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Monitoring the oxidative stability of virgin coconut oil during oven test using chemical indexes and FTIR spectroscopy

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Abstract: This study was conducted to evaluate the oxidative stability of virgin coconut oil (VCO) during oven test. VCO with and without antioxidants were subjected to oven test at 63°C over a 40 day-storage. The chemical parameters namely peroxide value (PV) and specific absorptivity of conjugated dienes (CDs) and conjugated trienes (CTs) were used to asses VCO stability. VCO samples treated with the mixture of butylated hydroxyanisole and butylated hydroxytoluene (BHA/BHT of 200 mg/kg) and citric acid (CA, 100 mg/kg) have lower PVs than control (VCO without antioxidants) and other treatments. The specific absorbtivities of CDs and CTs of VCO were also decreased due to the addition of antioxidants. In addition, Fourier transform infrared (FTIR) spectroscopy was used to monitor the peak changes during the thermal oxidation. The prominent peak change observed during thermal oxidation of VCO was at frequency 1739 cm^{-1} which corresponded to the carbonylic compounds (esters, aldehydes, ketones, lactones) resulted from the hydroperoxide decompositions during oven test.

Keywords: oxidative stability, virgin coconut oil, antioxidants, chemical indexes, FTIR spectroscopy

Introduction

Fats and oils are very important in the human diet due to the high contents of essential fatty acids, which are necessary for the appropriate development of human tissues (Moya Moreno et al., 1999). Virgin coconut oil (VCO), a relative new comer in the industry of fats and oils, is growing rapidly in the scientific field (Manaf et al., 2007). VCO contains a large amount of medium-chain fatty acids such as capric, caproic and caprylic acids which were also investigated to have antimicrobial and antiviral effects (Villarino et al., 2007). It has been claimed that VCO has several beneficial health effects. Nevin and Rajamohan (2004) reported that VCO lowered total cholesterol, triglycerides, phospholipids, low density lipoprotein (LDL) and very low density lipoprotein (VLDL) cholesterol levels and increased high density lipoprotein (HDL) cholesterol in serum and tissues.

It is generally known that fats and oils can deteriorate during storage in an oxidizing atmosphere, which is known as lipid oxidation. Lipid oxidation is probably the most important factors affecting the shelf life of edible oils. The hydroperoxides produced by lipid oxidation can decompose into various smaller molecules such as aldehydes, ketones, alcohols, and carboxylic acids. Some of these volatile products influence flavor, even at very low concentrations, in which both the oil and the food prepared from it become unpalatable (Richardsa et al., 2005). Lipid oxidation not only produces rancid flavor, but also can lower the nutritional value of food by the formation of oxidation products, which may play a role in the development of disease and can be harmful to human (Muik et al., 2005). Therefore, the evaluation of oxidative stability is a key factor in developing the new oil for food applications.

The oil stabilities during storage or upon heating are vital parameter for ensuring that oil appears the good performance at elevated temperature. Oxidation of unsaturated fatty acids is one of the major causes in the development of off-flavor compounds and in the reduction of nutritional value of food products (Hemalatha, 2007). During the thermal treatments, triglycerides in the oil can get a series of chemical reactions, namely hydrolysis, oxidation, isomerization, and polymerization, caused by the high temperature and the absorption of oxygen and water (Kowalski, 1991).

Several methods have been used to evaluate

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the extent of oxidative deterioration, which are related to the measurement of the concentration of primary or secondary oxidation products. The most frequently used are peroxide value (PV) and specific absorptivity in ultraviolet region at 232 and 270 nm (Frankel, 1998). PV is related to the concentration of hydroperoxide, meanwhile the specific absorptivity at 232 and 270 nm measures the contents of conjugated dienes (CDs) and conjugated trienes (CTs).

The oxidative deterioration of edible oils can be retarded by antioxidants, the main additives used to protect the quality of oil. Synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), are commonly added to oils in order to retard or prevent the oxidative changes during storage due to their effectiveness (Wanasundara and Shahidi, 1994).

