Reaction Conditions for Measuring Oxidative Stability of Oils by Thermogravimetric Analysis

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ABSTRACT

A method for evaluating the oxidative stability of oils based on heating the sample in an oven and periodically testing for weight gain has been known for over 100 years. Thermogravimetric analysis (TGA) with its highly sensitive recording electrobalance turns this simple method into a powerful technique for studying the relative thermooxidative stabilities of oils. This paper explores the potential of an isothermal TGA via evaluation of several freshly processed, unhydrogenated soybean oils. The objective was to define the parameters of the TGA experiment for fast routine measurement and to compare isothermal and dynamic experiments. The consideration of influence of temperature, specific surface area, air flow rate, sample volatilization and nature of the sample pan on the induction period (IP), which is a measure of the oil's resistance to oxidation, revealed that the temperature and specific surface area are the major parameters that affect the oxidation process. The Arrhenius plot in the range of 80-150 C has shown that the overall activation energy of the oxidation process for three freshly processed oils lies within the range of 21-22 kcal/mole. The rate of oxidation at 150 C is directly proportional to the specific surface area of an oil, suggesting that the rate of oxygen diffusion determines reaction rates at this temperature. A coefficient of variation of the IP better than 2% was found in a routine experiment (10 mg sample, 150 C, 60 ml/min air flow rate, aluminum pan) for typical oils which had an IP range of 25-31 min.

INTRODUCTION

Autoxidation is one of the major factors that affect the quality attributes of vegetable oils, even when oxygen is present in minute quantities. For this reason, many chemical and physical methods have been developed for assessing the extent of oxidation. A distinction should be noted between stability tests and methods of measuring the extent of oil oxidation. Stability tests measure the stability of an oil under conditions that attempt to accelerate the normal oxidation process (1). Oxidation curves thus obtained usually comprise an induction period (IP) which, in some cases, reflects the quality of an oil (2). The periodic determination of peroxide values (PV) in Wheeler's test (3), the active oxygen method (AOM) (4), automated AOM (5) and the ASTM oxygen bomb method (6, 7) are stability tests widely accepted in the oil industry. Microanalytical methods such as gas chromatography (8), differential scanning calorimetry (9, 10) and thermogravimetric analysis (10-15) have gained popularity in recent years.

One of the oldest methods for evaluating the oxidative stability of oils was based on heating the sample in an oven and periodically testing for weight gain (16). This is essentially the principle of isothermal TGA which continuously monitors changes in sample weight while the sample is held isothermally in a stream of flowing air or oxygen. A dynamic TGA was preferred for estimating the relative oxidative stabilities of the crambe oil (11), sperm whale oil and several wax esters (12). An isothermal as well as dynamic TGA were used to compare stabilities of several vegetable oils (10, 13-15). Coefficients of variation of 4.4-7% have been reported (10, 13-15) for the measurement of the IP in isothermal experiments.

Present work describes the reaction conditions used to measure the relative oxidative stability of freshly processed, unhydrogenated soybean oils. High sensitivity, maximum gravimetric accuracy and accurate temperature measurement, calibration and temperature stability of the TGA apparatus (17) suggest its application for such use.

EXPERIMENTAL

Apparatus

A Perkin-Elmer Thermogravimetric System, Model TGS-2 with System 4 Microprocessor Controller for temperature programming and Thermal Analysis Data Station, was used throughout this study. The analyzer was placed on a sturdy marble table close to a concrete wall in order to minimize environmental vibrations. The temperature calibration was performed automatically between 75 and 200 C with a thermocouple tip in close contact with the sample pan (17) and was cross-checked using a ferromagnetic calibration standard alumel (Perkin-Elmer Part No. 998-8015). During both calibration and experiment, dry air (zero-grade quality, Union Carbide) was passed through the balance at 60 ml/min.

The isothermal temperature stability of the TGA apparatus, which is absolutely necessary in this type of temperature sensitive experiment, was determined using a ferromagnetic standard alumel with magnetic transition temperature at 163 C (18). The maximum temperature fluctuation of 0.1 C/60 min was found at two temperatures of 160 and 161.5 C in the middle of magnetic transition. The balance calibration was checked occasionally using the 100 mg Class M calibrating weight (Perkin-Elmer Part No. 990-8397).

