Effect of Transesterification of Lard on Stability, Antioxidant-Synergist Efficiency, and Rancidity Development

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Abstract

Glyceride rearrangement of lard did not affect its resistance to oxidation or alter the efficiency of antioxidants and synergists. Changes in stability were due to the decomposition of tocopherol and the formation of reducing substances. The position of unsaturated fatty acids in the glyceride may influence the free volatile carbonyl compounds present in autoxidized lard and in rancidity development. Interesterification under vacuum produced an odorless and colorless randomized lard with natural stability in the range of the parent lard.

Introduction

TRANSESTERIFICATION is widely used in shortening technology, and reports concerning control (22,38), mechanisms (37), and technological problems (19,26) have been published. However there is little information on the effect of the interesterification on the stability of lard. Two publications have barely considered this possibility (31,32). Pohle, Gregory and Taylor (32), in a comparison of stability methods, observed some improvement in the stability of lard when crystal-modified. Neuwald and Eberhardt (31) reported that interesterified lard for use in cosmetics and pharmaceuticals was more stable than other fats, but they did not systematically investigate this observation.

There are three potential sources of changes in lard stability produced by interesterification. The first, and most relevant, could be due to fatty acid position. Unsaturated fatty acids in lard are located almost exclusively at the 1,3-positions of the glycerides (18, 36). During glyceride rearrangement some of these fatty acids are shifted from the 1,3- to the 2-position according to a random distribution (26). It is a well-known fact that steric hindrance can be a factor in oxidation reactions, and this could affect the rate and over-all mechanism of autoxidation (29). It might be expected that the shift from the 1,3- to the 2-position of some of the unsaturated fatty acids could produce steric hindrance and cause changes in oxidation and in the efficiency of antioxidants and synergists. Stereo specificity in action on 1,3-positions in glycerides exists in the hydrolytic reaction catalyzed by pancreatic lipase (28). However, Mattson and Volpenhein (27) have determined that the position of an unsaturated fatty acid in a triglyceride molecule does not influence its rate of catalytic hydrogenation.

A second source of change in stability might be the decomposition of tocopherols and the formation of antioxidants and synergists during a catalyst treatment, which is usually strongly alkaline in character (2).

The third source of differences might be the oxidation of the fat during treatment and alterations in the oxidized fractions. Such fractions serve as a main substrate for initiation of autoxidation (9,35), and their formation could affect stability and the effectiveness of antioxidants and synergists.

Apart from these stability considerations, there could be changes in rancidity development. This might be caused by differences in the course of autoxidation, hydroperoxide breakdown, and carbonyl formation. It is well known (34) that vegetable oils which have the unsaturated fatty acids predominantly in the 2-position of the triglycerides develop rancidity at a much higher level of autoxidation than lard, which has such labile fatty acids in the 1,3-positions. Ellis, Gaddis and Currie (7) and Gaddis, Ellis and Currie (16), in an examination of similarly oxidized lard and vegetable oils, observed distinct differences in the carbonyl fractions. Thus, random distribution of fatty acids in interesterified lard may affect rancidity development during storage and change the organoleptic threshold of rancidity.

The purpose of this investigation was to clarify these questions regarding the effect of the interesterification process on lard.

Procedure

The investigation was carried out on laboratory rendered and interesterified samples of lard and on commercially rendered and interesterified lard obtained from Swift and Company and Armour and Company. The samples from both companies (hereafter called "A" and "B" without respect to order) were rearranged under atmospheric pressure without protection from air. Both control and rearranged lards from Company B were deodorized. Antioxidants were not added to any of the commercial lards. The laboratory samples were derived from a mixture of 67% back fat and 33% leaf fat, which was dry-rendered at 60C, filtered through a Celite bed, and dried under vacuum at 0.7 mm Hg. Interesterification was accomplished by a modification of the method of Luddy et al. (25). In this procedure stirring was achieved by a rotary flask assembly. The catalytic treatment at 50C was conducted either in the presence of air or at 0.7 mm Hg vacuum. The procedure in the presence of air approximated the usual commercial practice. After the rearrangement process the product was filtered through Celite and dried under vacuum at 0.7 mm Hg. Control and interesterified laboratory samples were not deodorized.

Differential cooling curves were determined to evaluate the completeness of rearrangement or randomization achieved in the interesterification process (26,38). This was considered important since commercial purposes may frequently be satisfied by the crystal modification process in which there is little rearrangement. Iodine values were measured for better explanation of the shapes of the cooling curves.