Henna Lu and Tan (2009) have investigated the thermal stability of VCO at 190°C upon 40-day storage. The changes in fatty acid composition, FTIR spectra, iodine value and total phenolic content were determined throughout the period of study. However, the authors did not evaluate PV as well as CDs and CTs which are representative to primary oxidation products. Therefore, this study reported the oxidative stability of VCO during oven test (63°C) for 40-day storage period by assessing some chemical indexes, namely PV and the specific absorptivity of CDs and CTs. Furthermore, the change of FTIR spectra of oils and those treated with antioxidants was also highlighted.

Materials and Methods

Samples

Virgin coconut oil (VCO) was obtained from the local market in Jogjakarta, Indonesia. BHA and BHT were obtained from Sigma. Citric acid (CA) was purchased from E. Merck. All of the reagents and solvents used were of analytical reagent grade.

Sample preparation

Initially, VCO contained no added antioxidants (control). Furthermore, oils were directly added with the mixture of antioxidants of BHA/BHT, each at concentration of 100 mg kg^{-1} (BHA/BHT of 200 mg kg^{-1}), BHA/BHT at 200 mg kg^{-1} in the combination with CA at 100 mg kg^{-1}, and CA alone at concentration of 100 mg kg^{-1} before being subjected to oven test.

Oven test

Three samples (20 g of each oil treatment) were placed in a separate 50 mL open beakers (4 cm diameter and 6 cm height) and held in an oven (Memmert, Germany) at 63±1°C for up to 1, 2, 3, 5, 10, 15, 20, 30 and 40 days. After each storage period, oil samples were immediately analyzed. The temperature of 63°C was used as a rapid method to simulate the storage in real conditions (Besbes et al., 2004).

Chemical analyses

Lipid oxidation product of CDs and CTs was determined by specific absorptivity values at 232 and 270 nm, as described by Besbes et al. (2004) using UV-Vis spectrophotometer U-2810 (Hitachi, Tokyo, Japan). Oil samples were diluted in isooctane, and the absorbances obtained were used for calculating the specific absorptivity ($E^{1\%}_{1cm}$) as follows:

$$E^{1\%}_{1cm} = \frac{A_\lambda}{(c_L \times l)}$$

where $E^{1\%}_{1cm}$ is the specific absorptivity, A_λ is the absorbance measured at either 232 nm (for CDs) or 270 nm (for CTs), c_L is the concentration of the oil solution in g/100 ml, and 1 represents the path length of the cuvette in cm (Pegg 2005).

Acid value (Ca 5a-40), peroxide value (Cd 8-53), and iodine value (Cd 1d-92) were determined according to AOCS (1996) methods. Fatty acid compositions were determined according to Rohman and Che Man (2009).

FTIR studies

Absorption spectra of all oil samples were measured on a FTIR spectrometer (A Nicolet 6700 from Thermo Nicolet Corp., Madison, WI) using a deuterated triglycine sulphate (DTGS) as a detector and a KBr/Germanium as beam splitter, interfaced to Computer operating under Windows-based, and connected to software of the OMNIC operating system (Version 7.0 Thermo Nicolet). The rest procedure can be seen in our previous paper (Rohman and Che Man, 2010).

Results and Discussion

Quality of VCO

VCO used in this study has good initial quality. The free fatty acid (FFA) value obtained was relatively low, i.e 0.16±0.002 indicating that VCO has good quality, because FFA is responsible for undesirable favor and aroma in oils. FFA is formed by hydrolytic rancidity, which is the hydrolysis of an ester by lipase or moisture. The used VCO has iodine

Table 1. Chemical properties of virgin coconut oil (VCO)

Parameter†	
Acid value (% FFA as lauric acid)	0.16 ± 0.002
Iodine value-Wijs (g iodine per 100 g oil)	6.85 ± 0.098
Peroxide value (meq/kg oil)	0.42 ± 0.009
Fatty acid composition (% area)	
C6:0	0.06 ± 0.002
C8:0	7.73 ± 0.052
C10:0	6.59 ± 0.076
C12:0	50.01 ± 1.147
C14:0	19.26 ± 0.854
C16:0	10.01 ± 0.629
C18:0	4.81 ± 0.041
C18:1	0.90 ± 0.008
C18:2	1.05 ± 0.03
C18:3	0.10 ± 0.01