Standard aluminum DSC pans (6.5 mm ID × 1.6 mm deep, Perkin-Elmer Part No. 219-0041) used in this study were cleaned with n-hexane before use and discarded after each experiment. Platinum sample pans for TGS-2 (5.8 mm ID × 1.8 mm deep, Perkin-Elmer Part No. 319-0264) were wiped off and briefly heated in the flame after each experiment. Aluminum sample pans were used throughout this work except for an initial experiment in which platinum and aluminum pans were compared. The furnace was cleaned of decomposition products daily by raising the temperature to 800 C for 1 min.

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Oxidation

Freshly refined, bleached and deodorized, unhydrogenated soybean oils (PV=O) were obtained from oil refineries. Oils were stored frozen in the dark at −20 C under a dry, ultra high purity grade nitrogen (Union Carbide, less than 1 ppm of oxygen). Samples were melted slowly in the dark at room temperature, and 10.05 ± 0.05 mg of an oil was added to a tared pan using a disposable Pasteur pipette. The pan was then placed in the furnace and kept at 30 C for 10 min until the baseline had stabilized. In the isothermal experiments the temperature was then raised to the reaction temperature at a heating rate of 40 C/min. The collection of isothermal data was initiated as soon as the digital display on the System 4 Controller indicated that the programmed isothermal temperature had been reached. In the dynamic mode, the sample was loaded at 30 C and programmed at a heating rate of 5, 1 and 0.2 C/min. A sample size of 10 mg, temperature of 150 C, air flow rate of 60 ml/min and aluminum pan were selected as standard reaction conditions for routine measurement of the IP.

RESULTS AND DISCUSSION

A typical thermogravimetric curve in isothermal mode is shown in Figure 1. During the induction period (IP), minimal weight changes are observed (phase I). The length of this IP, which is a measure of the oil's resistance to oxidation, is determined through extrapolation of the baseline and upward portion of the curve. An oxidation phase during which a marked weight gain is observed is typical of autocatalytic oxidation (phase II). The maximum rate of weight gain (R_{WG}) can be calculated from the slope of upward portion of the curve. A decomposition phase is characterized by continuous weight loss due to secondary reactions of hydroperoxides and formation of volatile products including aldehydes, ketones, alcohols, esters, etc. (phase III). The maximum rate of weight loss (R_{WL}) is calculated from the slope of the downward portion of the curve.

Standard platinum sample pans supplied with the TGS-2 instrument had been selected initially for an oil oxidation study. A coefficient of variation of 10% was found for the IP of one oil measured in four new platinum pans at standard reaction conditions (10 mg sample weight, 150 C, 60 ml/min air flow rate). Similarly poor reproducibility was found for two other oils. Moreover, the reproducibility of the IP as measured in one new sample pan was found to be affected by cleaning in the flame as presented in Figure 2. After the initial 18% increase over a period of 12 days (60 cleaning operations), the IP leveled off at 30.0 ± 0.3 min (n=8) between 15-40 days of testing (75-200 cleaning operations). However, after 40-56 days of testing (200-280 cleaning operations), the IP was increased to 30.2 ± 1.2 min (n=10).

The initial increase of IP was attributed to the thermal modification of the pan surface. This was verified by heating another new pan in the flame for 30, 45 and 60 min. Subsequent measurement of the IP showed a 19% increase after 30 min of heating and no further change was observed after 45 and 50 min. For such reasons, standard disposable aluminum DSC pans were tested for oil oxidation studies. A coefficient of variation of the IP better than 2% was found for an oil having an IP mean of 28.6 min (n=11). Similarly, the coefficients of variation of the R_{WG}, R_{WL} and % total weight gain were determined to be 1.7, 2.2 and 1%, respectively, for the same set of samples. Thus, using aluminum pans for oil oxidation studies clearly is preferable to platinum, resulting in a better reproducibility of measurement and eliminating cleaning operations.

The IP could be affected by sample volatilization due to excessive weight loss during the early stages of oxidation, especially at higher temperatures. In a control experiment oil samples weighing 10 mg were heated at 150 and 190 C under nitrogen atmosphere. There were no weight changes observed under these experimental conditions during the experimental time which typically was needed to complete the oxidation in the air. These results indicate that the sample volatilization does not affect the measurement of the IP at the chosen temperature.

