig. 4 Arrhenius plot of the autoxidation of oils

log $\tau = E_a/2.303R(1/T) + \text{constant}$ (where, τ , E_a , R , and T are IP, activation energy, gas constant, and absolute temperature, respectively). Fig. 4 shows the Arrhenius plots for the autoxidation of soybean, sunflower, and olive oils. A slope of the Arrhenius equation, $E_a/2.303R$, gives the information on the E_a of the oil autoxidation. Since R is 1.987 cal/mol K, E_a for the autoxidation of soybean, sunflower, and olive

oils was 17.6, 19.0, and 12.5 kcal/mol, respectively. A reaction with high E_a is regarded as temperature-sensitive [27], and the sunflower oil was more temperature-dependent than soybean and olive oils in the autoxidation, in this study. The autoxidation of olive oil was less temperature-dependent.

Changes in PAV of soybean, sunflower, and olive oils during oxidation at 25, 40, 60, and 80 °C in the dark are shown in Table 3. As the oxidation time and temperature increased, PAV of the oils increased due to the aldehydes formation in the oil by decomposition of hydroperoxides. The rate of PAV increase with respect to the oxidation time of oils increased as the oxidation temperature increased, as was expected. It is very interesting that soybean oil whose initial PAV (0.8) was low showed a big increase during oxidation, and this was more clearly shown at high temperature. This might be partly due to high amount of PUFA, especially linolenic acid, in soybean oil and faster decomposition of hydroperoxides at higher temperature. Linolenic acid produces more aldehydes than linoleic acid during oxidation [28]. Olive oil did not show a big increase in PAV during autoxidation, and PAV changes were influenced a little by the oxidation temperature. The results clearly show that the autoxidation of olive oil

Table 3 Effects of oxidation temperature on *p*-anisidine values of soybean, sunflower, and olive oils during oxidation in the dark

| Oxidation temperature (°C) | Oxidation time (days) | Soybean oil | Sunflower oil | Olive oil |
|----------------------------|-----------------------|-------------|---------------|------------|
| 25 | 0 | 0.8 ± 0.19 | 6.9 ± 0.34 | 5.8 ± 0.53 |
| | 30 | 1.3 ± 0.57 | 5.5 ± 0.16 | 3.4 ± 0.12 |
| | 60 | 1.7 ± 0.12 | 5.7 ± 0.30 | 3.2 ± 0.23 |
| | 90 | 1.5 ± 0.12 | 5.9 ± 0.39 | 3.5 ± 0.22 |
| | 120 | 0.9 ± 0.08 | 5.5 ± 0.79 | 2.9 ± 0.14 |
| | 150 | 2.0 ± 0.11 | 5.6 ± 0.51 | 3.2 ± 0.31 |
| | 180 | 2.1 ± 0.31 | 6.1 ± 0.87 | 3.7 ± 0.70 |
| 40 | 0 | 0.8 ± 0.19 | 6.9 ± 0.34 | 5.8 ± 0.53 |
| | 7 | 1.0 ± 0.32 | 7.2 ± 0.10 | 5.4 ± 0.10 |
| | 14 | 1.5 ± 0.01 | 7.4 ± 0.31 | 5.9 ± 0.00 |
| | 21 | 1.5 ± 0.11 | 7.6 ± 0.03 | 6.5 ± 0.42 |
| | 28 | 1.6 ± 0.24 | 7.8 ± 0.08 | 6.7 ± 0.56 |
| | 35 | 1.7 ± 0.02 | 8.0 ± 0.01 | 6.0 ± 0.22 |
| | 42 | 2.4 ± 0.05 | 8.1 ± 0.07 | 7.5 ± 0.27 |
| 60 | 0 | 0.8 ± 0.19 | 6.9 ± 0.34 | 5.8 ± 0.53 |
| | 3 | 1.8 ± 0.08 | 7.4 ± 0.00 | 4.1 ± 0.34 |
| | 6 | 2.2 ± 0.11 | 7.8 ± 0.25 | 4.5 ± 0.00 |
| | 9 | 5.9 ± 0.05 | 7.8 ± 0.16 | 5.0 ± 0.17 |
| | 12 | 11.1 ± 0.40 | 8.4 ± 0.68 | 5.3 ± 0.02 |
| | 15 | 17.1 ± 0.39 | 9.7 ± 0.03 | 5.6 ± 0.37 |
| | 18 | 22.8 ± 0.61 | 10.8 ± 0.86 | 6.2 ± 0.11 |
| 80 | 0 | 0.8 ± 0.19 | 6.9 ± 0.34 | 5.8 ± 0.53 |
| | 1 | 1.6 ± 0.08 | 7.7 ± 0.34 | 7.5 ± 0.92 |
| | 2 | 5.3 ± 0.06 | 8.6 ± 0.35 | 7.9 ± 0.32 |
| | 3 | 11.8 ± 0.57 | 10.2 ± 0.06 | 7.8 ± 1.27 |
| | 4 | 19.4 ± 0.19 | 12.7 ± 0.61 | 7.6 ± 0.77 |
| | 5 | 25.4 ± 0.39 | 16.0 ± 0.02 | 7.7 ± 0.05 |
| | 6 | 36.1 ± 0.79 | 23.6 ± 0.52 | 8.1 ± 0.04 |