†Each parameter is from at least three replicates. Standard deviation (SD) is given after ±

value of 6.85 iodine/100 g oil and peroxide value of 0.42±0.009 meq/kg oil, respectively (Table 1). Oils with iodine value more than 130 (g iodine per 100 g) such as safflower or sunflower oils stored in the dark exhibited a significantly shorter induction period than coconut or palm kernel oils whose iodine values are less than 20 (Tan et al., 2002). The fatty acid composition of VCO showed that VCO had a reasonably high content of saturated fatty acids, especially lauric acid (50.01±1.147%) compared with unsaturated fatty acids. The low degree of unsaturation leads to the high resistance to oxidative rancidity (Onyeike and Acheru 2002).

Peroxide value

Peroxide value (PV) is a common method used to measure lipid oxidation, and is suitable for measuring the peroxide formation in early stages of oxidation. The effects of antioxidants on PV of VCO during oven test for 40-day storage were shown in Figure 1. PV of the oils increased during storage (Figure 1). All VCO samples (control and that added with antioxidants) showed a gradual increase in PV. The PVs of control oils and those treated with citric acid (CA) became higher. Samples treated with BHA/BHT with or without CA significantly decreased the PV values after 40 day-storage at 63°C than control samples. BHA and BHT can act as primary antioxidants and its combination showed the synergistic effects. CA is often added to oil in order to reduce its oxidation during storage before being processed (Choe and Min 2006).

Determination of conjugated dienes (CDs) and conjugated trienes (CTs)

The formation of peroxides is concurrent with conjugation of double bonds in polyunsaturated fatty acids, which can be measured using the specific absorptivity of CDs and CTs at 232 and 270 nm in the UV spectrum (Wanasundara et al., 1995). The detection of CDs and CTs in unsaturated lipids is a sensitive assay, but the magnitudes of changes in absorption are not easily related to the extent of oxidation. However, during the early stages of oxidation, the increase in UV absorption due to the formation of CDs and CTs is proportional to the uptake of oxygen and to the generation of peroxides. For this reason, the content of CDs and CTs can serve as a relative measurement of oxidation (Pegg, 2005).

Figure 2 showed the specific absorptivity values of CDs and CTs of VCO samples (control and that added with antioxidants) during storage period for 40 days. All VCO samples revealed the increase of specific absorptivity values of CDs and CTs with time. The addition of antioxidants in the oils lowered these values (Figure 2). The gradual increase of VCO samples during oven test suggested that VCO was resistant to oxidation. This can be explained by two reasons. Firstly, the used VCO has low level of polyunsaturated fatty acid (PUFA) such as linoleic (C18:2) and linolenic acids (C18:3). The studied VCO contained monounsaturated fatty acid (MUFA) of oleic acid (C18:1) and saturated fatty acid (SFA) as shown in Table 1. PUFA is more prone to oxidation