The influence of air flow-rate on the IP at 150 C was also investigated using 10 mg oil samples. It was

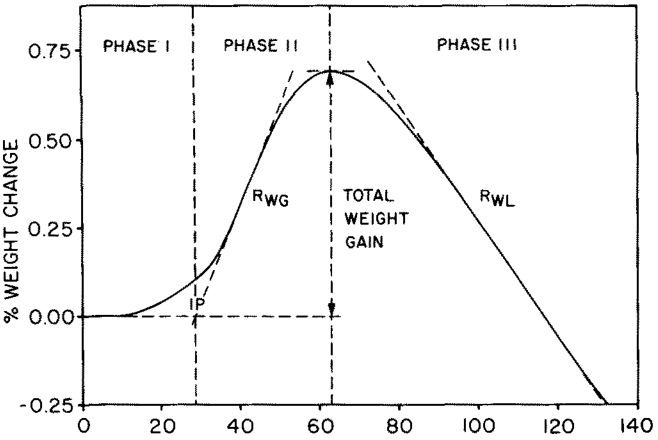

FIG. 1. Thermogravimetric curve of a soybean oil as measured isothermally under standard reaction conditions (temperature 150 C, sample weight 10 mg, air flow-rate 60 ml/min).

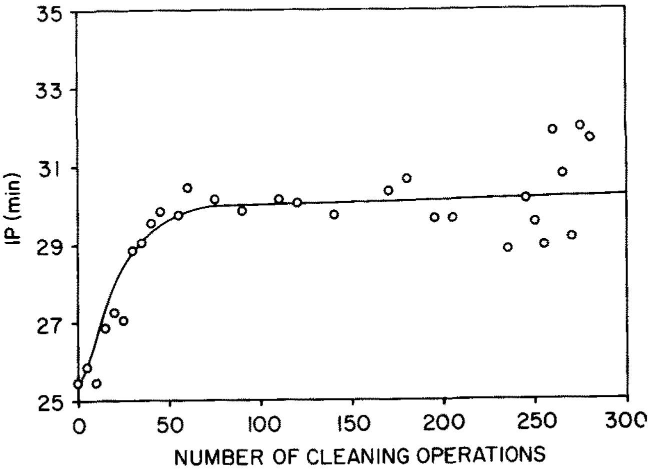

FIG. 2. Effect of flame cleaning of the platinum pan on the IP of a soybean oil as measured isothermally under standard reaction conditions (temperature 150 C, sample weight 10 mg, air flow-rate 60 ml/min).

found that at flow-rates of 20, 40, 60 and 80 ml/min the IP values were constant, indicating that the air flow-rate has no effect on the oxidation process. This is not unexpected because the oxygen concentration is not a rate limiting step in autoxidation reactions, except at very low concentrations (2). Moderate flow-rates, however, are to be preferred in order to minimize the interaction of decomposition products with the sample.

It has been shown by several investigators that the oxidation of an oil is not only a function of temperature and time, but also depends on the specific surface area of the sample used for testing (11, 19-21). The rate of oxidation as measured by PV (20), viscosity and titratable acidity (21) was found to be directly proportional to the specific surface area of the oil. It was concluded that the rate of oxygen diffusion across the air-oil interface is the limiting factor which determines the rate of oxidation (20, 21). Although a high surface area-to-weight ratio was recommended for dynamic TGA oxidation studies (12), no details have been published on how the sample size affects the results in an isothermal TGA experiment.

Table I illustrates the effect of the sample size on oxidation characteristics of an oil as measured isothermally at 150 C. Data shown here represent a single measurement for each sample weight. Both the R_{WG} and R_{WL} are markedly affected by varying the sample weight. The R_{WG}/R_{WL} ratio increases with increasing sample weight. Especially noteworthy is the observation that the R_{WL} becomes greater than the R_{WG} for samples weighing less than 3 mg and vice versa. Because the formation and breakdown of hydroperoxides occur simultaneously, the R_{WG} and R_{WL} must be composites and should not be mistaken for rates of oxidation and decomposition. Generally, as the sample weight is decreased both oxidation and decomposition reaction rates become faster, resulting in shorter IP and greater R_{WG}, R_{WL} and % total weight gain. The IP was found to be inversely proportional to the specific surface area (SSA) of the oil, which is given by the ratio SSA = (cross sectional area)/(sample weight). This dependence is well described by the linear equation $IP = 32.35 - 0.989 \times SSA$ (correlation coefficient $r = -0.99$), suggesting that diffusion is the factor which limits reaction rates. The differences in IP were found to be statistically insignificant for samples weighing 8, 10 and 12 mg, respectively. Sample weight of 10 mg was chosen for routine analysis.