Stability was determined by the oven method at 60C on 1-in. layers of lard. All stability tests were repeated. Tocopherol was removed from samples for base-line stability tests by a molecular distillation (33) at 190C and 20 μ Hg pressure. After such treat-

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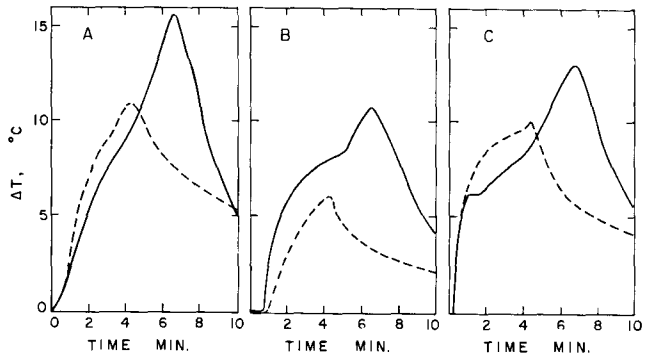

FIG. 1. Control of glyceride rearrangement in investigated samples of lard:
A. Laboratory rendered and rearranged lard
B. Samples of lard obtained from Company A
C. Samples of lard obtained from Company B
——— Control lard before rearrangement
– – – – Rearranged lard

ment all samples of lard showed no induction period, and tocopherol content was below 2 ppm. The molecular distillation technique also removed free fatty acids and methyl esters from the lard.

Peroxides. The iodometric method was employed with the exclusion of air and light as routinely used in this laboratory (23). Values were expressed as milliequivalents per 1,000 g of fat.

Total Carbonyls. The Henick (20) procedure, according to Fioriti (10) and with Chipault (4) modifications and formula (4), was employed. In order to decrease peroxide decomposition interference in the samples oxidized above PV 10, the Mizuno and Chipault (30) peroxide reduction procedure was used.

Total Volatile Carbonyls. Total volatile carbonyls as 2,4-dinitrophenylhydrazones were determined by the vacuum-distillation method of Lea and Swoboda (24), including the modifications of Gaddis et al. (15,17).

Volatile Monocarbonyls. The total volatile monocarbonyl hydrazones were obtained by fractionation of the total volatile carbonyl derivatives on an alumina column as described by Gaddis, Ellis and Currie (13). The volatile monocarbonyl 2,4-dinitrophenylhydrazones were separated into classes by the Gaddis and Ellis (14) paper chromatographic method, and the proportions of each class determined as indicated by Ellis and Gaddis (6) and practiced by Ellis et al. (7).

Individual Compounds in Classes. Individual hydrazones in each class were separated by the paper chromatographic methods described by Ellis, Gaddis and Currie (5), and the proportion of each identified compound in a class was estimated visually as done by Ellis et al. (7).

Oxidized Fractions. The Frankel et al. (11) silica column chromatographic method, including a later modification (12), was used. This method allowed the investigation of "hidden oxidation" (9), which can exist when peroxides have been decomposed. To increase the sensitivity of the Frankel et al. (11) method, larger samples were used, and the formula of the column was changed to 50:90:50 for complete separation.

Free Fatty Acids. Free fatty acids were estimated in ether-ethanol solution by employing the Iwanska method (21).

Tocopherol. Tocopherol in lard was determined by the Bieri et al. (2) and the Erickson and Dunkley (8) column chromatographic methods. The Erickson and Dunkley method displayed the best reproducibility, and data are based on findings obtained.

Iodine Value. The AOCS CD-1-25 method was used.

TABLE I
Effect of Glyceride Rearrangement Process on Tocopherol, FFA, and Peroxide Content in Samples of Lard

	Tocopherol ppm	FFA %	PV
Laboratory rendered lard			
Control	10	0.294	0.0
Randomized in vacuum	8	0.023	—1.0
Randomized in air	5	0.029	—1.0
Company A samples			
Control	23	0.205	5.5
Randomized	11	0.034	3.0
Company B samples			
Control	4[a]	0.014[a]	2.0[a]
Randomized	7[a]	0.029[a]	1.5[a]

[a] Data obtained from Company B samples indicate that the deodorization conditions applied to the control sample were more severe than those for randomized lard, and for that reason results are not directly comparable.