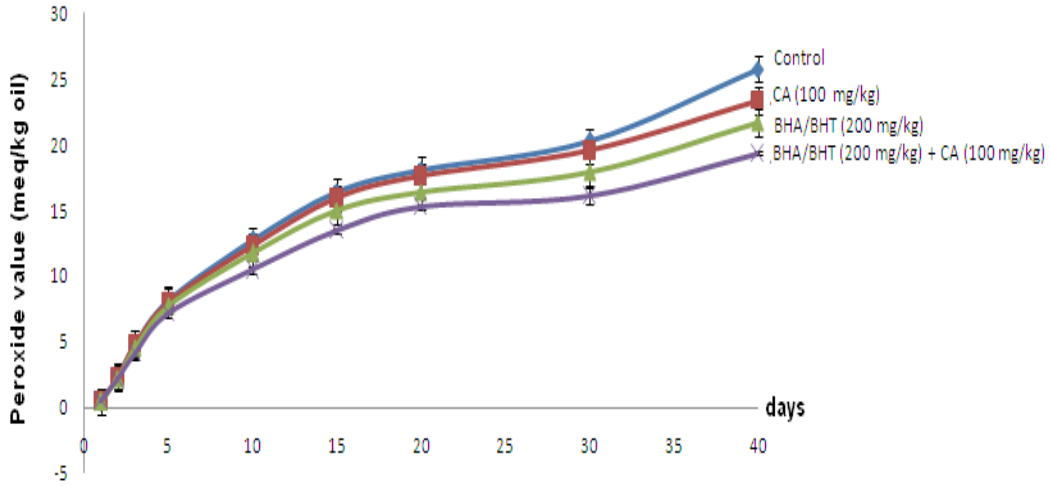

Figure 1. Peroxide values of VCO during oven test for 40 days.

