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RESEARCH OF EFFECTIVE METHODS FOR ASSESSING THE QUANTITY OF OXIDIZED PRODUCTS IN VEGETABLE OILS

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Annotation: Four vegetable oils with typical fatty acid compositions were chosen to determine their indicators of lipid oXidation under the conditions of accelerated oXidation. Good linear correlations were observed between the total nonpolar carbonyl amount and the total oXidation value (TOTOX, R2 = 0.89−0.97) or peroXide value (POV, R2 = 0.92−0.97) during 35 days of accelerated oXidation.

***Keywords*:** nonpolar aldehydes/ketones, oxidation indicator, total oxidation value, fatty acid, oil oxidation.

It is well-known that hydroperoxides are the primary products in lipid oxidation, but they are unstable and can be further decomposed into many secondary compounds.1 Beltran et al1. detected 22 compounds including 7 nonpolar aldehydes from oxidized almond oils (100 °C for 20 days) by HS-SPME-GC- MS. Using the same technique, Poyato et al. analyzed 21 nonpolar aldehydes from 7 vegetable oils (180 °C for 4 h), and Petersen et al. identified a total of 55 volatile oxidation compounds from rapeseed oil (40 °C for 26 days). Additionally, 32 toxic oxygenated α,β-unsaturated aldehydes in virgin olive, sunflower, and virgin linseed oils (190 °C for 20 h) were found by Guillen and Uriarte. Their team also analyzed many types of secondary products in corn oil and sunflower oil stored at room temperature with limited air and found that themost numerous group of volatiles was the nonpolar aldehydes.

On the other hand, Seppanen and Saari Csallany8 determined simultaneously 17 nonpolar and 13 polar lipophilic aldehydes from soybean oil (185 °C for 8 h) using HPLC combined with 2,4-dinitrophenylhydrazine (DNPH) derivatization. Zhu et al.9 identified nine characteristic nonpolar aldehydes/ketones in virgin olive oil (heated to 45 °C) by UHPLC-MS and found this method provided comparable linearity and repeatability with SPME-GC. Reasonably, GC/HPLC-MS has become the common method for analyzing carbonyl compounds in oil samples, also in other lipid matrices such as ham, seafood, and biological material.

Generally, the above studies mainly focused on the separation and identification of secondary lipid oxidation products under high-temperature condition. Although high temperature can provide energy to break double bonds in oil molecules more easily than low temperature,13 autoxidation of lipid at room temperature actually is also the main cause of deterioration. The Schaal oven test at 60−70 °C could be used to simulate the oxidation process at room temperature.14 In addition, it was reported that there were some diff erences in the aldehyde compositions of oleic, linoleic, and linolenic acids during oxidation.15,16 The structure of the fatty acids, especially the position and number of double bonds in

1 Choe, E.; Min, D. B. Mechanisms and factors for edible oil oxidation. Compr. Rev. Food Sci. Food Saf. 2016, 5, 169−186.

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them, is the main cause. Thereby, oils having different fatty acid compositions may show different oxidation patterns[2].

The main objectives of this study therefore were to (a) monitor the oxidation of vegetable oils with typical fatty acid compositions with limited air; (b) compare the types and amounts of nonpolar aldehyde/ketone products from these oils during accelerated oxidation; and (c) establish models from peroxide value, p-anisidine value, and aldehyde products to explore good and sensitive oxidation indicators for the evaluation of oil oxidation.

Oil Samples. The oils chosen for this study were palm oil, camellia oil, sunflower oil, and perilla oil with different fatty acid compositions. All four were purchased from local shops (Nanchang, China), and they complied with the legal requirements in China.