Results and Discussion

Interesterification Process. The differential cooling curves in Fig. 1 show that randomization was complete in each interesterified sample (38). Iodine values of the laboratory lard were unaltered by the interesterification. A similar finding for the commercial lard indicated the probability that the rearranged lard came from the same batch as the control lard. There appeared to be a tendency toward a direct relationship between peak height of the cooling curves and degree of saturation.

The laboratory lard interesterified in air had a yellow color, an unpleasant aroma, and, as indicated in Table I, considerable loss in tocopherols. Significantly, laboratory lard interesterified under a vacuum had only a small loss in tocopherols. The interesterification process caused complete decomposition of peroxides and removed most of the free fatty acids as soaps. The laboratory rearranged lards, whether in air or under vacuum, had negative peroxide values. This might be explained by the formation of reducing substances during the process. It is well known that alkaline treatment at elevated temperatures forms reducing substances from carbohydrates and proteins. Budslawski (3) applied such a technique in the improvement of butter fat stability. Full evaluation of the amount of reducing fraction is hindered by lack of a sensitive method. Curiously, negative peroxide values were not observed in the commercial samples. This might be due to change since interesterification or to differences in the lard-rendering processes. An example of the effect of interesterification on peroxide values is shown for a moderately oxidized laboratory lard in Table II. Even with a starting peroxide value 8.0, the rearrangement process yields a product with a negative peroxide value.

Since the interesterification treatment decomposes peroxides, a means for the determination of the oxidative condition of the lard would be useful. Therefore total carbonyls, volatile carbonyls, and oxidized fractions have been used as indicators of oxidative changes before and after interesterification. As shown in Table III, there was little difference in the laboratory

TABLE II
Peroxide Values at Various States of Transesterification Process

Stage of process	PV
Before treatment	8.0
Catalyst added and mixed	6.0
After randomization	—2.5
Soaps removed and filtered	—1.5
Vacuum redried	—1.0

TABLE III
Effect of Rearrangement Process on Carbonyls and Oxidized Fractions in Lard Samples

Sample of lard	Total Carbonyls				Volatile Carbonyls				Oxidized Fraction	
	λ Max.	Absorption 1 g/50 ml	Unsaturated ppm	Saturated ppm	λ Max.	Absorption 1 g/50 ml	Unsaturated ppm	Saturated ppm	Nonpolar %	Polar %
Laboratory										
Control	434	2.40	0.46	5.34	440	0.03	0.015	0.057	0.2	0.4
Rearranged in vacuum	435	2.45	0.44	5.50	425	0.03	0.003	0.071	0.2	0.6
Rearranged in air	437	2.65	0.88	5.41	425	0.04	0.021	0.066	0.4	0.3
Company A										
Control	437	2.2	1.1	4.3	450	0.07	0.1	0.05	0.8	0.4
Rearranged	435	2.1	0.7	4.3	435	0.06	0.05	0.1	1.0	0.5
Company B deodorized										
Control[a]	437	2.7	1.7	4.9	no det.	0.02	0.004	0.07	0.6	0.7
Rearranged[a]	437	3.4	1.6	6.6	no det.	0.02	0.003	0.05	0.4	0.6

[a] Footnote is the same as for Table II.

lard values for oxidized fraction and carbonyls when interesterification took place under vacuum conditions. However laboratory lard rearranged in air showed increases in some of these measurements. The total carbonyl and its unsaturated fraction, the unsaturated component of volatile carbonyl compounds, and the nonpolar part of the oxidized fraction were higher. This possibly may be related to the unpleasant flavor of this lard. Generally, the wavelength of maximum absorption of volatile carbonyls decreased as a result of interesterification. The commercial lards, as might be expected from their peroxide values, had higher carbonyl and oxidized fraction values than the laboratory lards. There were fairly large differences between the commercial lards. Company A lard had higher volatile unsaturated carbonyls and nonpolar oxidized fractions. Deodorized Company B lard had high unsaturated total carbonyl values but otherwise lower values than those of Company A.