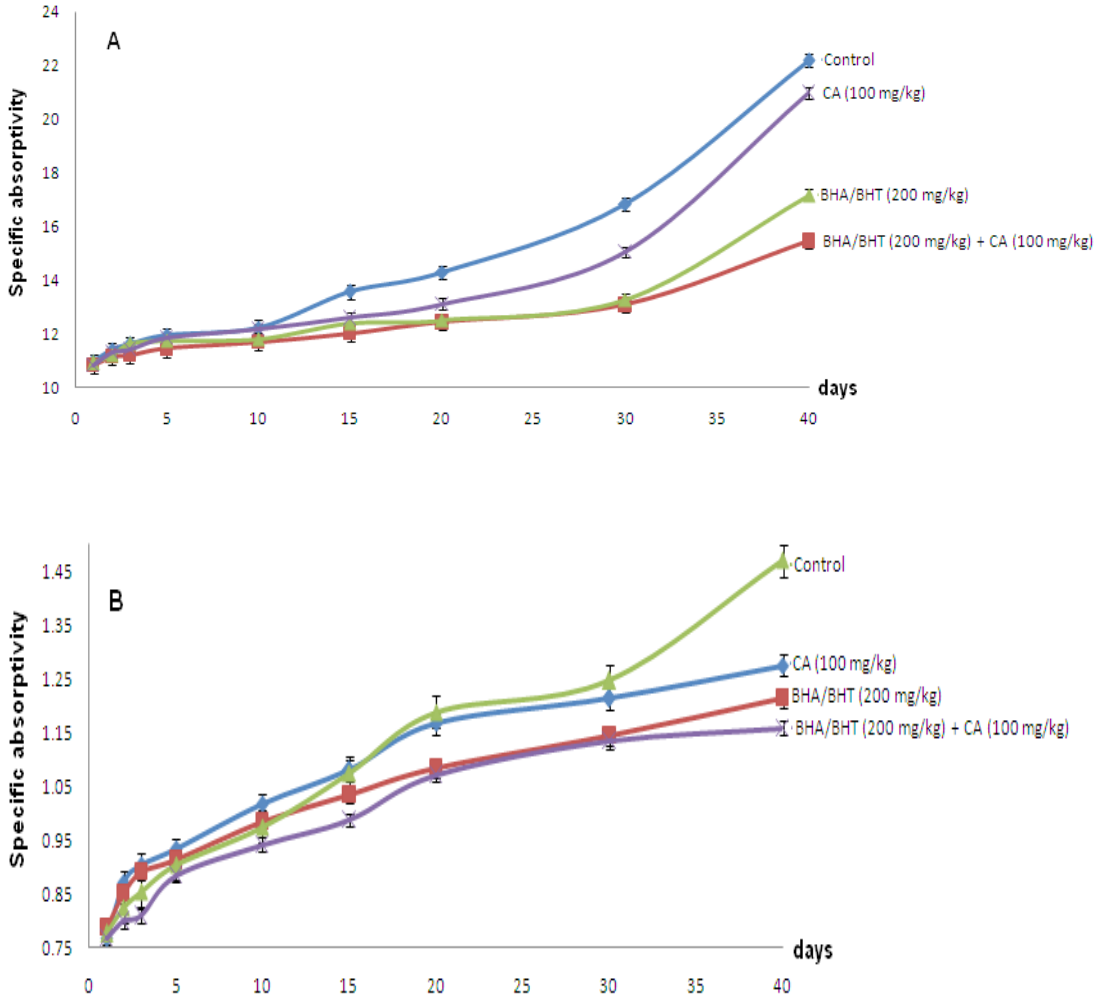

Figure 2. The relationship between the specific absorptivity values of CDs (A) and CTs (B) during oven test over 40-day storage

