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Synthesis of natural antioxidants by oligomer technique in epoxidized sunflower and palm oil and comparison of the effects of rosemary extract and synthetic antioxidants with citric acid in sunflower oil

Mohadese Khojir
Master's student in food industry engineering, food quality control,
mohadesekhojir@gmail.com
Leila Baha
Master's student in food industry engineering, food technology,
leilabaha58@gmail.com
Taherah Harsij sani
Master's Degree in Analytical Chemistry,
Tahereh.shimi@gmail.com
Masoumeh Qutbi
Member of the Faculty of Agriculture, Chalous Branch, Islamic Azad University, Chalous,
Iran.Masoumeh.ghotbi@gmail.com

Abstract

Antioxidant is one of the most important additives in oil. In this article, it has been tried to determine the relationship between antioxidant and citric acid and what effects these two additives have on each other so that the product is of high quality. Also, the presence of a natural extract and its effect instead of synthetic antioxidants on the quality of oil. Rosemary extract has been extracted by HPLC method and the same amount as the antioxidant was added to the oil. The result was seen in two graphs that the effect of the natural antioxidant, which is the extract, has a significant effect on the nutritional value and stability. And after that, the synergism of antioxidants with citric acid by the method of this XRD pattern can show the interactions of the components through the change of the crystal structure of the XRD patterns of starch and biocomposites prepared in Figure 3. Raw starch displayed A-type diffraction pattern with characteristic peaks at 2θ of 14.9, 17.3, 18.0 and 23.1◦. During processing, plasticizers penetrate into starch grains, replacing starch intramolecular and intermolecular hydrogen bonds with starch-plasticizer hydrogen. Binds and changes the crystal structure, attributed that the carboxyl groups of CA contributed to the additional interactions with starch/fiber and disrupted the cross-linking reaction of the ordered array of molecules.

Key words: synergy, natural antioxidants, epoxidized, oligomer, extract

Introduction

One of the main causes of deterioration of food quality is the oxidation of unsaturated lipids by free radicals when lipids are exposed to the environment. Factors such as air, light and temperature, oxidation reactions begin to produce unpleasant flavors, spoil odors.

Discoloration and other forms of spoilage are the primary oxidation products of the hydroperoxides themselves, which are tasteless, but their decomposition products (aldehydes, ketones…) have very strong flavors and flavor modifiers. (Gordon, 1991)

Antioxidants are added to food to delay or prevent oxidative deterioration. Added antioxidants maintain the quality and increase the useful life of many food products. Antioxidants can be of synthetic or natural origin. The use of synthetic antioxidants has been restricted in several countries due to their possible adverse effects on human health (Brannen, 1975; Chen, Shi and Hu, 1992; Kahl and Kapus, 1993).

As a result, there is a large. Using antioxidants from natural sources is assumed to be safe since they are found in plants. Today, the most important natural antioxidants from a technological point of view are: ascorbic and citric acid and their salts, tocopherols and spice extracts (Weinreich, 1998).

Natural antioxidants from plants and spices have been widely studied for their antioxidant properties (Che Man & Tan, 1999; Chipault, Mizuno, Hawkins, & Lundberg, 1952; Economou, Oreopoulos, & Tomopoulos, 1991;

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Madsen, Sorensen, Skibstad, & Bertelsen, 1998)
Most of the attention in herbs and spices has focused on rosemary. Many studies have been conducted to investigate the antioxidant activity of raw rosemary and various rosemary extracts.

In addition to evaluating the antioxidant activity of rosemary extracts, the antioxidant compounds responsible for the antioxidant activity of rosemary, mainly phenolic diterpenes, such as carnosic acid, carnosol, rosmanol, epirosmanol, isorosmanol, methyl carnosate (Kovlier, Brest and Richard, 1994; Schwartz & Terence, 1992) and other phenolic acids, such as rosmarinic acid (Frankel, Huang, Aeschbach & Prior, 1996).