TABLE I

Effect of Sample Size on Oxidation Characteristics[a] of a Soybean Oil as Measured by TGA at 150 C[b]

Sample weight (mg)	IP (min)	$R_{WG} \times 10^2$ (%/min)	Total weight gain (%)	$R_{WL} \times 10^2$ (%/min)	R_{WG}/R_{WL}
3.082	21.4	7.12	1.03	7.38	0.96
5.076	26.5	5.25	0.95	3.98	1.32
8.020	28.6	3.80	0.86	2.36	1.61
10.054	28.7	2.74	0.69	1.63	1.68
12.081	29.4	2.55	0.76	1.36	1.88

[a] Abbreviations refer to induction period (IP); rate of weight gain (R_{WG}); rate of weight loss (R_{WL}).

[b] Other reaction conditions included the air flow-rate of 60 ml/min.

In order to select the most suitable temperature for routine studies, a temperature range of 80-190 C was examined. In addition it also was interesting and useful to investigate how different phases of oil oxidation are affected by temperature, and whether an activation energy of the oxidation process can be calculated. The results are summarized in Table II. In general, with increasing temperature the IP becomes shorter and the total weight gain is reduced. The R_{WG} passes through the maximum, whereas the R_{WL} increases exponentially with temperature. These results indicate that the volatile products already are generated during the oxidation phase II of the process, and thus, the R_{WG} must not be confused with the rate of oxidation or of oxygen uptake. As the hydroperoxides concentration increases during phase II of the oxidation process, the apparent weight gain due to the oxygen uptake is offset by the accelerating formation of volatile decomposition products such as aldehydes, ketones, alcohols, etc.

The induction phase I of the oxidation process seems to be least affected by the formation of volatile decomposition products. Because the IP is inversely proportional to the rate of oxidation (22), the Arrhenius equation can be written as $IP = IP_o.e^{E/RT}$, where E is activation energy of the process, R is gas constant and T is absolute temperature. The overall activation energy of the oxidation process was calculated from a temperature dependence of the induction period in the range of 80-150 C, as shown in Figure 3. The slope of the line E/R gives the activation energy 21.0 kcal/mole. Similar temperature dependences of the IP were found for two other freshly processed, unhydrogenated soybean oils giving activation energies of 21.3 and 22.0 kcal/mole. The activation energy of 23.2 kcal/mole was calculated for the oxidation of sunflower oil based on data reported by Buzás et al. (13). This value is of the same order as that for the oxidation of unhydrogenated soybean oil. According to Emanuel (22), the

TABLE II

Effect of Temperature on Oxidation Characteristics[a] of a Soybean Oil as Measured by TGA[b]

Temperature (°C)	IP (min)	$R_{WG} \times 10^2$ (%/min)	Total weight gain (%)	$R_{WL} \times 10^2$ (%/min)
80	4071.0	1.27	4.35	0.28
100	961.5	2.20	3.19	0.52
120	229.7	2.67	2.09	0.85
130	110.1	3.01	1.60	1.04
140	56.5	3.34	1.11	1.30
150	28.7	2.74	0.69	1.63
160	13.0	2.46	0.42	2.10
170	5.2	1.87	0.22	2.98
180	2.4	2.28	0.11	3.94
190	1.1	2.09	0.05	5.46

[a] See Table I for key to abbreviations.

[b] Other reaction conditions included the sample size of 10 mg and the air flow-rate of 60 ml/min.