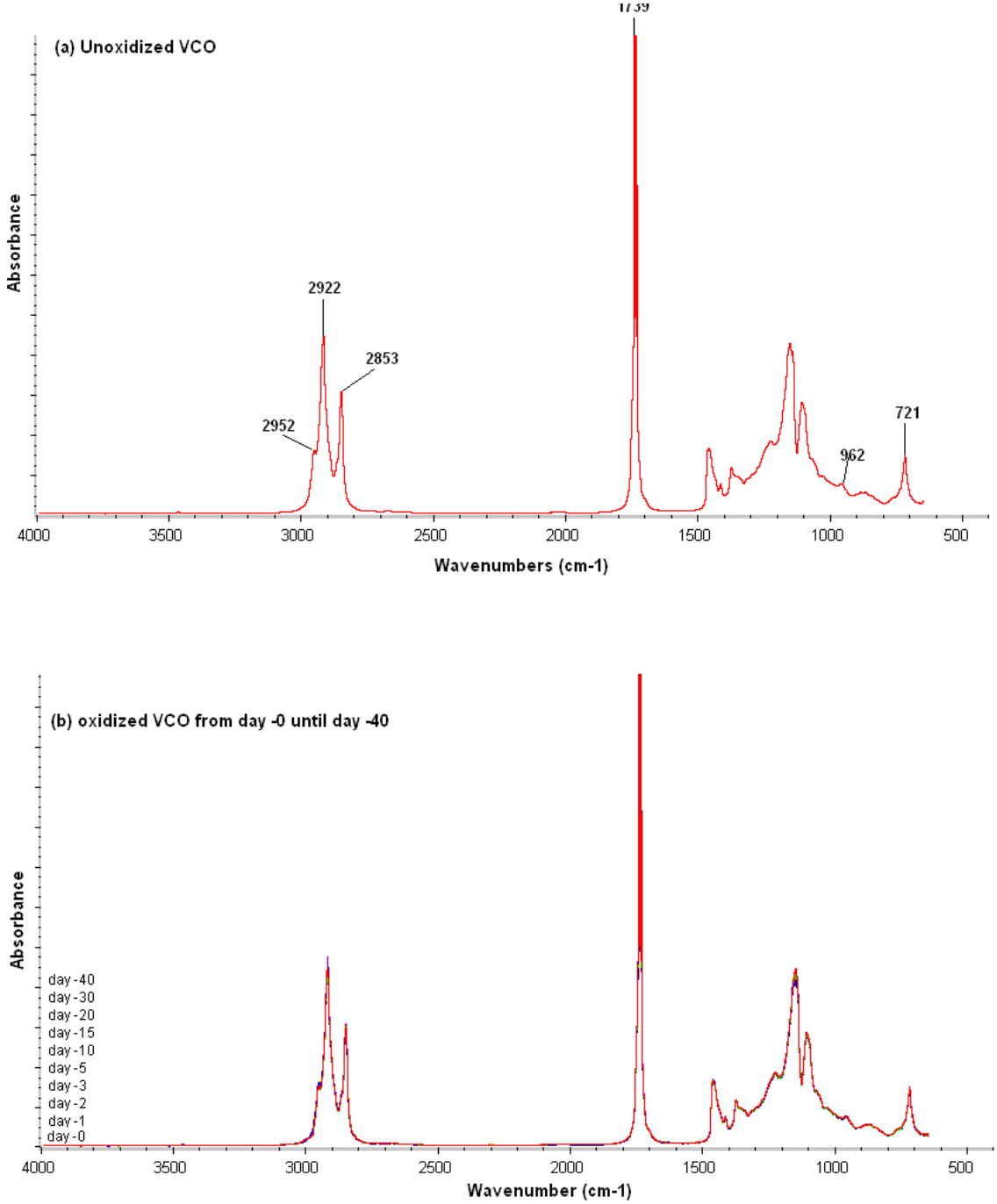

Figure 3. FTIR spectra of non-oxidized VCO (b) and VCO subjected to thermal oxidation (b)