A number of rosemary extracts are available on the market for use in food systems today (Bauman, Hadolin, Riz˘ner Hras˘& Knez, 1999)a-, b-, g- and d-tocopherols appear as a mixture inside. Vegetable oils are the main natural antioxidants and fats (Gordon, 1991). The most abundant and biologically active tocopherol in food is a-tocopherol (White and Xing, 1997)

A variety of food systems research has evaluated the effectiveness of various natural antioxidants on sustainability (Pongraz, Wieser, & Matzinger, 1995; Reichheimer, Bernhardt, King, Kent, & Bailey, 1996).

There is a lot of evidence for this. The synergistic effect of various compounds in foods, the synergistic effect of rosemary extract with other antioxidants, especially tocopherols, has been investigated and conflicting results have been reported (Banias, Oreopoulos, & Tomopoulos, 1992; Nish and Wada, 1993). ; Hopia, Huang, Schwarz, German, and Frankel, 1996; Wada and Nish, 1992).

Therefore, more information is needed to fully assess the synergistic effects of rosemary extract and other natural antioxidants. This study compares the effectiveness of rosemary extract (ROS.CON), α-tocopherol (TOC), ascorbyl palmitate (AP) and citric acid (CA) in sunflower oil.

In the same experiment, the ability of α-tocopherol, ascorbyl palmitate and citric acid to improve the antioxidant activity of rosemary extract was also tested. The conditions of the prepared samples were kept at 60 degrees for 11 days.

The results of the primary oxidation were measured by the iodometric peroxide value method and the results of the secondary oxidation by the peroxide value.Cross-linking is one of the methods to improve the compatibility-to-physical or chemical interactions between the components (Gunathilake) . et al., 2018, 2017; Liu et al., 2019; Zhao et al., 2018).

The use of epoxidized vegetable oils (EO) is a suitable approach to develop biocomposites with superior hydrophobic and mechanical performance (Ballart et al., 2016; Belhassen et al., 2014; Lee and Lee, 2014). EO, containing epoxy structures, can undergo various reactions.

Generate cross-linked products with many other functional compounds such as amines and carboxylic acids through nucleophilic epoxy ring-opening reactions (Belhassen et al., 2014; Tan et al., 2014) .

Epoxidized linseed oil was used as a cross-linking agent to bridge hazelnut shell flour and poly(lactic acid), where EO created a cross-linking network and apparently enhanced the properties of the composites (Ballart et al. , 2016).

Epoxidized sunflower oil (EAO) has been shown to be used as a starch surface modifier and softener by reacting epoxy groups with hydroxyl groups (Belhassen et al., 2014).

Palm oil (PO) is one of the most widely used and cheapest vegetable oils in Malaysia

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(Goncalves et al., 2012). Epoxidized palm oil (EPO) is considered as a reactive component to produce a mixed product with desirable mechanical, thermal and water resistance properties (Ng et al., 2017; Saleh et al., 2015; Sarono et al., 2012).

However, the use of EPO as a modifier for starch/fiber-based bioplastic composites has rarely been investigated. Unlike oil-based epoxies (usually terminal epoxides), the epoxy groups in EO molecules are not located at the ends of the fatty acid chains, which greatly limits its reactivity to it.(Meng et al., 2019; Xiong et al., 2013).

The low content of epoxy groups in EO can only cause low reactivity. Starch, in addition, it is not easy to uniformly disperse EO in composites due to poor compatibility between EO and starch (Ge et al., 2019).

Consequently, the interfacial adhesion between EO and starch needs further improvement. Compatibilizers such as polyethyleneimine, maleic anhydride, tannic acid, stearic acid and citric acid (CA), to improve the compatibility between hydrophobic polymers and hydrophilic starch (Kadam et al., 2015; Meng et al., 2019)

For example, starch-based bioplastics were modified by EAO using a reactive melt compound with tetrabutylammonium bromide (TABA) as a catalyst, which significantly increased the stiffness and strength of biocomposites (Belhassen et al., 2014)

In order to create water-resistant coatings for starch-based biocomposites, polyethyleneimine was used to improve the surface adhesion between starch and acrylated epoxidized sunflower oil. (Meng et al., 2019)

Linking multifunctional groups on EO is also a practical strategy because groups can act as mutual interfaces to build a strong cross-connection network with improved performance (Pawar et al., 2016; Zhao et al., 2018).

