Comparative Study of Physical Methods for Lipid Oxidation Measurement in Oils

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ABSTRACT

For the determination of lipid oxidation in oils, electrical, optical, spectroscopic and extraction methods were investigated using rice bran oil and doubly-fractionated palm olein as model systems. The oxidized polar components and dielectric constant of rice bran oil increased very similarly with those of double-fractionated palm olein. In the case of rice bran oil, all of the test methods were shown to possess good statistical correlations. Polar components, dielectric constant, refractive index and polymer content showed relatively better correlations. It was shown that diene and triene content determined by spectroscopic methods was not suitable for more saturated oils such as palm olein.

INTRODUCTION

The major cause of deterioration of lipids and lipid-containing foodstuffs is known to be lipid oxidation. In spite of many assessments to measure the lipid oxidation in oils, no single method has yet been established to represent all oxidative qualities of lipids because of the complexity of the reactions between lipids and other substances (1,2). The degree of lipid oxidation can be measured by chemical and/or physical methods (1). Among chemical methods, peroxide value, TBA test, carbonyl compound, Kreis test and anisidine value have been widely used. In the case of physical methods, conjugated diene content, infrared spectroscopy, refractive index and gas chromatographic method have been used to measure lipid oxidation. In recent years, measurement of the dielectric constant of lipids is reported to be very effective in determining the quality of oils due to its reproducibility and the simplicity of the measuring procedure (3,4). The progress of lipid oxidation also can be measured by the increase of oxidized polar lipid content itself (5,6).

In this study, attempts were made to examine physical measurement methods for lipid oxidation in rice bran oil and double-fractionated palm olein and to compare relationships among them.

EXPERIMENTAL PROCEDURES

Materials

The refined, bleached and deodorized (RBD) rice bran oil and RBD double-fractionated palm olein (DF palm olein) were purchased from local markets in Korea and Malaysia, respectively. Acid value and iodine value of rice bran oil were 0.35 and 101.2, respectively, and those of DF palm were 0.45 and 61.5. Cloud point of DF palm olein was 3.6 C and that of rice bran oil was -5 C. All other reagents used were of analytical grade unless otherwise specified.

Heating Conditions and Sampling Method

Heating of oil was conducted in a Valentine batch fryer (working volume, 2-4 l) at 180 ± 5 C for 50 hrs without forced agitation. An aliquot of 250 ml oil was collected for each sampling at the geometric center of residual oil. Refills of new oil were not made after sampling. To avoid the increase of specific area (area contacting air per unit weight or volume of oil) during successive sampling without refills, a fryer with inclined side wall was used. Thus, the specific areas of oil were maintained in the range of 0.17 ± 0.01 cm^2/ml oil.

Analytical Methods

Polar and nonpolar components in oils were separated by column chromatography (6). Column-packing material used was silica gel 60, and polar components were eluted with a solvent mixture comprised of 87% light petroleum (boiling point 40-60 C) and 13% diethyl ether. Dielectric constants of oils were measured by using Foodoil Sensor NI-22 (Northern Instruments Corp., Lino Lakes, Minnesota). Conjugated diene and triene contents of oils were determined by spectrophotometer (Varian Series 634) at 232 nm and 268 nm, respectively. In UV spectroscopy, oil samples were diluted in iso-octane to a final concentration of 2 mg/10 ml. Using Abbe 2L refractometer (Bausch & Lomb Co., Rochester, New York), refractive indices of oils were measured at 25 C. The polymer content of oil was determined as the chloroform insoluble portion after methanolysis according to Peled (8).

RESULTS AND DISCUSSION

For the determination of lipid oxidation, DF palm olein and rice bran oil were used. Oxidized polar lipid components increased significantly as the heating time increased (Fig. 1). Contents of polar components in fresh oils were 6% or less and reached 26% after 50 hr heating. Polar substances separated by column chromatography also included mono- and diglycerides and unaltered free fatty acid, whereas nonpolar components were mostly unaltered triglycerides. There was no significant difference in polar components between rice bran oil and DF palm olein.

For the measurement of dielectric constants of oils, the instrument was calibrated according to Fritsch et al. (3) with test oils whose readings were between 0.0 and 4.0. The dielectric constants of both fresh oils were about 2.1 and

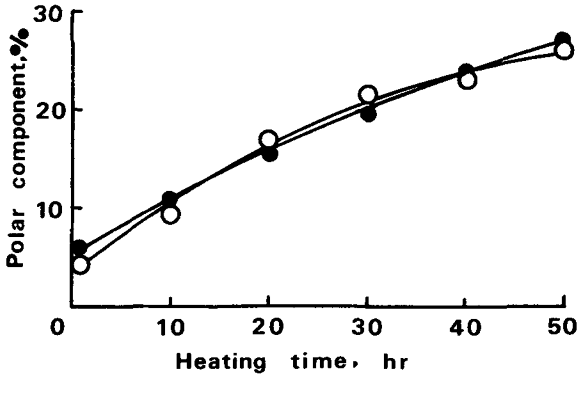

FIG. 1. Effect of heating time on the oxidized polar components of rice bran oil (●) and double-fractionated palm olein (○).