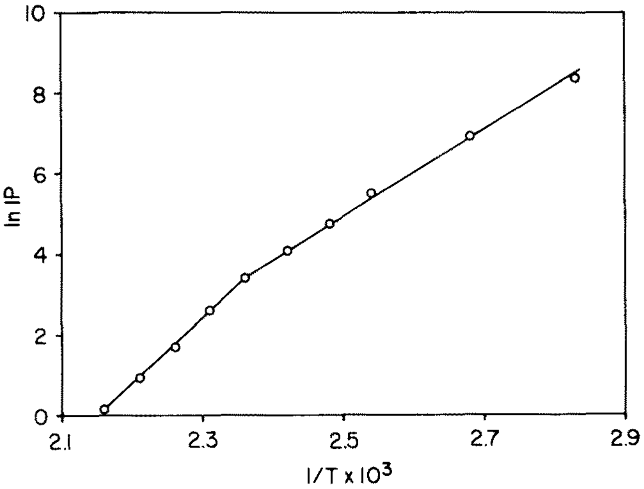

FIG. 3. Effect of temperature on the IP of a soybean oil (sample weight 10 mg, air flow-rate 60 ml/min).

activation energy for the oxidation process of various samples of fat lies within the range of 20-25 kcal/mole. Figure 3 shows the linear dependence of the IP on temperature between 80-150 C, indicating that the same kinetic mechanism governs the oxidation in this range. The activation energy, however, changes at temperatures above 150 C, indicating that the reaction mechanism changes or the IP is affected by the accelerating generation of secondary volatile products above this temperature. Based on these results, the isothermal temperature of 150 C was selected for fast routine analysis. The results obtained at this temperature also can be applied to lower temperatures in the range of 80-150 C.

A method which can be used successfully for measuring the relative thermooxidative stability of freshly processed, unhydrogenated soybean oils is expected to provide differentiation among the samples which have initially light color, bland flavor and zero PV. Six freshly produced oils were evaluated under standard reaction conditions by isothermal TGA, and the results are summarized in Table III. As can be seen, the IP vary from 25.1 to 31.3 min. A statistical multiple range test comparing the IP revealed that sample 1 was significantly different from all others, sample 2 was significantly different from 5 and 6 and samples 3 and 4 were significantly different from 6. When comparing the R_{WG} values, only sample 1 was significantly different from sample 2. When comparing the R_{WL} values, only sample 1 was significantly different from sample 6. Finally, when comparing % total weight gain the differences were statistically insignificant. This implies that only the IP of all measured parameters has a practical value for comparing the relative oxidative stabilities of different samples of the same freshly processed oil. In initial stages of the oxidation process the induction phase I reflects the resistance of an oil toward the oxidation which is related to the fine differences in the composition of triglycerides, extent of previous oxidation (PV), natural antioxidant content, presence of heavy metal catalysts, etc. However, as the oil is somewhat oxidized during phase II of the oxidation process, these fine differences disappear and all samples undergo similar changes upon further oxidation.

TABLE III

Oxidation Characteristics[a] of Six Selected Soybean Oils as Measured by Isothermal TGA at 150 C[b]

Sample No.	IP (min)	$R_{WG}\times10^2$ (%/min)	Total weight gain (%)	$R_{WL}\times10^2$ (%/min)
1	25.1	2.83	0.71	1.56
2	27.8	2.66	0.69	1.62
3	28.4	2.75	0.69	1.64
4	29.1	2.74	0.69	1.63
5	30.0	2.74	0.69	1.64
6	31.3	2.76	0.69	1.69

[a] See Table I for key to abbreviations.

[b] See Table II for other reaction conditions.

TABLE IV

Oxidation Characteristics[a] of Three Selected Soybean Oils as Measured by Dynamic TGA at a Heating Rate of 0.2 C/min[b]

Sample No.	T_i[c] (C)	R_{WG} (%/C)	Total weight gain (%)	R_{WL} (%/C)
1	140.9	0.154	1.19	0.128
2	142.4	0.151	1.12	0.129
6	143.1	0.148	1.10	0.133

[a] See Table I for key to abbreviations.

[b] See Table II for other reaction conditions.

[c] Abbreviation T_i refers to the initiation temperature of weight gain.

Three of the above mentioned samples also have been tested in dynamic conditions using the heating rates of 5, 1 and 0.2 C/min. The initiation temperature of weight gain (T_i) that is analogous to the IP of isothermal methods is used for estimating the realtive thermooxidative stability under dynamic conditions (12). Although the slowest heating rate provides the best differentiation among the samples, there is only a 2 C temperature difference for the T_i, as illustrated in Table IV. This compares with 6 min time difference for the IP of the same samples as measured under standard reaction conditions. Moreover, the isothermal experiment at 150 C takes 40-50 min compared to the dynamic experiment lasting several hr. The R_{WG}, R_{WL} and total weight gain remained unchanged as in isothermal experiment, and the differences also were found to be statistically insignificant. Based on these results, it can be concluded that the isothermal TGA is a more suitable technique for fast, routine evaluation of the relative oxidative stability of freshly processed, unhydrogenated oils.

