The stability of palm oils during heating in a rancimat

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ORIGINAL PAPER



The stability of palm oils during heating in a rancimat

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Abstract

The crude palm oil (CPO) and refined palm oil (PO) not only have a balance of saturated and unsaturated fatty acids but also have the highest β -carotene and vitamin E compared to others vegetable oils. A series of aliphatic aldehydes starting from hexanal to decanal was identified by LC-MS/MS and quantified as DNPH derivatives. In addition, the total amount of carbonyls was determined based on the calibration with hexanal. Looking at the kinetic profile of the carbonyl formation in crude palm oil and refined palm oil, both of the oils were still stable until 10 h of oxidation with the Ranzimat at 120 °C. The analytical method for quantifying the vitamin E and β -carotene are quick, reliable, precise, economical and suitable for the routine analysis. For both analyses, a simple dilution of the oil was necessary. The quantitative analysis showed that β -carotene in the oxidized crude palm oil decreased from 2.34 mg/g to 0.33mg/g within 7.5 h of oxidation. However, after 7.5 h, no more β -carotene in the crude palm oil was validated. The coefficient of determination (0.999) of the linear regression indicates a good correlation between the peak area and the amount of β -carotene. The linearity of the β -carotene analysis was tested in the range 0.00078–0.05 µg/cm³. The limit of detection (LOD) was 2.65 µg/cm³ and the limit of quantification (LOQ) was 8.83 µg/cm³ for β -carotene.

Vitamin E in both refined and crude palm oil, δ -tocotrienol and γ -tocotrienol, have the long shelf life compared to α -tocopherol and γ -tocopherol. The δ -tocotrienol is degraded slowly and can be found even after 15 h of oxidation with 0.035 mg/g remaining in the oxidized crude palm oil. However, in refined palm oil, the δ -tocotrienol could be determined until 11 h of oxidation with 0.49 mg/g.

 $\label{eq:crude} \begin{array}{l} \mbox{Keywords} \ \mbox{Crude palm oil} \cdot \mbox{Refined palm oil} \cdot \mbox{Lipid oxidation} \cdot \mbox{Aldehydes} \cdot \mbox{DNPH} \cdot \mbox{Antioxidants} \cdot \mbox{β-carotene} \cdot \mbox{Tocopherol} \cdot \mbox{Tocotrienol} \end{array}$

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Introduction

Palm oil is derived from the fruit of the palm tree (Elaeis guineensis). Palm oil is consumed in the world so that it can be replaced with animal fats related to the cost and health concerns [1]. The leading country which exported palm oil are Malaysia and Indonesia around 86% of global production. Crude palm oil is produced from palm fruits. The crude palm oil is known as red palm oil, RPO represents the richest

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source of natural β -carotene. It contributes to the stability and nutritional value of the oil [2].

On the other hand, palm oil is well known as the African oil and red palm oil in its crude form largely used in West African. It has a typical smell like an overripe mushroom and tastes very pungent so it does not taste good. In addition, it has free fatty acids (FFA), moisture, trace metals and other impurities that limit it's shelf life. The way to increase the utility with refined which can remove odors, flavors, and impurities, as well as that some consumers did not like the red color because it is unappetizing [3]. Palmitic acid is the main saturated fatty acid naturally occurring in animal fats and vegetable oil, as well as the main component of human breast milk fat [4].

Crude palm oil are extracted either by wet or dry processes, contains 1% of minor components both healthy beneficial compounds, such as vitamin E, carotenoids,

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phytosterols, as well as impurities, such as phospholipids, free fatty acids (FFAs), gums, and lipid oxidation products. The unuseful content can be removed by refining [5]; the dried oil is then cooled and stored in appropriate containers [6].

Crude palm oil not only has high carotenoid content (500–700 mg/kg) that makes dark orange color [7], but also has vitamin E with 600–1200 ppm which composes by approximately 24% of tocopherol and 76% of tocotrienol. It contributes to its stability and nutritional properties [5, 8–12]. Crude palm oil has to be refined to produce palm oil which has desirable characteristics, such as a light color, bland taste and good oxidative stability [13, 14].