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increased to about 9.0 after 50 hr heating (Fig. 2). The increasing modes of both oils were very similar, and little difference in dielectric constant between the two oils was observed throughout the heating period.

Content of conjugated dienes and trienes was determined (Fig. 3). To calibrate the spectrophotometer, rice bran oil heated for 50 hr was used. The absorbance at 232 nm varied linearly between 0.0-0.8, corresponding to 0.0-22.0 ppm rice bran oil in iso-octane. In this range of rice bran oil concentration, the absorbance at 268 nm varied between 0.0-0.16. The value of A_{232} of fresh rice bran oil (0.27) was higher than that of DF palm olein (0.06). The results indicate that fresh rice bran oil has more conjugated diene hydroperoxide than DF palm olein. The values of A_{232} of both oils increased rapidly for the first 20 hr heating, and the rates of increase decreased thereafter. The triene contents also increased, but very slowly in both oils.

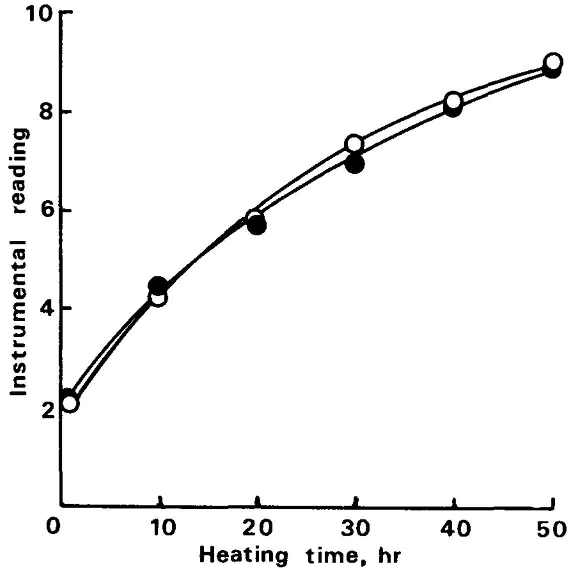

FIG. 2. Effect of heating time on changes in dielectric constant of rice bran oil (●) and double-fractionated palm olein (○).

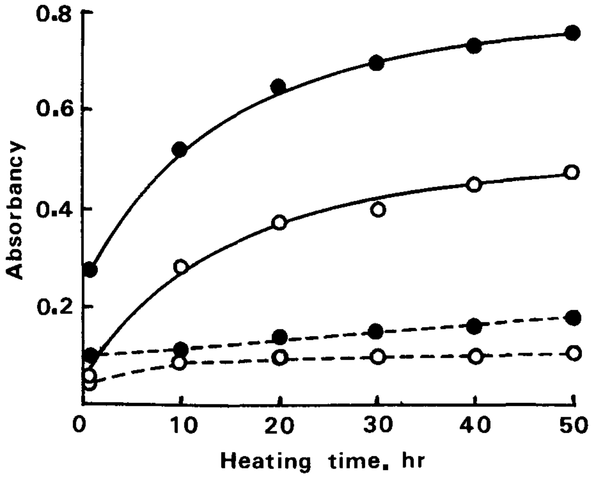

FIG. 3. Effect of heating time on changes of absorbances at 232 nm (solid line) and 268 nm (dotted line) of rice bran oil (●) and double-fractionated palm olein (○).

One of the convenient and simple methods to measure oil deterioration was determination of RI (9). Refractive indices of both oils increased almost linearly with the increase in heating time (Fig. 4). RI values of rice bran oil were higher than those of DF palm olein, as expected.

It is well known that, as oxidation of oil proceeds, the polymer content increases (7). The polymer contents in both fresh oils were nearly zero, increased slowly until 10 hr and more rapidly after 10 hr heating (Fig. 5). After 50 hr heating, rice bran oil was determined to include 20%

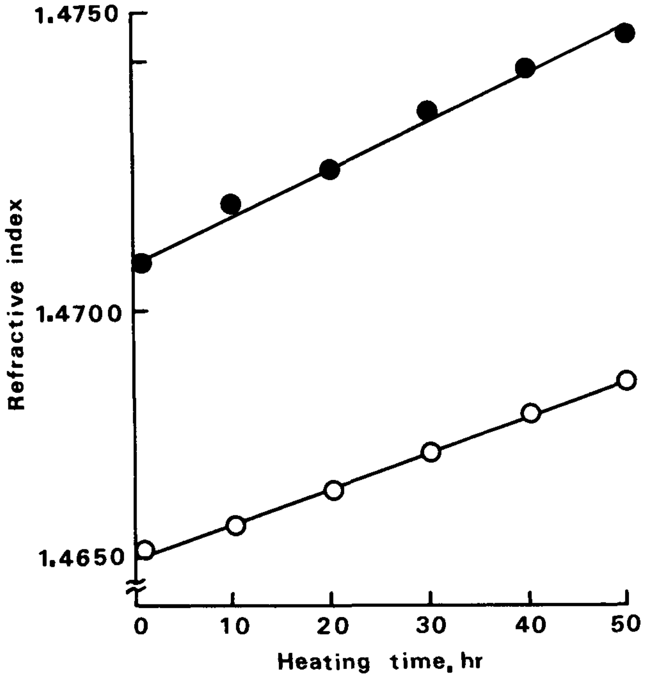

FIG. 4. Refractive indices of rice bran oil (●) and double-fractionated palm olein (○) vs. heating time.