Bamboo fiber-reinforced poly(lactic acid) biocomposites were toughened with tannic acid-linked EAO oligomer via reactive extrusion (Liu et al., 2019).

Zhao et al. (2018) used sunflower oil containing epoxy and phosphate groups as a multifunctional binder that reacts synergistically with soy flour-based adhesive and kenaf fibers.

The reaction of carboxylic acids with non-terminal epoxy groups has also been proposed as an attractive method to improve the compatibility of biopolymers and EO by β-hydroxyester linkages (Gogoi et al., 2015b; Zeng et al., 2017).

Zhao et al. (2017) An efficient method for dynamic vulcanization of EAO with poly(lactic acid) and sebacic acid with excellent heat processing and tensile properties.

A green bio-based nanocomposite was prepared by introducing acidic functionalized multi-walled carbon nanotubes into an EAO oligomer cured with CA. (Gogoi et al., 2015b)

Li et al. (2018) lignocellulose prepared biocomposites by modifying lignocellulosic fibers with CA-ESO oligomers and biocomposites were obtained that showed high hydrophobicity and tensile strength.

Food fats and oils spoil quickly under the influence of oxygen and pollution. The amount of oxidation caused by air or autooxidation varies. And it depends on the ease of removing hydrogen ions from the substrate molecule. Unsaturated lipids have more allyl hydrogen than saturated lipids and are prone to oxidation (Akaranta O and T.O Odozi, 1986).

Vegetable oils are obtained from fatty tissue of plants. They are liquid and are triglycerides. (McMurray John, 1992). The structure of the

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triglyceride molecule has been studied (Litterfield, C, 1992).

Some of the fatty acids found in vegetable oils are: lauric acid, myristic acid, stearic acid, ricinoleic acid and linoleic acid. Fats and oils are easily degraded as a result. Poor storage and handling methods identified two major types of deterioration due to microorganisms and that due to atmospheric oxidation and hydrolysis (Krishnamurthy, R., 1982)

The latter is a very serious storage problem that leads to a process simply as oxidative pickling, with a consequent reduction in product quality. Citric acid is usually used as a preservative in vegetable oils.

A metal chelator, in other words, citric acid binds to metal ions that would otherwise contribute to souring and catalyzes free radical oxidation of lipids. Most formulations contain citric acid, which in addition to its chelating abilities acts as an antioxidant synergist (Eastern Chemical Company, 2003).

Most vegetable oil refineries add citric acid dissolved in either propylene glycol or water in the final stages of refining (Robards, K et al, 2004). Citric acid, next to coffee, has the highest antioxidant activity among beverages (Nicoletta et al., 2003).

Synergy

When we say that synergy has occurred, we mean that several resources or capabilities have been combined and a new resource or capacity has been created that exceeds the sum of those resources or capabilities. Synergy is usually defined as: when two or more elements, flows or agents work together in cooperation and interaction (interaction), usually an effect is created. If that effect is greater than the sum of the effects that those individual elements can create, a synergy is created.

Oligomer

From ancient Greek: ὀλίγοι oligoi, méros μέρος) is a molecule made of several identical or similar structural units. If there are more structural units, it is called a polymer.

Epoxidized oil

Epoxyd oil is an inexpensive, non-toxic and environmentally friendly compound. Which is considered a good substitute for toxic petroleum derivatives available in the market, especially softeners such as DOP.

Citric acid

Citric acid or lemon essence is one of the organic acids found in both lemons and oranges. Its chemical formula is $C_6H_8O_7$; And its IUPAC name is 2-Hydroxypropane-1,2,3-tricarboxylic acid.

Citric acid is a weak organic acid with the chemical formula C6H8O7, which is used in both industrial and edible grades and can be found in many foods such as fruits and vegetables.

Citric acid with the chemical formula C6H8O7, molecular mass of 192.027 grams and melting point of 153ºC is a weak organic acid. It has a sour and special taste and it is the same acid found in citrus fruits (oranges and lemons). This weak acid exists in both dry and aqueous forms. Citric acid is used in the food industry as a preservative, food acidity regulator and an antimicrobial agent.