Table 4 Polyphenol contents (ppm) of olive oil during oxidation in the dark

| Oxidation temperature (°C) | Oxidation time (days) | Polyphenols (retention %) ^a |
|----------------------------|-----------------------|--|
| 25 | 0 | 180.8 ± 8.8 (100) |
| | 30 | 167.1 ± 6.9 (92.4) |
| | 60 | 159.4 ± 2.9 (88.1) |
| | 90 | 167.8 ± 7.0 (92.8) |
| | 120 | 174.2 ± 6.0 (96.3) |
| | 150 | 150.1 ± 5.2 (83.0) |
| 40 | 180 | 160.2 ± 3.7 (88.6) |
| | 0 | 180.8 ± 8.8 (100) |
| | 7 | 168.5 ± 7.4 (93.2) |
| | 14 | 147.7 ± 9.1 (81.7) |
| | 21 | 146.7 ± 7.0 (81.1) |
| | 28 | 151.2 ± 4.3 (83.6) |
| 60 | 35 | 146.7 ± 10.5 (81.1) |
| | 42 | 138.0 ± 7.1 (76.3) |
| | 0 | 180.8 ± 8.8 (100) |
| | 3 | 153.3 ± 13.8 (84.8) |
| | 6 | 144.3 ± 23.6 (79.8) |
| | 9 | 143.5 ± 32.0 (79.4) |
| 80 | 12 | 135.6 ± 9.7 (75.0) |
| | 15 | 134.0 ± 14.3 (74.1) |
| | 18 | 131.3 ± 6.6 (72.6) |
| | 0 | 180.8 ± 8.8 (100) |
| | 1 | 139.6 ± 6.6 (77.2) |
| | 2 | 138.9 ± 10.1 (76.8) |
| | 3 | 133.9 ± 2.5 (74.1) |
| | 4 | 113.6 ± 8.1 (62.8) |
| | 5 | 113.6 ± 8.2 (62.8) |
| | 6 | 102.7 ± 7.6 (56.8) |

^aResidual polyphenols in %.

was less temperature-dependent than soybean or sunflower oil.

Effects of temperature on the degradation of polyphenols and tocopherols during the autoxidation of oils

Olive oil originally contained polyphenols at 180.8 ppm in addition to tocopherols, as shown in Table 4. Polyphenols could contribute to the high autoxidative stability of olive oil. Phenolic compounds are powerful inhibitors in lipid oxidation, breaking the chain reaction and chelating metal ions [29–31]. Velasco and Dobarganes [32] reported synergistic antioxidation of α -tocopherol and phenolic compounds in olive oil. Contents of polyphenols in olive oil decreased from 180.8 to 160.2 ppm after 180-day oxidation of the oil at 25 °C, and to 138 ppm after 6-week oxidation at 40 °C, to 131.3 ppm after 18-day oxidation at 60 °C, and to 102.7 ppm after 6-day oxidation at 80 °C due to degradation. This clearly shows that degradation of polyphenols became fast at high oxidation temperature of oil.