Reagents and Standards. Standard solutions of the following carbonyl-DNPHs were obtained as reference solutions in acetonitrile (15 μg/mL of each carbonyl) from Supelco Inc. (TO11/IP-6A Mix, Supelco Inc., Bellefonte, PA, USA): formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexaldehyde, and 2,5-dimethylbenzalde- hyde. Standard fatty acid methyl esters (FAME, GLC-463) were obtained from Nu-Chek Prep Inc. (Elysian, MN, USA). Tocopherol standards (α, β, γ, and δ) were purchased from Sigma (Sigma Chemicals, Shanghai, China). Methanol, n-hexane, acetonitrile, and isopropanol (HPLC grade) were purchased from Merck (Darmstadt, Germany). Water was purified using a Milli-Q system from Millipore (Bedford, MA, USA). All other solvents were of analytical reagent grade. Potassium hydroxide, phenolphthalein, ethyl alcohol, acetic acid, isooctane, soluble starch, potassium iodide, sodium thiosulfate, and p-anisidine were of analytical grade.

Table 1. Initial Fatty Acid Composition (Area %), Tocopherol Content (mg/kg), Acid Value (mg KOH/g), Peroxide Value (mequiv O2/kg), and p-Anisidine Value of Vegetable Oila

sample	palm oil	camellia oil	sunflower oil	perilla oil
palmitic acid	38.23 ± 1.18a	7.80 ± 0.01b	6.27 ± 0.02c	6.02 ± 0.10c
stearic acid	4.49 ± 0.07a	2.42 ± 0.07d	3.94 ± 0.07b	2.76 ± 0.07c
oleic acid	43.05 ± 0.88b	80.14 ± 0.08a	29.50 ± 0.03c	21.97 ± 0.25d
linoleic acid	10.33 ± 0.35c	6.98 ± 0.01d	55.24 ± 0.11a	12.73 ± 0.12b
α-linolenic acid	0.14 ± 0.01b	0.22 ± 0.01b	0.07 ± 0.01b	54.37 ± 0.29a
total SFA	44.52 ± 1.25a	10.36 ± 0.05bc	11.46 ± 0.07b	9.17 ± 0.25c
total MUFA	43.41 ± 0.88b	80.89 ± 0.09a	29.75 ± 0.05c	22.28 ± 0.14d
total PUFA	10.51 ± 0.35c	7.22 ± 0.03d	55.55 ± 0.11b	67.18 ± 0.41a
α-tocopherol	191.1 ± 2.8b	199.0 ± 3.5b	1106 ± 39a	37.22 ± 4.98c
β-tocopherol	nd	nd	nd	nd
γ-tocopherol	2.26 ± 0.07c	nd	7.63 ± 0.23b	128.3 ± 2.3a
δ-tocopherol	nd	nd	nd	19.51 ± 0.20
total tocopherol	193.4 ± 2.8b	198.7 ± 3.5b	1113 ± 39a	185.0 ± 3.8b
AV	0.06 ± 0.02b	0.04 ± 0.02b	0.04 ± 0.01b	0.72 ± 0.04a
POV	5.11 ± 0.57a	2.89 ± 0.65b	2.16 ± 0.38b	0.41 ± 0.06c
p-AV	4.07 ± 0.69a	2.15 ± 0.01b	3.81 ± 0.05a	0.22 ± 0.01c

2 Poyato, C.; Ansorena, D.; Navarro-Blasco, I.; Astiasarań, I. A novel approach to monitor the oxidation process of different types of heated oils by using chemometric tools. Food Res. Int. 2014, 57, 152− 161.

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[a]Data are mean values ± SD, n = 3. nd, peak not detected under this analysis condition; SFA, saturated fatty acid; MUFA, monounsaturated fatty acid; PUFA, polyunsaturated fatty acid; AV, acid value; POV, peroxide value; p-AV, p-anisidine value. Values followed by the same letter in the same row are not significantly different ($p < 0.05$)3.

In summary, in this work, palm, camellia, sunflower, and perilla oils were selected in oxidation assays in consideration of their typical fatty acid compositions. Camellia (20 types), sunflower (19 types), and palm (19 types) oils were found to have more types of nonpolar carbonyls than perilla oil (14 types) on the 35th day. Besides, alkanal contained a higher proportion of nonpolar carbonyl than alkenal and alkadienal in the four oils. Interestingly, the four oils had their own characteristic carbonyl products, which could be used as markers to monitor the oxidation state of oils.

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