Antioxidants

Antioxidants are compounds that prevent oxidation. Oxidation is a chemical reaction that can produce free radicals, thereby leading to a chain reaction that may damage the cells of living organisms.

Materials and ways

Tocopherol-free sunflower oil purchased from Gea, Slovenska Bistrica, Slovenia was determined to be tocopherol-free by high-performance liquid chromatography (Mayne, Taylor & Parker, 1988).

The composition of sunflower oil fatty acids using gas chromatography (GC) is as follows:

۶/۳۸٪16:0 ۶۲/۳۶٪ ;۱۸:۱ ۲۵/۷۰٪ ;۱۸:۰ ۴/۰۲٪ ; ۰/۲۲٪ ;۱۸:۲

18:3 ۲۲:۰ ٪۰/۲۶ و ۲۰:۱ ۰/۶۸٪ ;۲۰:۰ ۰/۳۸٪ ;

Rosemary extract (ROS.CON) was obtained

Pinus, Chemie, Slovenia, the contents of the two main antioxidant components of rosemary, carnosic acid and carnosol were 36.33 and 4.79%, respectively. Natural a-tocopherol (T 3634) and citric acid (C0759) were purchased from Sigma, Germany. Used without purification, all chemicals and other solvents used were analyzed.

Methods

HPLC analysis was performed to isolate the extract. This method was similar to the method used by Richeimer et al. (1996). The HPLC system consisted of a ConstaMetric 3000 pump (Milton Roy), Spectro Monitor 3100, UV-VIS detector (Milton Roy).

Sample preparation method

Antioxidants or their mixture were added to sunflower oil in the following amounts: 0.02% by weight of rosemary extract (ROS.CON), 0.01% by weight of a-tocopherol (TOC), 0.01% by weight of ascorbyl palmitate (AP).

۰/۰۱٪by weight of citric acid (CA), 0.02% by weight of rosemary extract and 0.01% by weight of a-tocopherol (ROS.CON+ TOC), 0.02% by weight.

The percentage by weight of rosemary extract and 0.01% by weight of ascorbyl palmitate (ROS.CON+AP), 0.02% by weight of rosemary extract and 0.01% by weight of citric acid (ROS.CON+CA).

For control, the sample without added antioxidant (control) was used. After careful mixing, the samples (0.1 ± 50.0 g) were placed in an oven kept at 60 degrees Celsius.

For a quick storage study of 11 days. Triplicate samples were stored. Oxidative stability was determined by measuring peroxide values every 24 hours.

Amount of peroxide

The primary oxidation products – hydroperoxides – were determined by measuring the amount of peroxide. 0.1 ± 1 g of oil was weighed and the amount of peroxide was determined by iodometry (AOCS, 1990).

The induction period was considered as the number of days required for the peroxide value of the sample to become 20 mEq/kg of fat (Economo et al., 1991). This is consistent with a general opinion that oils go rancid at peroxide values above 20.

Discuss

The peroxide values of sunflower oil with single antioxidant addition at 60°C are presented in Figure 1.

Rosemary extract (ROS.CON) significantly delayed the formation of hydroperoxide ($P<0.05$).

The addition of ROS.CON reduced the final peroxide value from 200 after 11 days. As seen by the control sample, it is 120 milliequivalents/kg.

The stabilizing effect of ascorbyl palmitate (AP) shows a small amount but is not significant ($P<0.05$). Citric acid antioxidant effect towards the oxidative stability of sunflower oil. A-Tocopherol (TOC) showed a slight prooxidative effect.

After 9 days of storage at 60°C, the peroxide value of the sample started to increase with the addition of a-tocopherol.

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The amount of sunflower oil peroxide with antioxidant mixture of a-tocopherol rosemary extract with (ROS.CON+TOC)

Ascorbyl palmitate (ROS.CON+AP) and citric acid (ROS.CON+CA) at 60 °C reduced the oxidation rate by all three tested antioxidant mixtures. Peroxide values from samples with ROS.CON+CA and ROS.CON+ added AP are lower than samples added to ROS.CON.