Contents of tocopherols in soybean, sunflower, and olive oils during oxidation at 25, 40, 60, and 80 °C in the dark are shown in Table 5. Soybean oil contained high amount of tocopherols, which could contribute to the oxidative stability during storage in the dark. Tocopherols can decrease the lipid oxidation by donating the phenolic hydrogen to lipid peroxy radicals [33] or slowing down the decomposition of hydroperoxides [34]. Contents of tocopherols in soybean oil decreased from 687.5 to 464.2 ppm after the oil oxidation at 25 °C for 180 days due to their degradation. Degradation of tocopherols during the oil oxidation was also shown in sunflower and olive oils. It was reported that 60% of tocopherols present in rapeseed oil was degraded after 5-week autoxidation at 40 °C [35]. Yosida and others reported 40% degradation of tocopherols in safflower oil during 20 min microwave heating [36].

Degradation rates of tocopherols in oils, as determined on the basis of percentage of retained tocopherols, increased as the oil oxidation temperature increased as shown in Table 6. Degradation rates of tocopherols during the autoxidation of soybean oil at 25, 40, 60, and 80 °C were 2.1×10^{-3} , 1.3×10^{-2} , 8.9×10^{-2} , and 3.2×10^{-1} %/day, respectively, which were higher than those of sunflower and olive oils. Olive oil whose tocopherol content was low showed slow degradation of tocopherols. The degradation rates of tocopherols in olive oil were 5.0×10^{-4} , 3.6×10^{-3} , 1.9×10^{-2} , and 2.6×10^{-1} %/day at 25, 40, 60, and 80 °C, respectively. Slow degradation of tocopherols in olive oil might be partly due to polyphenols. Pellegrini and others reported the stabilization of α -tocopherol by polyphenols in extra virgin olive oil [10].

Table 6 also shows that the degradation rate of tocopherols increased with the oil oxidation temperature. An Arrhenius plot of the logarithm of tocopherols degradation rate versus reciprocal of the oxidation temperature yielded a good straight line as shown in Fig. 5. E_a for the degradation of tocopherols calculated from Arrhenius equations was 19.2, 20.0, and 23.0 kcal/mol, in soybean, sunflower, and olive oils, respectively. This indicates that the degradation of tocopherols was more temperature-sensitive in olive oil than in sunflower and soybean oils.

Table 7 shows relationships between the antioxidants degradation rate and the autoxidation of oils as expressed by IP calculated on the basis of POV. As the degradation rates of antioxidants increased, the IP in the autoxidation of oils decreased. Tocopherol degradation rates affected the IP with a correlation coefficient of 0.92, 0.86, and 0.78 for soybean, sunflower, and olive oils. Correlation coefficient between polyphenols degradation rates and the IP in olive oil was 0.82. In olive oil, the gradient of $\ln[IP]$ with respect to polyphenols degradation rate (-22.5) was higher than

Table 5 Total tocopherol contents (ppm) of soybean, sunflower, and olive oils during oxidation in the dark