The main aim of this work was to establish an analytical method for a quantitative determination of the carbonyls in the lipid (oxidized oil) phase for determination of the alimentary exposure. As we know, the crude palm oil (CPO) and refined palm oil (PO) not only have a balance of saturated and unsaturated fatty acids but also have the highest β -carotene and vitamin E compared to other vegetable oils. The formation of carbonyls during oxidation of crude palm oil (CPO) and refined palm oil (PO) in the oil phase which were non-evaporating. On the basis of reversed-phase chromatography with UV and MS detection, the non-evaporating carbonyl compounds formed during oxidation of CPO and PO were identified and quantified. Both oils were not compared because they came from different sources.

In addition, the relationship between the reduction of antioxidants contains to the stability of the oils which have focused on the carbonyls form which was, hexanal, heptanal, octanal, nonanal, and decanal were done.

Materials and methods

Reagents

2,4-Dinitrophenylhydrazine (2,4-DNPH) was purchased from Sigma-Aldrich (St. Louis, USA), hydrochloric acid (HCl 37%) was purchased from Merck (Darmstadt, Germany), all solvents (e.g., methanol, ACN, acetone) used were of HPLC grade and were purchased from Merck (Darmstadt, Germany), acetic acid was purchased from Roth (Karlsruhe, Germany), β -carotene and α -tocopherol were from Sigma-Aldrich (St. Louis, USA).

Palm oil materials

Crude palm oil was purchased from Asia Markt in Graz, Austria, and refined palm oil was purchased in a local market in Medan-North Sumatera, Indonesia.

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Analysis of secondary oxidation products in oil

These analysis included standardized oxidation of crude palm oil (CPO) and refined palm oil (PO), derivatization with 2,4-dinitrophenylhrazine (DNPH) and liquid chromatography-mass spectrometry condition for aldehydes identification.

Standardized oxidation of crude palm oil (CPO) and refined palm oil (PO)

The oil samples were oxidized in a Rancimat (679, Metrohm, Herisau, Switzerland). For this, 11 g of oil were used. The temperature was set to 120 °C and the air flow to 20 l/h. CPO was treated for up to 18 h and PO for up to 11 h. The range hour oxidation was set related to the vitamin E decreased with the Rancimat process.

Derivatization with 2,4-dinitrophenylhrazine (DNPH)

For the carbonyls, it was analyzed by 2,4-dinitrophenylhydrazine (DNPH) derivatization with a commonly known derivatization reagent for carbonyls that would give the possibility to identify and quantify single components as well as the total carbonyl content. The derivatives are stable and can be analyzed by HPLC with ESI-MS in the negative mode or by its absorption at 400 nm [15–17].

To 1 ml of the oxidized oil samples, 4 ml of acetonitrile were added and mixed with 3 ml of the reagent 2,4-DNPH (3.48 mg/ml in 2 N HCl). The reaction mixture was kept at room temperature in the dark for 1 h. After completion of the reaction, 2 ml of ethyl acetate were added for extraction and 1 g of KCl for better phase separation. This mixture was thoroughly shaken for 30 s and centrifuged for phase separation. The organic layer on the top was analyzed without further treatment by HPLC.

Liquid chromatography–mass spectrometry condition for aldehyde identification

The analyses of the DNPH derivatives of the carbonyls formed during oxidation were done by an HPLC (Agilent 1100, Waldbronn, Germany) using a reversed-phase column (Kinetex, EVO C18, 150×3 mm (Phenomenex, Aschaffenburg, Switzerland). For elution, a gradient was used starting with a mixture of methanol (45%), water (30%), and acetonitrile (25%) changing to methanol (6%), water (4%), and acetonitrile (90%) linearly within 15 min. The absorption of the eluent was measured at 400 nm for the presence of the DNPH derivatives.

