

Effects of Eugenol on Thermal Autoxidation of Palm Oil

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ABSTRACT

The effects of eugenol on the thermal autoxidation of palm oil were studied in the 40 – 97°C range under atmospheric air system. The antiperoxidative action of eugenol was indexed by measuring peroxide number and methyl esters of fatty acids from palm oil. The eugenol isolated from clove leaf oil exhibited activity as a potential antioxidant for use in mild temperature against thermal autoxidation.

INTRODUCTION

Palm oil is gaining importance in the food industry. Palm oils are used as frying media in household and industrial friers. During the life of a frying oil the development of brown color is normally associated with oxidation and polymerization.

Deterioration of lipid is expedited by oxidation, enzyme and contamination of trace metal. The thermal autoxidation and composition of palm oil has been studied (Goh, 1985). However, the study of addition of natural antioxidant to palm oil has not been reported.

Many naturally occurring substances of potential antioxidant activity are of particular interest. Relationship between the structure of an antioxidant and its antioxidative activity has been investigated by several workers. Letan (1966) reported the relation of structure to antioxidative activity of quercetin and some of its derivatives. Das and Pereira (1990) studied the antioxidative effect of a number of flavonoids in palm oil. Their potency of antioxidative activity is affected by location and number of the hydroxyl group in the ring. Eugenol, which occurs naturally in clove, has potential as a compound to inhibit autoxidation in lipids. Clove has been mostly used in food industry as a flavoring (Coulter, 1990). Therefore, eugenol could be added to foods as a flavoring and antioxidant.

The experiments described here are a further

contribution to the study of antioxidative activity of eugenol on thermal autoxidation.

MATERIALS AND METHODS

Palm oil was purchased from a local market in Yogyakarta. The eugenol used in this study was isolated from clove leaf oil. Other chemicals used were obtained from E. Merck, Germany. The oxygen gas was supplied by air pump.

Treatment of the palm oil: Palm oil was treated as follows:

1. Palm oil without eugenol (control) and with eugenol (200 ppm) were stored at 40, 60 and 75°C for 1 month. Oil samples were withdrawn periodically and analyzed for peroxide content.
2. The palm oils were placed in a tube inserted in an oil bath. A carefully controlled flow (2.3 ml/sec) air was bubbled through the sample while the entire bath and samples were held at a temperature of 97°C. Oil samples were withdrawn periodically and analyzed for peroxide content by reaction with a starch-iodine indicator.
3. The palm oils treated in part 1 were esterified for fatty acid analysis.

Determination of peroxide value: A small portion of oil (5 g) was dissolved in a 30 ml of (2 : 3 v/v) chloroform-acetic acid mixture. Approximately 0.5 ml solution of KI was added to the solution which liberated blue color. This blue mixture was titrated to a colorless end point with 0.1 N standard sodium thiosulphate solution. Peroxide value was stated as milliequivalents per kilogram of oil. Peroxide value (POV) = $(A \times 0.1 \times 1000) / G$
where :

A = ml of sodium thiosulphate solution needed in titration.

B = palm oil sample weight.

Preparation of fatty-acid methyl ester: 0.2 gram of sodium was dissolved in 25 ml of absolute methanol, and the solution was refluxed for 3.0 h with 10 g of palm oil. The methanol was then driven off in vacuo below 50°C, and the residual esters were washed with warm water until free from alkali, and dried over anhydrous Na₂SO₄. Methyl esters of fatty acids obtained were identified with gas chromatography.

Gas chromatography (GC): Methyl esters were analyzed on a Hitachi gas chromatograph equipped with a flame ionization detector. Data were collected and integrated on Shimadzu integrator. The column was diethyleneglycol succinate (DEGS). Nitrogen was the carrier gas at 30 ml/min. The oven temperature was 60 – 200°C and programmed at 15°C/min. The injector temperature was 225°C.

RESULTS AND DISCUSSION

Determination of oxidative level: Samples were withdrawn from the flask at suitable intervals and subjected to peroxide number determination by iodometric determination. Figure 1 and 2 show, for illustration only, a very small fraction of the actual results (autoxidation value versus time).