| Oxidation temperature (°C) | Oxidation time (days) | Total tocopherol contents (retention %) ^a | | |
|----------------------------|-----------------------|--|----------------------|---------------------|
| | | Soybean oil | Sunflower oil | Olive oil |
| 25 | 0 | 687.5 ± 25.4 (100) | 290.0 ± 14.3 (100.0) | 128.5 ± 4.1 (100) |
| | 30 | 630.0 ± 9.4 (91.6) | 264.8 ± 0.3 (91.3) | 128.5 ± 1.5 (100) |
| | 60 | 580.3 ± 20.4 (84.4) | 252.5 ± 20.0 (87.1) | 121.5 ± 6.7 (94.6) |
| | 90 | 573.2 ± 25.7 (83.4) | 241.3 ± 13.5 (83.2) | 119.1 ± 4.5 (92.7) |
| | 120 | 543.8 ± 37.92 (79.1) | 230.9 ± 3.1 (79.6) | 121.3 ± 2.2 (94.4) |
| | 150 | 491.0 ± 5.0 (71.5) | 221.8 ± 3.4 (76.5) | 119.8 ± 2.8 (93.2) |
| 40 | 180 | 464.2 ± 45.9 (67.5) | 221.3 ± 2.4 (76.3) | 118.4 ± 6.8 (92.1) |
| | 0 | 687.5 ± 25.4 (100) | 290.0 ± 14.3 (100.0) | 128.5 ± 4.1 (100) |
| | 7 | 630.0 ± 31.8 (91.6) | 274.3 ± 6.7 (94.6) | 128.5 ± 6.2 (100) |
| | 14 | 618.4 ± 15.6 (89.9) | 259.2 ± 19.4 (89.4) | 126.5 ± 7.8 (98.4) |
| | 21 | 606.0 ± 3.5 (88.2) | 245.3 ± 18.6 (84.6) | 120.7 ± 5.8 (93.9) |
| | 28 | 590.2 ± 34.7 (85.9) | 244.0 ± 11.3 (84.1) | 115.5 ± 1.9 (89.9) |
| 60 | 35 | 521.0 ± 50.1 (75.8) | 226.7 ± 14.9 (78.2) | 114.6 ± 3.9 (89.2) |
| | 42 | 347.3 ± 1.8 (50.5) | 214.1 ± 9.8 (73.8) | 112.7 ± 2.8 (87.7) |
| | 0 | 687.5 ± 25.4 (100) | 290.0 ± 14.3 (100) | 128.6 ± 4.1 (100) |
| | 3 | 556.7 ± 4.7 (81.0) | 276.9 ± 11.4 (95.5) | 119.6 ± 1.7 (93.0) |
| | 6 | 518.3 ± 9.6 (75.4) | 252.0 ± 4.0 (86.9) | 116.4 ± 6.5 (90.6) |
| | 9 | 391.3 ± 58.5 (56.9) | 241.5 ± 8.5 (83.3) | 112.4 ± 1.0 (87.5) |
| 80 | 12 | 313.2 ± 58.5 (45.6) | 220.8 ± 0.0 (76.1) | 100.7 ± 1.5 (78.3) |
| | 15 | 214.2 ± 18.6 (31.2) | 144.2 ± 12.8 (49.7) | 96.6 ± 3.5 (75.2) |
| | 18 | 126.1 ± 0.0 (18.3) | 4.0 ± 0.0 (1.4) | 91.7 ± 1.4 (71.4) |
| | 0 | 687.5 ± 25.4 (100) | 290.0 ± 14.3 (100) | 128.5 ± 4.1 (100.0) |
| | 1 | 526.3 ± 61.6 (76.6) | 250.2 ± 19.3 (86.3) | 117.8 ± 1.8 (91.7) |
| | 2 | 421.0 ± 5.5 (61.2) | 225.2 ± 6.1 (77.7) | 95.8 ± 3.5 (74.5) |
| | 3 | 317.8 ± 17.4 (46.2) | 143.0 ± 39.1 (49.3) | 78.0 ± 1.3 (60.7) |
| | 4 | 226.0 ± 17.4 (32.9) | 100.1 ± 5.7 (34.5) | 54.7 ± 4.2 (42.5) |
| | 5 | 157.9 ± 12.6 (23.0) | 65.6 ± 18.6 (22.6) | 34.5 ± 4.8 (26.8) |
| | 6 | 98.4 ± 8.9 (14.3) | 2.2 ± 0.0 (0.8) | 10.7 ± 2.4 (8.3) |

^aResidual tocopherols in %.