For mass selective detection, a QTRAP 2000 (AB Sciex, Framingham, MA, USA) was used. Ionization was done using the APCI mode with a gas drying temperature of 250 °C, capillary voltage of 4000 V, and a fragmentor potential of 150 V.

Analyses of vitamin e and β-carotene

The antioxidant (β -carotene, α -tocopherol) analysis can be done by 25 mg of the oil (CPO and PO) were extracted with 1 ml of methanol in 2 ml reactions vials (Eppendorf, Wien, Austria). The samples were shaken for 2 min vigorously and centrifuged. Under these conditions, both α -tocopherol and β -carotene were extracted quantitatively. The methanolic extract was used directly for HPLC analysis on a reversedphase column (Kinetex, EVO C18, 150 × 3 mm), using a flow of 0.6 ml/min. α -Tocopherol was separated isocratically using 5% water in methanol as eluent and UV detection at 292 nm. β -Carotene was chromatographed with DAD HPLC with Kinetex EVO C18 2.6 µm; 100 × 3 mm (Phenomenex, Aschaffenburg, Switzerland) column using a flow of 1 ml/ min of 100% acetonitrile with detection at 450 nm.

Gas chromatography condition for fatty acid identification [18]

25 mg of palm oil were put in a Pyrex glass tube and hydrolyzed with 1.5 ml M of NaOH in methanol. The samples were closed tightly and vortexed for 1–2 min. After that, the samples were heated at 100 °C for 1–2 min. The free fatty acids were methylated with 2 ml of BF₃ in methanol at 100 °C for 30 min. After cooling to temperature 30–40 °C, iso-octane was added to the solution, and then FAMEs (fatty acid methyl esters) were extracted in the presence of 5 ml of saturated NaCl. The isooctane layer was analyzed for the fatty acids by GC (Shimadzu Q Plus 2010, Columbia, USA) using column DB-23; 30 m × 0.25 mm, column max. temperature 250°, column length 30 m, pressure 100 kPA, column flow 1.04 ml/min, stop time 31.87 min with mobile phase with Hexan.

Results and discussion

It is known from the literature that palm oil contains 50% saturated fatty acids mostly palmitic acid (ca. 44%) and lower amounts of stearic acid (5%); 40% of the fatty acids are monounsaturated fatty acids (mostly oleic acid) and 10% polyunsaturated fatty acids (mostly linoleic acid) [5, 7, 9].

The gas chromatographical analysis showed that the refined palm oil which was used for the experiments

described here had a fatty acid composition which was comparable to the literature values. It contained 44.5% oleic acid, 12.2% linoleic acid, 37.3% palmitic acid, and 3.81% stearic acid. The crude palm oil had a different composition with 41.9% oleic acid, 9.30% linoleic acid, 0.21% linolenic acid, 43.1% palmitic acid, and 4.18% stearic acid. The presence of vitamin E (tocopherols and tocotrienols) and the comparably low content of linoleic acid increase the stability of palm oil.

The oxidative and thermal stability of palm oil and crude palm oil was evaluated using Rancimat 679. During oxidation, formic acid is formed which is transferred with the air stream to the measurement vessel filled with water and detected by an increase of the conductivity. A chromatogram of the DNPH derivatives is shown in Fig. 1. The oxidation of crude palm oil is similar to triolein. The dominant peaks of the derivatized carbonyls eluted at the same time resulting in a similar pattern. When measuring the absorption of the eluent at 400 nm, practically no other substances could be observed.