Therefore, in sunflower oil at a temperature of 60 degrees Celsius, combinations of rosemary extract with citric acid and especially ascorbyl palmitate have synergistic effects in preventing hydroperoxide..

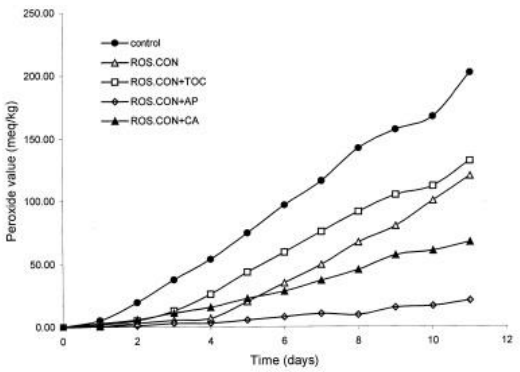
Formation, compared to rosemary extract. Calculated synergy: 2.61% for ROS.CON+CA and 56.0% for ROS.CON+AP. The effect of ROS.CON+ AP was significantly ($P<0.05$) better than AP. The result of ROS.CON.

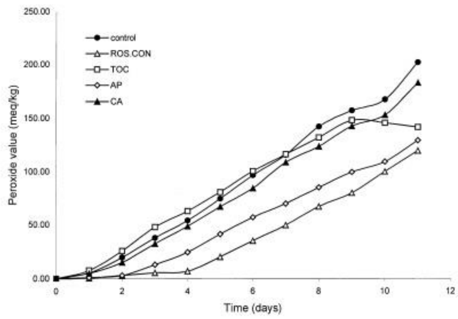
A mixture of rosemary extract with citric acid showed weak synergistic activity. Compared to the control sample, ROS.CON, ROS.CON+AP and ROS.CON+CA reduced hydroperoxide. Formation significantly ($P<0.05$).

On the other hand, the calculated synergy is ROS.CON+TOC. 0.21% of a-tocopherol reduces the antioxidant effect of rosemary extract, but rosemary extract increased. The stability of a-tocopherol is in agreement.

The findings of Hopia et al. (1996) who found that a-tocopherol reduces the oxidative stability of the two main.

Rosemary carnosol and carnoic acid compounds in Banias et al. (1992) also reported that α-tocopherol had strong negative effects with different plant extracts.





Chemists procedure (Official Methods of the Society of Official Analytical Chemists, 1984).

The extract solvent was concentrated in a water bath and dried in air. The oil samples were directly treated with the plant extract according to the method adopted by Blatina (Blatina, J and G. Manus, 1961)

The peroxide values of the oil samples were measured using a titrimetric method

Materials and methods

The vegetable oil used was obtained from General International Oil Company, Port Harcourt. Dried onion skin was obtained from Chuba market.

The extract was ground. Sample weight was measured using Mettler. Solvent extraction analytical balance was performed with the aid of a Soxhlet extraction unit using the Society of Official Analytical

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plotted as a function of time. Comparative studies on the effectiveness of citric acid and its extract on the oxidative stability of vegetable oils.

Vegetable oil samples (100 g) with a mixture of 0.1 g of citric acid and 0.1 g of extract in a reaction vessel at different temperatures of 60 °C , 80°C, 150°C and 180°C, respectively. Oxidative stability of treated oil samples was tested. Peroxide values obtained at each temperature based on time plot. The extracts were tested for their antioxidant potential.

First, they were compared in terms of their ability to protect vegetables. Oil against extensive oxidation in the environment was obtained by relative comparison.

Increase in peroxide content (initial surface oxidation) of treated and control samples of vegetable oil. The percentage increase in peroxide value (PV) during the experimental period was checked using.

and Sharma (2012). The epoxy value and equivalent weight of EPO and EAO epoxy were determined to be 2.95% and 542 g/eq, respectively.

Glycerol was obtained from Sigma-Aldrich and used as emollient. Acetic acid (CH_3COOH), acetone, anhydrous sodium sulfate (Na_2SO_4).