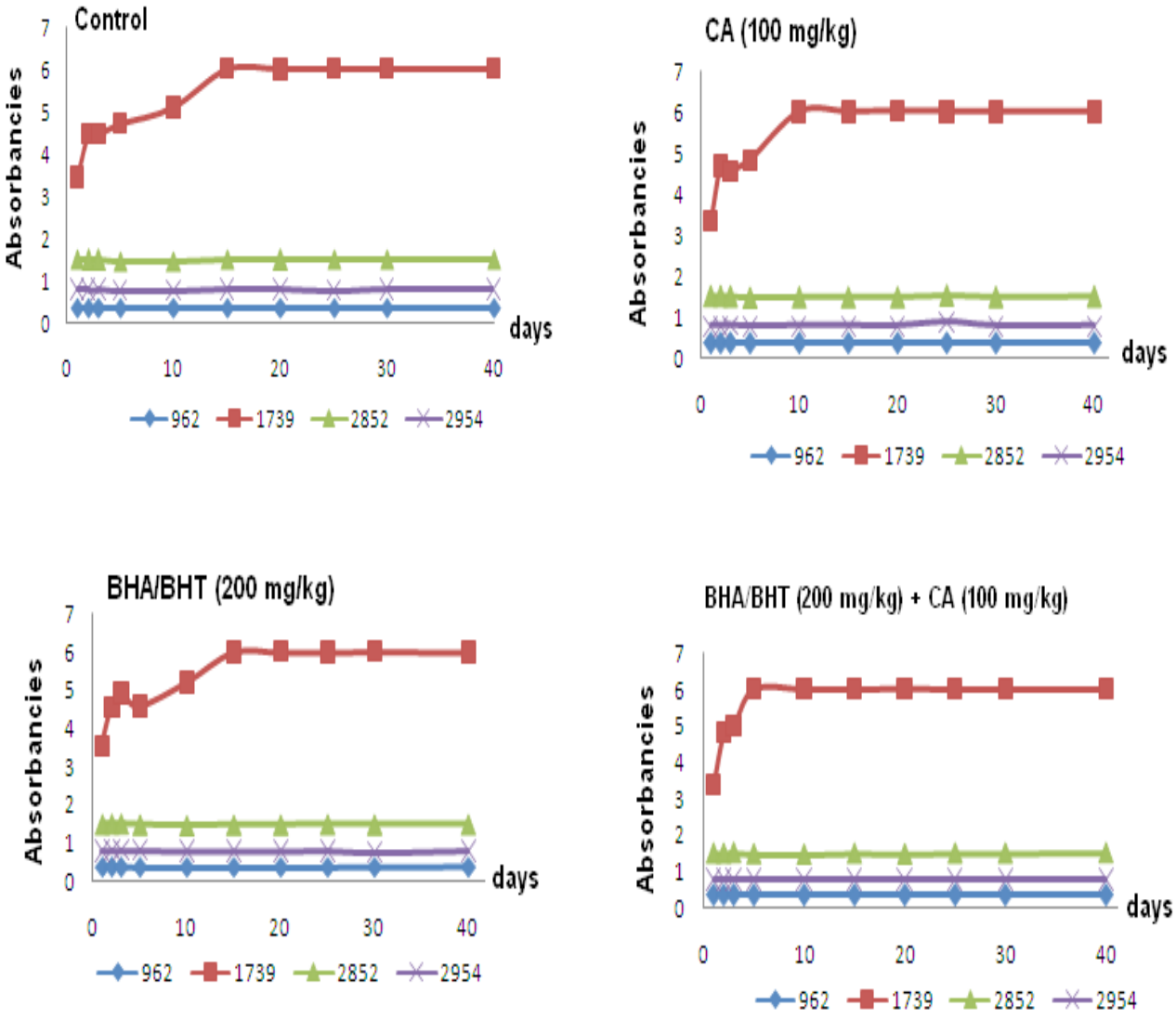

Figure 4. The changes of FTIR spectra of VCO and that added with antioxidants at frequencies of 2922, 2852, 1739, and 962 cm^{-1} during oven test for 40 days

than MUFA and SFA. Secondly, VCO contained some natural antioxidants such as phenolic compounds as reported by Marina et al. (2009) which can inhibit the peroxide formation.

FTIR studies

FTIR spectra spectroscopy can be used to follow the course of oxidation, during the oxidation of oils (Gray, 1978). Figure 3 showed FTIR spectra of non-oxidized (a) and oxidized VCO (b), during oven test without the addition of any antioxidants. The functional groups responsible for infrared absorption at each frequency in VCO spectrum are as reported by Rohman et al. (2009).

Muik et al. (2007) reported that during thermal oxidation of edible oils, there are several changes in the peak intensities (absorbances) observed as follows: intensity at frequency 710 cm^{-1} was decreased, two peaks at 970 and 987 cm^{-1} were increased, the bands at 1160 and 1462 cm^{-1} remained constant, and absorbance in the region 1660-1735 cm^{-1} was increased. Goburdhun et al. (2001) reported that FTIR spectra of soybean oil subjected to thermal oxidation have changed, namely an increased in peak intensity at frequency of 3800-3200 cm^{-1} due to OH stretching vibration of hydroperoxides or free fatty acids and at 1740 cm^{-1} corresponding to carbonyl group, and a decrease intensity at 2922 and 2825 cm^{-1}.

The changes of VCO spectra which take place during oven test at frequencies of 3300, 2922, 2852, 1739, and 962 cm^{-1} have been investigated. Using FTIR spectra, all VCO samples evaluated did not reveal peaks around 3300 cm^{-1} (Figure 3) indicating no hydroperoxedis or fee fatty acid could be detected, which may be formed during thermal oxidation. The peak intensities (absorbances) of VCO control and

that treated with antioxidants can be seen in Figure 4. The treatment of antioxidants to VCO relatively did not alter the peak intensities at these studied frequencies.

All VCO samples, either control or those treated with antioxidants, showed an increase in absorbances at frequency 1739 cm^{-1} until day-10 (for VCO and VCO+CA) and day-15 (for VCO+BHA/BHT and VCO+BHA/BHT+CA), and relatively unaltered for subsequent days of storage. These changes can be explained by the amount of carbonylic compounds such as aldehydes, esters, ketones, and lactones present in the oils formed during oxidation. The higher the intensities at 1739 cm^{-1}, the more carbonylic compounds present. Carbonylic compounds are the major secondary products during hydroperoxide decomposition (Smith et al., 2005). Furthermore, the treatment of antioxidants in VCO did not show a significant effect to lower the intensity of carbonylic compounds. Intensities at frequencies of 2852, 1739, and 962 cm^{-1} were relatively constant for all samples evaluated (Figure 4).

Conclusion

In conclusion, based on data obtained from this study, antioxidants (BHA/BHT and CA) added to VCO can lower PVs after 40 day-storage during oven test at 63°C. The specific absorptivity values of CDs and CTs were also decreased due the addition of antioxidants. Furthermore, the change of peak intensities at 1739 cm^{-1} corresponding to change of carbonylic compounds from hydroperoxide decompositions could be detected using FTIR spectroscopy.

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