In the vegetable oil industry there is a continuing need for a reliable and fast analytical method which could be used in production and product control for monitoring refining processes, for assessing the effectiveness of antioxidants, for studying the effect of light on the oxidation process, for evaluating the deleterious effect of metal catalysts and for monitoring numerous storage studies. The TGA approach to measuring the relative thermooxidative stability of oils is by no means new, but still unique in using extremely small samples, in being fast and in providing good reproducibility of results. Such an analytical method, which is capable of measuring the relative thermooxidative stability, is potentially useful not only in the oil and food industry, but also in cosmetics production, the plastics and petrochemical industries and many others.

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Flavor and Oxidative Stability of Continuously Hydrogenated Soybean Oils

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ABSTRACT

Soybean oil was partially hydrogenated in a continuous system with copper and nickel catalysts. The hydrogenated products were evaluated for flavor and oxidative stability. Processing conditions were varied to produce oils of linolenate contents between 0.4 and 2.7%, as follows: oil flow, 0.6-2.2 liters/hr; reaction temperature, 180-220 C; hydrogen pressure, 100-525 psig, and catalyst concentration, 0.5-1% copper catalyst or 0.1% nickel catalyst. *Trans* unsaturation varied from 8 to 20% with copper catalyst and from 15.0 to 27% with nickel catalyst. Linolenate selectivity was 9 with copper catalyst and 2 with nickel catalyst. Flavor evaluation of finished oils containing 0.01% citric acid (CA), appraised initially and after accelerated storage at 60 C, showed no significant difference between hydrogenated oils and nonhydrogenated oil. However, peroxide values and oxidative stability showed that hydrogenated oils were more stable than the unhydrogenated oil. CA+TBHQ (tertiary butylhydroquinone) significantly improved the oxidative stability of test oils over oils with CA only, but flavor scores showed no improvement. Dimethylpolysiloxane (MS) had no effect on either flavor or oxidative stability of the oils.

INTRODUCTION

Currently most of the acceptable soybean salad oils and shortening-base stocks having good shelf-life are produced by batch hydrogenation processes. Partial hydrogenations in batch convertors with nickel or copper catlyst are reported to improve flavor and oxidative stability of oils for cooking, frying and baking (1-4). The potential of effective continuous slurry hydrogenation with nickel or copper catalyst has been reported by several authors (5-8); however, the oils produced by these processes were not evaluated for flavor and oxidative stability.

This study extends our previous work (8) and considers the relationship of flavor scores and oxidative stability of test oils to the operating conditions for continuous production of partially hydrogenated oils.

EXPERIMENTAL

Materials

Commercial alkali refined and bleached soybean oil (SBO) from Central Soya Inc., Ft. Wayne, Indiana, was used as base and control oil. Commercially hydrogenated and processed oil (Ni-4.6) was included for comparison purposes in the sensory testing program. Analyses of SBO and commercial oils are shown in Table I.

Hydrogenation catalysts, Cu1106P (39% CuO, 43.5% Cr_2O_3, 10% BaO), Nysel (25% nickel in tristearin) and Super-filtrol bleaching earth were obtained from Harshaw/Filtrol Partnership, Cleveland, Ohio.

Additives in deodorized test oils, added during the cooling stage, included: citric acid (CA) (J.T. Baker Chemical Co., Phillipsburg, New Jersey) dissolved in distilled water; tertiary butylhydroquinone (TBHQ) (Eastman Chemical Products, Inc., Kingsport, Tennessee) dissolved in ethyl alcohol, and dimethylpolysiloxane (MS) (Dow Corning Corp., Midland, Michigan).

Analytical Methods

Methyl esters of fatty acids were prepared by transesterification of the sample oil with sodium methoxide in methanol (9). Fatty acid compositions were determined by gas liquid chromatography (GLC) of methyl esters on a column packed with

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