Citric acid monohydrate (≥ 99.5%, CA), ethanol (95%), hydrogen peroxide (30% H_2O_2), potassium bromide (KBr), sodium carbonate (Na_2CO_3).

Sodium chloride (NaCl), and sulfuric acid (95–97% H_2SO_4) from Friendemann Schmidt Chemicals (Parkwood, Australia). Chemical reagents were all of analytical grade. And were used if received.

Method

X-ray diffraction (XRD)

following the procedure of the American Oil Chemists' Society (AOCS) (American Oil Chemists' Society, 1960).

The effect of synthetic citric acid, extract and a mixture of citric acid and extract in different temperature ranges on the oxidative stability of vegetable oil samples was investigated by the titrometer method.

The effect of temperature on the efficiency of synthetic citric acid.

To ensure the oxidative stability of acidic vegetable oil, an oil sample (100 grams) was treated with citric acid (0.2 grams). And concentrations at 60°C in paraffin wax using the unrefined oil sample as a control oil sample.

The peroxide is removed every hour for measurement. Values for samples treated at different temperatures, 60 °C, 80 °C, 150 °C and 180 °C, respectively, during the five-hour reaction period. The amounts of peroxide obtained at each temperature were

Method and materials

Materials

Native cassava starch (moisture 11.43% and amylose content about 21.20%), oil palm fiber empty fruit bunch (EFB) (moisture content 9.30%, powder).

And commercial refined palm oil (minimum purity 99.00%, molecular weight 849 g/mol, 1.50 mol double bonds per mol palm oil) by LGC Scientific SDN BHD located in Selangor (Malaysia).

EFB fibers were exposed to heat and alkali. Treatment according to our previous research (Yang et al., 2020). The resulting fibers consist of 44.70% cellulose, 24.55% hemicellulose.

and 15.45% lignin. Epoxidized palm oil (EPO) with a molecular weight of 873 g/mol was synthesized according to Kim

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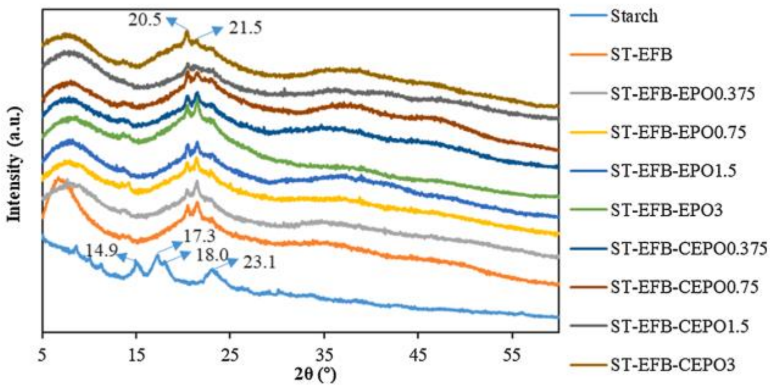
a scan speed of 2/min. The XRD pattern can reveal the interactions of the components through the change of the crystal structure. The XRD patterns of the prepared starch and biocomposites are shown in Figure 3.

Diffraction of the samples was recorded using an X-ray diffractometer (Empirin Panalytics) operating in Cu-Kα radiation produced at 40 mA and 40 kV.

The diffraction patterns were measured in the range of 5-60◦ at room temperature with



Conclusion

The results of the above studies show that citric acid and extract act as antioxidants.

For the oxidative stability of vegetable oil, citric acid is more effective than the extract. However, the mixture of citric acid and the extract has a better result than the use of the extract alone, as the peroxide values of citric acid/extract are comparable to those of citric acid, this shows that citric acid has a synergistic effect on the extract.

Therefore, it is recommended to mix the extract with citric acid. So, this mixture can be used instead of citric acid to use only the extract. This helps to reduce production as citric acid is more expensive than extracts which can be obtained at a very low price.

In the case of ixoradia epoxidized oil, we concluded that as the CEPO concentration increased.This may be because CA carboxyl groups contributed to further interaction with starch/fibers and group cross-linking reaction in the undisturbed molecule.

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