Table 6 Degradation rate of tocopherols in oils during the oil oxidation in the dark

| Oxidation temperature (°C) | Degradation rate of tocopherols (%/day) ^a | | |
|----------------------------|--|---------------------|---------------------|
| | Soybean oil | Sunflower oil | Olive oil |
| 25 | 0.0021 | 0.0015 | 0.0005 |
| 40 | 0.0126 | 0.0069 | 0.0036 |
| 60 | 0.0893 | 0.0402 ^b | 0.0188 |
| 80 | 0.3165 | 0.3039 ^c | 0.2596 ^c |

^aDegradation rate was determined from a slope (*a*) of the regression equation, $\ln[\text{tocopherol retention, \%}] = a \times [\text{oxidation time, days}] + b$.

^bData of the 18th day were omitted due to a big deviation from the regression line.

^cData of the 6th day were omitted due to a big deviation from the regression line.

that of $\ln[\text{IP}]$ with tocopherols degradation rate (-6.2), indicating a higher correlation between IP and polyphenols than between IP and tocopherols. This strongly supports a protection of tocopherols from degradation by polyphenols during the autoxidation of olive oil as reported by Pellegrini et al. [10].

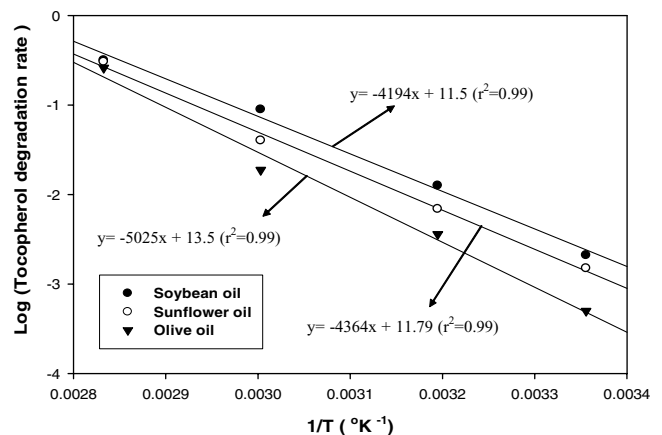


Fig. 5 Arrhenius plot for the degradation of tocopherols in soybean, sunflower, and olive oils during oxidation in the dark

The results clearly indicated that the autoxidation of sunflower oil was temperature-sensitive, possibly due to both low amount of tocopherols and their relatively high degradation rate during the oil oxidation in the dark.

Table 7 Linear regression analysis between the degradation rate (%/day) of antioxidants and IP (days) based on POV during the oil oxidation in the dark

| Oxidation temperature (°C) | Soybean oil | | Sunflower oil | | Olive oil | | |
|----------------------------|-------------------------------|--------|-------------------------------|--------|-------------------------------|-------------------------------|--------|
| | [Tocopherol degradation rate] | ln[IP] | [Tocopherol degradation rate] | ln[IP] | [Tocopherol degradation rate] | [polyphenol degradation rate] | ln[IP] |
| 25 | 0.0021 | 4.564 | 0.0015 | 4.469 | | | |
| 40 | 0.0126 | 3.109 | 0.0069 | 2.728 | 0.0036 | 0.0054 | 3.564 |
| 60 | 0.0893 | 1.668 | 0.0402 | 1.281 | 0.0188 | 0.0154 | 2.015 |
| 80 | 0.3165 | −0.105 | 0.3039 | −0.693 | 0.2596 | 0.0825 | 1.308 |
| Gradient ^a | −12.6 | | −13.0 | | −6.2 | −22.5 | |
| r ^b | 0.92 | | 0.86 | | 0.78 | 0.82 | |

^aSlope (*a*) of the regression line, $\ln[\text{IP}] = a \times [\text{antioxidant degradation rate}] + b$.

^bCorrelation coefficient of the regression line.

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