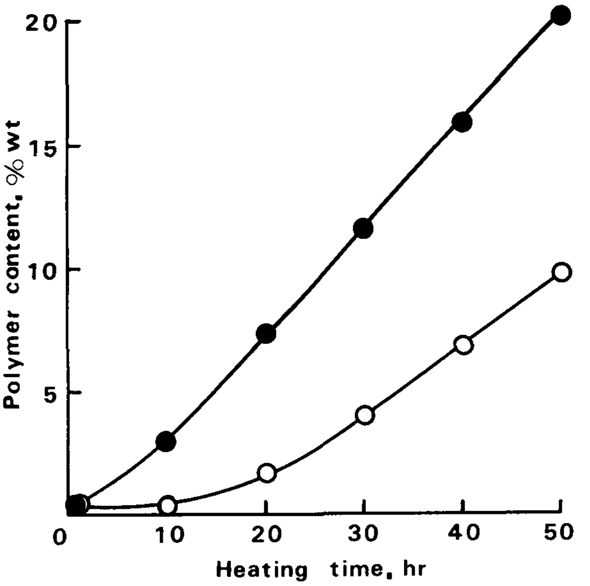

FIG. 5. Effect of heating time on changes in polymer contents of rice bran oil (●) and double-fractionated palm olein (○).

TABLE I

Correlations between Analytical Values of Rice Bran Oil and Double-Fractionated Palm Olein

	Double-fractionated palm olein					
Rice bran oil	Polar components	Dielectric constant	A_{232}	A_{268}	Refractive index	Polymer content
Polar components	–	0.981	0.928	0.827	0.953	0.877
Dielectric constant	0.984	–	0.952	0.883	0.977	0.909
A_{232}	0.904	0.964	–	0.972	0.889	0.774
A_{268}	0.971	0.988	0.947	–	0.821	0.711
Refractive index	0.995	0.993	0.927	0.976	–	0.975
Polymer content	0.995	0.975	0.882	0.974	0.990	–

polymer and DF palm olein only 9%. As shown in Figure 5, the polymerization occurred more rapidly in rice bran oil than in DF palm olein.

Among analytical methods tested, conjugated diene content, refractive index and polymer content discriminate clearly between the two oils after 10 hr heating, whereas oxidized polar components and dielectric constant do not discriminate each other even in absolute abuse level.

The correlation coefficients between every two analytical values were obtained by linear regression analysis and are given in Table I. In the case of rice bran oil, polar components, dielectric constant, refractive index and polymer content were shown to have a high correlation. Dielectric constants especially appeared to possess correlation coefficients of 0.96 or higher with all methods. In the case of DF palm olein, polar components, dielectric constant and refractive index were shown to have relatively good correlation. However, spectroscopic methods measuring the existence of double bonds appeared not to be suitable for DF palm olein, which is composed of less unsaturated fatty acids than is rice bran oil.

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[Received November 28, 1984]

A Mathematical Model for the Prediction of Triglyceride Molecular Species by High Performance Liquid Chromatography

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ABSTRACT

The physicochemical and theoretical relationships between the traditional equivalent carbon number (ECN) and a proposed elution theory for triglyceride molecular species that has been expressed as a matrix model were demonstrated by multiple regression analysis. It was concluded that the ECN expression has two independent variables, that is, the total acyl carbon number (CN) and the total double bonds (DB), and one dependent variable , the relative retention time (RRT). In the proposed elution equation, there are six independent variables, including the carbon numbers and number of double bonds in each acyl group to be considered.

INTRODUCTION

Equivalent carbon numbers (ECN) or partition numbers (PN) have been widely accepted as empirically derived values for determining the molecular species of triglycerides when using reverse-phase high performance liquid chromatography (HPLC) (1-7). The definition of ECN or PN is ECN(PN)= CN−2•DB where CN is the total acyl carbon number and DB is the total number of double bonds in the molecule. In addition, a matrix model for the identification of lipid molecular species has been proposed by the authors (8,9). The matrix model (For ease in expressing the constants and variables among the acyl groups in triglyceride molecules; it does not follow mathematical operations.) can be written as:

$$CN=p_1 \cdot \log(RRT)+q_1 \qquad CN=\begin{vmatrix} x & d_1 \\ c_2 & d_2 \\ c_3 & d_3 \end{vmatrix}$$

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