The dominant peaks that could be identified were hexanal, heptanal, octanal, nonanal, and decanal. These are degradation products of oleic acid which were described earlier in the triolein. The result from previous experiment showed that the similar concentration range with maximum concentrations of 56.8 ppm of hexanal, 81.65 ppm of heptanal, 88.75 ppm of octanal, 113.6 ppm of nonanal, 142 ppm of decanal after 6 h. The total amount of carbonyls reached a maximum after 6 h being 958 ppm for triolein without antioxidant. All these result referred to the calibration with hexanal, all other dominant substances were in [19]

Carbonyl compounds are the most abundant secondary oxidation products formed in edible oils at higher temperatures. The position of double bond in unsaturated fatty acid

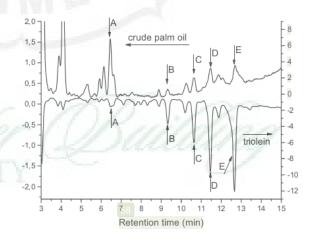


Fig. 1 Chromatogram of DNPH derivatives of carbonyls from triolein and crude palm oil (A, hexanal; B, heptanal; C, octanal; D, nonanal; E, decanal) after oxidation at 120 °C for 15 h measured at 400 nm

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was correctly localized based on the fact that double bonds are more prone to cleavage than a single bond [20]. The ease of hydroperoxidation depends on the number of double bonds present [21].

Some of aldehydes and carboxy aldehydes that could possibly result from fatty acid oxidation have been identified in sea buckthorn berry (Hippophae rhamnoides) samples. Mathew and co-workers [22] concluded that the lower carbonyls such as formaldehyde, acetaldehyde and acetone were found to predominate in the berries, whereas longer aldehydes and carboxy aldehydes were dominant in oxidized oil. Our results show that the longer aldehydes are formed to a greater extent. Both of the oils, CPO and PO show that octanal is produced after hexanal.

The reason might be that the longer aldehydes are less volatile and remain in the oil phase during air sparging. These aldehydes were produced by thermal decomposition via homolytic cleavage about the oxidation functional group atoms such as hydroperoxy, keto, epoxides and dimer oxygen linkages [23–27]. The oxidized oleic volatile produced octanal and nonanal, while the aldehydes such as pentanal and hexanal usually expected from linoleic hydroperoxide were produced. Another compound which associated with oxidized linoleic acid such as 2-pentyl furan and 4-octene-3one were produced in heated triolein and the HPLC fraction [25]. Those secondary products decompose the same way as monohydroperoxides to produce similar volatile compounds.

From the kinetic profile, the carbonyls compound still reach the highest amount until 18 h oxidation times with Rancimat with 120 °C in crude palm oil (Fig. 2). For 18 h oxidation, the carbonyls which detected were hexanal 1.6 mmol/g, heptanal 0.61 mmol/g, octanal 1.36 mmol/g,

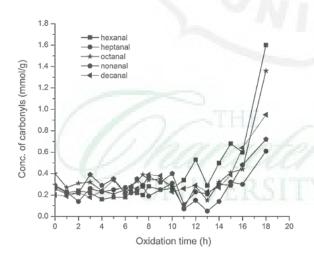


Fig.2 Formation kinetics of single compounds during oxidation of CPO (containing the natural antioxidants vitamin E and β -carotene) at 120 °C with constant air sparging for up to 18 h

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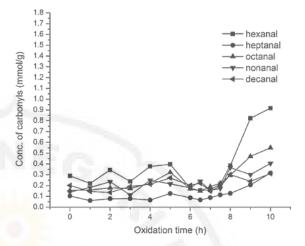


Fig. 3 Formation kinetics of single compounds during oxidation of refined palm oil in the presence of lipid soluble antioxidants at 120 °C with constant air sparging for 10 h (hexanal; heptanal; octanal; nonanal; decanal)

nonanal 0.72 mmol/g and decanal 0.95 mmol/ g for CPO (Fig. 3). This corresponds to the research undertaken by Reindl [28] focused on the oxidative degradation of unsaturated fatty acids which isolated from meat which shows that hexanal is the main product from oleic, linoleic and arachidonic acid.