Effect of Interesterification on Stability and Antioxidant-Synergist Efficiency. Stability tests on laboratory lards shown in Fig. 2A indicate that the interesterification process in air decreased stability about 50%. However, when the parent and air-rearranged lards were freed of tocopherol, there was no difference in the rates of autoxidation. The performance of Company A lards was similar to the laboratory lards. The pattern of Company B lards shown in Fig. 2C differs because these samples were deodorized and had lost much of the tocopherol. Referral to Table I shows that the stabilities of thes lards correlate well with tocopherol content. Apparently, when the level of tocopherol detected dropped below 5 ppm, there was little influence on stability. The similar stability of parent and rearranged lards when tocopherol-free seems to indicate little effect of the position of the unsaturated acids in the glycerides after interesterification. Results in Fig. 3A show that interesterification protected from air produced a randomized lard with better stability than the parent lard.

Tocopherol content was obviously not a factor in this result since there was a small decrease due to the treatment (Table I). Apparently, the increase in stability was caused by products formed by the interesterification process. The formation of reducing compounds or reductones by such a treatment and the presence of negative peroxides have already been referred to. These reductones may be formed in the rearrangement process whether protected from air or not. As shown in Table I, both methods of randomization produced lard with negative peroxide values. However, with decreased or no tocopherol, as shown in Fig. 3A and 3B, the reductones did not provide improvement in stability. The effect on stability, by interesterification in air, of an oxidized laboratory lard is shown in Fig. 3B. Negative peroxide values were obtained, and there was no improvement in stability in this example, in which tocopherols had been destroyed.

Fig. 4A, B, and C show the effect of random glyceride rearrangement on antioxidant and synergistic efficiency of tocopherol-free lard samples. Each parent and randomized lard sample showed the same stability with 0.01% BHA. There was no evidence of a synergistic action by compounds formed in the interesterification process. These reductones evidently are not effective with BHA. The addition of the

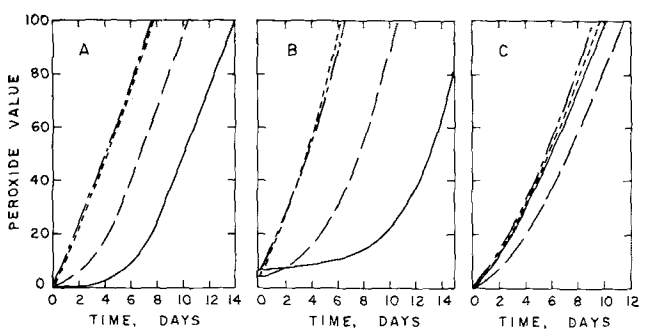

FIG. 2. Effect of glyceride rearrangement process on stability of lard samples in oven test at 60C:
A. Laboratory samples
B. Company A samples
C. Company B samples (deodorized)
——— Control unrandomized lard
– – – – Randomized lard
- - - - - - Control unrandomized lard, tocopherol removed
– – – – – Randomized lard, tocopherol removed

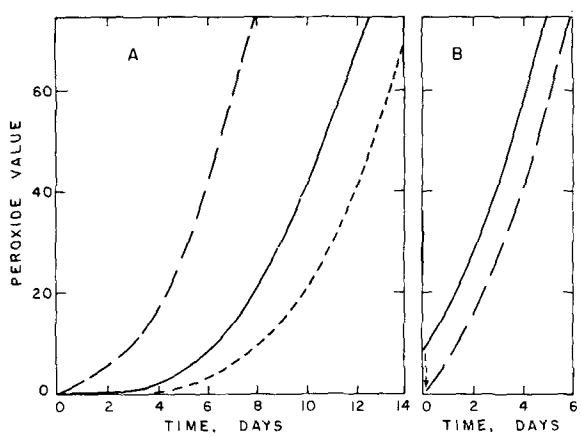

FIG. 3. A. Effect of rearrangement conditions on stability of lard:
——— Control lard
– – – – Rearranged in atmospheric pressure
- - - - - - Rearranged in vacuum 0.7 mm Hg
B. Effect of decomposition peroxides during transesterification on rate of oxidation

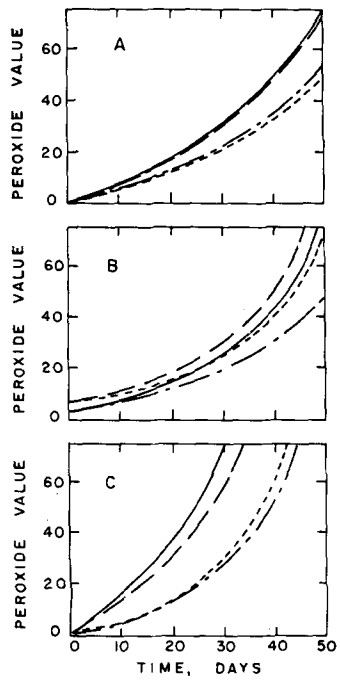

FIG. 4. Effect of glyceride rearrangement process on antioxidant and synergist efficiency in lard samples in oven test at 60C:

A. Laboratory samples
B. Company A samples
C. Company B samples
——— Control lard + 0.01% BHA
– – – – Rearranged lard + 0.01% BHA
· · · · · · Control lard + 0.01% BHA and 0.03% citric acid
– · – · – · Rearranged lard + 0.01% BHA and 0.03% citric acid

synergist, citric acid, increased stability without significantly altering relationships.