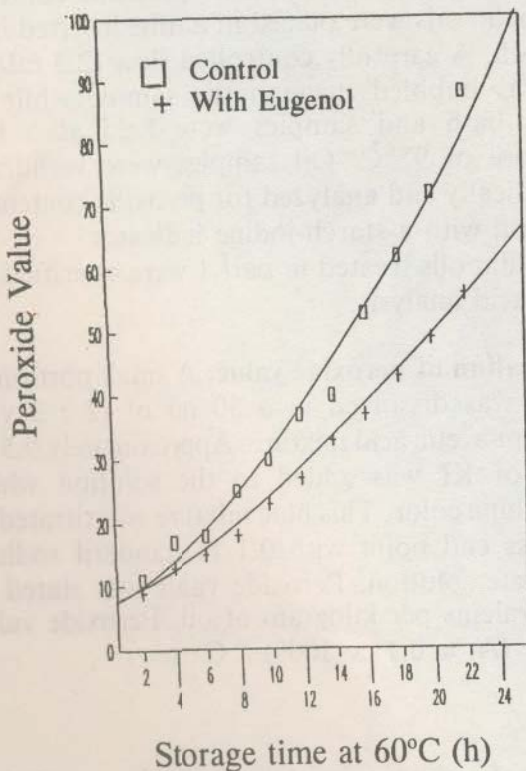


Figure 1. Antioxidative activity of eugenol on autoxidation of palm oil at 60°C

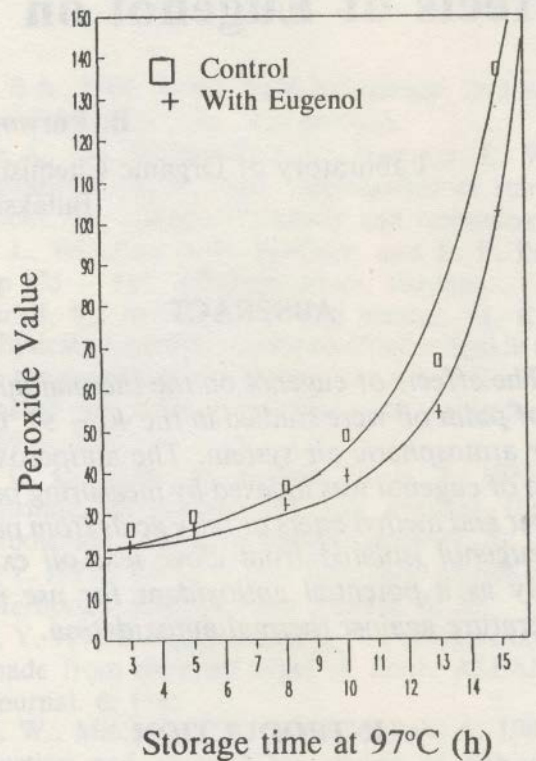


Figure 2. Antioxidative activity of eugenol on autoxidation of palm oil at 97°C

Calculation of Protection Factor:

The antioxidative activity of eugenol was measured by protection factor (PF). The PF is defined as $PF = (t_a - t_c)/t_c$ where:

t_a = time to reach an arbitrarily peroxide level, with eugenol.

t_c = ditto, without antioxidant (control)

The calculation results of the experiment are summarized in table 1.

Table 1. Protection factor of eugenol at 40, 60, 75 and 97°C

Antioxidant	Protection Factor (PF) at:			
	40°C	60°C	75 - C	97°C
Eugenol	0,35	0,28	0,25	0,06

Calculation of methyl ester composition:

The methyl ester composition was analyzed by gas chromatography equipped with integrator. The results of the calculation are shown in table 2.

Table 2. Gas chromatography analyses of methyl ester derived from palm oil

methyl ester	Palm oil heated at:					
	40°C		60°C		75°C	
	C ^a	E	C	E	C	E
C ₁₂ : 0	tr	tr	tr	tr	tr	tr
C ₁₄ : 0	tr	tr	tr	tr	1.19	1.29
C ₁₆ : 0	7.78	37.84	46.73	42.10	49.22	48.92
C ₁₈ : 1	41.83	43.03	42.24	45.75	35.64	39.12
C ₁₈ : 2	7.60	7.05	3.45	4.17	4.46	5.64

^aRelative amounts computed from peak areas (%)

tr : trace (< 1%)

C : control (oil without eugenol)

E : oil with eugenol (200 ppm)

Early works (Sherwin, 1968; Kikugawa, 1987) clearly demonstrated methods of determining antioxidative activity. In their procedures oil was allowed to oxidize in presence of the air and progress of the oxidation was followed by determination of peroxide content. Antioxidative activity, i.e., the ability to inhibit oxidation of oil was measured and compared with that of controls containing no antioxidant. The results are shown in figure 1 and 2. The plots shown are average value from three samples tested over certain period while oil was kept at 40, 60, 75 and 97°C. Statistical analysis of the data for a certain period indicated that peroxide value of samples (control and treated with eugenol) did not differ significantly. Calculation of data (not shown) displayed in table 1 indicates that protection factor of eugenol to autoxidation of palm oil was not high enough to be effective. At a low temperature of 40°C a PF (0.35) higher than that of high temperature was obtained. The losses in protection factor maybe due to high temperature conversion of the eugenol the quinone compound which has no antioxidative activity.

Effects of changes in composition of fatty acid methyl esters from treated palm oil were measured and shown in table 2. There were some differences in the relative composition in that the methyl esters (treated with eugenol) were somewhat higher in unsaturated

fatty acids than that of control. This may be the result of the protection against oxidation by the presence of eugenol. The higher antioxidative activity was noted in the slowest moving unsaturated methyl esters to saturated methyl ester.

CONCLUSION

From the comparative study on determination of peroxide content and composition of methyl ester in these experiments, the following conclusion can be drawn: Eugenol is effective in inhibiting autoxidation at low temperature (40 – 60°C). Eugenol has low protection factor therefore exhibits relatively weak antioxidative activity.

ACKNOWLEDGMENT

The authors are grateful for financial support provided by Food and Nutrition Development and Research Center, Gadjah Mada University.

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