On the other hand, oleic acid produced octanal, nonanal, 2-nonenal, and 2,4-decadienal. Thus, the main secondary oxidation product of oleic acids in the CPO was hexanal, octanal and decanal which has the higher percentage than others. The decanal is produced by homolytic cleavage B of the alkoxyl-intermediate group from the 8-hydroperoxide. Octanal is normally formed from the 11-hydroperoxide [29]. However, the percentage of linoleic acid is just 9.3% so the production of heptanal was lower with 0.61 mmol/g. The other carbonyls which produced from linolenic acid, was 2,4-heptadienal from, and 2,4-nonadienal from arachidonic acid.

Autoxidation of 2,4-decadienal at ambient conditions has been shown to produce a mixture of volatiles including hexanal, butenal, heptenal, octenal, benzaldehyde and glyoxal [22], while oxidation of 2-nonenal produced C2, C3, C7, C8 alkanals, glyoxal, and a mixture of C7, C8 and C9 α -keto aldehydes [30].

In addition, the kinetic profile of the carbonyl compound in refined palm oil until 11 h oxidation still want to reach the highest amount of secondary oxidation products with Rancimat at 120 °C (Fig. 3). For 11 h oxidation, the carbonyls which detected were hexanal 0.92 mmol/g, heptanal 0.32 mmol/g, octanal 0.55 mmol/g, nonanal 0.41 mmol/g and decanal 0.31 mmol/g for CPO (Fig. 3). from autoxidized oleate. The octanal from the 11-hydroperoxide and the nonanal from either 9- or 10-hydroperoxide [25]. The other fatty acids which contain in the palm oil is linoleic acid 12.2% and palmitic acid 37.3%.

The carotenoids α -carotene, β -carotene, and lycopene contribute to the color of red palm oil. Red palm oil is a form of processed palm oil in which ca. 80% of the original carotenoids are retained. This means that it is a remarkable source of vitamin A [31]. The quantitative analysis showed that β -carotene is completely oxidized in the oil decreased with a natural content of 2.34 mg/g within 8 h of the Rancimat treatment (Fig. 4).

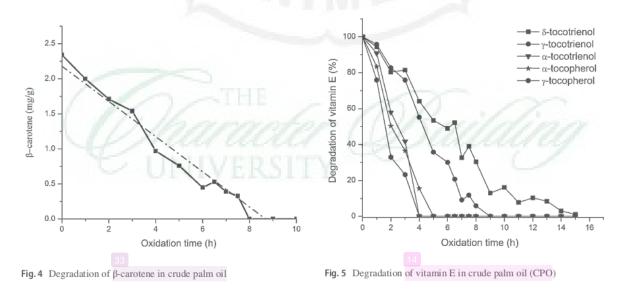
β-Carotene plays an important role during the oxidation of oils and fats. Some studies have been done to the stability of β-carotene. Henry et al. [32] studied the thermal and oxidative stability of all-E-β-carotene, 9-Z-β-carotene, lycopene, and lutein in safflower seed oil at 75, 85 and 95 °C for 24, 12 and 5 h, respectively. The carotenoids were found to degrade following a first-order kinetic model. The rates of degradation were lycopene > all-E-β-carotene ≈ 9-Z-βcarotene > lutein. Another issue was published by Bezbradica and co-workers who found carotenoids were degraded with a first-order kinetics model, which was dependent on concentration. The highest degradation rates were observed in extracts prepared with linoleic acid containing oils such as sunflower, soybean oil and grapeseed oil [33].

β-Carotene was found to degrade in the first few hours of thermal treatment [34]. This statement can be strongly supported from the experiment which has been done. The β-carotene completely oxidized at 8 h oxidation of CPO. The concentration of β -carotene at 0 h oxidation was 2.34 mg/g and ends at 7.5 h with 0.33 mg/g. However, the formation of secondary oxidation products still tried to reach the highest amount till 18 h of heating.

Previous results [35], have shown that β -carotene was more stable in the corn oil than in olive oil and model TAGs. The β -carotene degraded completely before 12 h in the corn oil of the thermal treatment in the Rancimat at 110 °C. However, β -carotene can act as prooxidant and has a lower stability compared to astaxanthin during thermal degradation in olive oil [34].

The HPLC-DAD method developed for the β-carotene in the CPO was validated according to Kazakavich and Labrutto [36]. In this study, the β -carotene was re-spike in the CPO. The concentration of the β -carotene in CPO was 7.8 mg/g. The quantification was performed using five-point best fit standard calibration plot. The coefficient of determination (0.999) of the linear regression indicates a good correlation between the peak area and the amount of β -carotene. The regression equation was: Y = 1235.1X - 0.405. The respike of the CPO is done in the concentration of 0.05 mg/g. The extracted and quantified amount of β -carotene in the pre-spike sample was 0.0494 mg/g which shows the high accuracy of this methode. The linearity of the oil β-carotene analysis was tested in the range 0.00078-0.05 µg/cm³ according to Mandel [37]. The limit of detection (LOD) was 2.65 µg/ cm³ and the limit of quantification (LOQ) was 8.83 μg/cm³ for β-carotene.

The results show that the tocotrienols are more stable than the tocopherols in crude palm oil (Fig. 5). The δ -tocotrienol content was 3.01 mg/g in the fresh oil. It is still remaining in the oxidized oil after 15 h in the Rancimat with 0.03 mg/g δ -tocotrienol or 1.13% compared to the fresh oil. It has been



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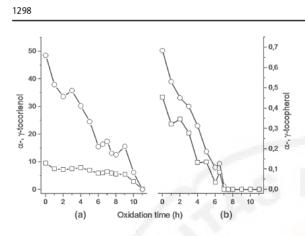


Fig.6 Degradation of tocotrienols (a) and tocopherols (b) in refined palm oil

shown that half of the δ -tocotrienol was destroyed after 5 h of oxidation.

The γ -tocotrienol with an original content of 11.48 mg/g was less stable. 50% of it was degraded after 4 h of oxidation with remaining 0.68 mg/g after 8 h (5.89%) (Fig. 5). As we already know, tocotrienols have been found to have antioxidant and anti-cancer activities. γ and δ -tocotrienol derived from palm oil exhibit a strong activity not only against tumor promotion but also inhibit certain types of cancer, such as breast cancer cell [38].

In addition, the α -tocotrienol was completely degraded after 4 h which still remained 0.2 mg/g in 3 h with the started contain in the 0 h with 0.48/g. Furthermore, for α -tocopherol at 0 h with 39.96 mg/g still remained until 4 h with 6.18 mg/g. Both α -tocotrienol/tocopherol have degraded half percentage from 0 h at 2 h oxidation. γ -tocopherol just remained until 3 h with 0.22 mg/g compared to the 0 h with 0.94 mg/g. At low concentration $\leq 100 \,\mu$ g/g for tocopherol, α -tocopherol appeared to be the most effective antioxidant [39–45].

The oxidation experiments of PO showed that δ -tocotrienol were 2.10 mg/g at 0 h to 0.49 mg/g at 11 h. On the other hand, γ -tocotrienol were present until 11 h with 0.18 mg/g from the starting point at 0 h with 9.45 mg/g, while α -tocotrienol was completely oxidized after 10 h of oxidation. The δ -tocotrienol, γ -tocotrienol and α -tocotrienol has a good stability against the oxidation of refined palm oil. They still remained in the oil until 10 until 11 h oxidation. The δ -tocotrienol itself stayed in the 11 h of palm oil oxidation with 23.35%. α -Tocopherol and γ -tocopherol were completely oxidized within 6.5 h (Fig. 6).

The HPLC-UV method was developed for determination of α - and γ -tocopherol in the palm oil. The validation showed that the method could be used for palm oil. The coefficient of correlation (0.999) of the linear regression indicates a good correlation between the peak area and the

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amount of α -tocopherol and γ -tocopherol, respectively. The limit of detection (LOD) was 0.14 µg/cm³ and limit of quantification (LOQ) was 0.47 µg/cm³ for γ -tocopherol. In addition for α -tocopherol, the limit of detection (LOD) was 460 µg/cm³ and the limit of quantification (LOQ) was 1530 µg/cm³.

The absence of carotenoids in refined palm oil is not only due to the various refining steps (bleaching). It could also be reduced because of thermal deterioration which is able to remove the β -carotene from crude palm oil [46, 47].

Conclusion

Looking at the kinetic profile of the carbonyl compound of crude palm oil and refined palm oil, both of the oil are still stable until 10 h of oxidation times with Rancimat at 120 °C. The quantitative analysis showed that β -carotene in the oxidized crude palm oil decreased from 2.34 mg/g to 0.33 mg/g at 7.5 h of oxidation. However after 7.5 h of oxidation, no β -carotene was detected. In addition, β -carotene was not detected in refined palm oil.

Vitamin E in both refined and crude palm oil, δ -tocotrienol and γ -tocotrienol, have the long shelf life compared to α -tocopherol and γ -tocopherol. The δ -tocotrienol is degraded slowly and can be found even after 15 h of oxidation with 0.035 mg/g remaining in the oxidized crude palm oil. However, in refined palm oil, the δ -tocotrienol could be determined until 11 h of oxidation with 0.49 mg/g.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Research involving human participants and/or animals This article does not contain any studies with human or animal subjects.

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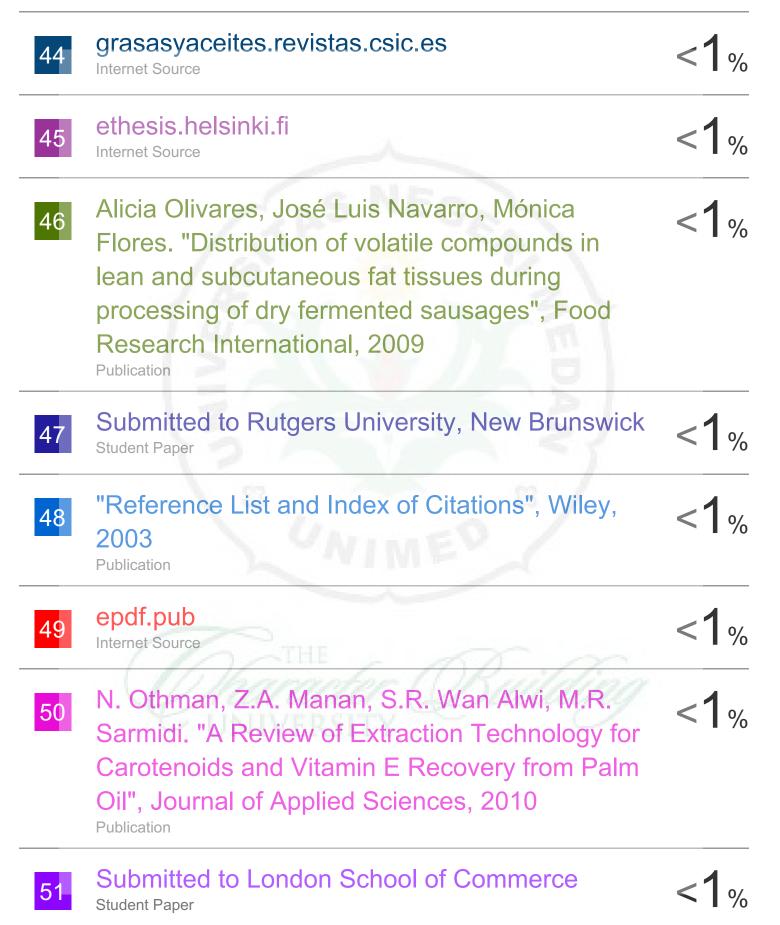
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