Fig. 5 shows the effect of natural antioxidant (tocopherol) content in lard on the performance of added BHA-citric acid. In the interesterification in air, the BHA-citric acid system was partially inactivated or destroyed. As indicated in Table I, heavy losses of tocopherol also occur. The BHA-citric acid combination was most effective in the parent lard, which was more stable than the air-rearranged lard with

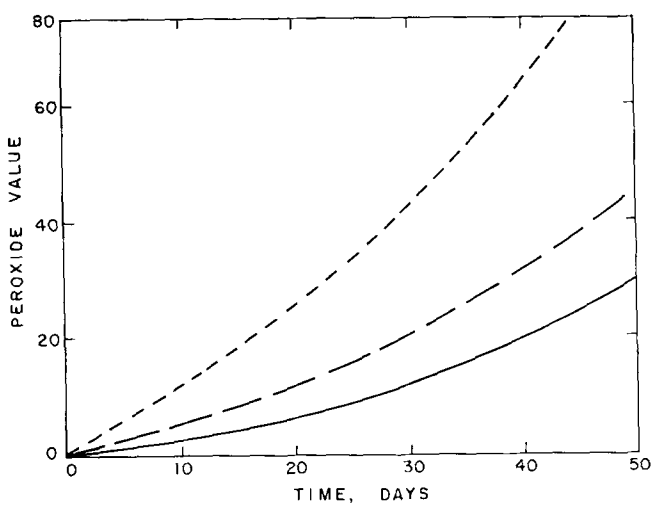

FIG. 5. Effect of natural antioxidants and rearrangement treatment on antioxidant-synergist efficiency in lard samples in oven test at 60C:

——— Control + 0.01% BHA and 0.03% citric acid
· · · · · · Rearranged + 0.01% BHA and 0.03% citric acid (added after transesterification)
– – – – Rearranged + 0.01% BHA and 0.03% citric acid (added before transesterification)

TABLE IV
Effect of Glyceride Rearrangement Process on Total Carbonyl and Volatile Monocarbonyl Content in Lard Samples Stored to PV 38 at 60C with 0.01% BHA Added

	Control lard	Randomized lard
Total carbonyls		
Total		
λ Max.	440	440
Absorption 1 g/50 ml	4.07	3.95
Classes in ppm		
Unsaturated	3.0	2.8
Saturated	6.5	7.0
Volatile monocarbonyls		
Total monocarbonyls		
λ Max.	352	354
Absorption 1 g/50 ml	0.100	0.116
Monocarbonyls in classes %		
Saturated	48	33
2-Enals	30	41
2,4-Dienals	22	26

added antioxidant. The differences seem principally caused by the destruction by interesterification in air of natural and added antioxidants. The BHA-citric acid efficiency in the interesterified lards was exactly the same when they were tocopherol-free (Fig. 4A). This indicates the destruction, by the interesterification procedure in air, of not only tocopherols but possibly other natural oxidation-inhibitors.

In summary, differences in stability as the result of interesterification appear to be attributable to changes in the amount of natural antioxidants and destruction and/or formation of substances possessing synergistic influence. This seems satisfactorily demonstrated by the equal stability of parent and interesterified lards when tocopherol-free. Consequently, it can be concluded that there was no appreciable effect on initiation of oxidation and autoxidation rates due to position of unsaturated fatty acids at 1,3-positions or randomization toward the 2-position in pork fat glycerides.

Rancidity Development. There is ample evidence that the appearance of rancidity is related to the amount of hydroperoxide decomposition and the quantity and kind of carbonyl compounds formed.

Study of the effect of interesterification under vacuum on carbonyl formation was carried out on tocopherol-free control and rearranged lard samples which contained 0.01% BHA. Oxidation at 60C was allowed to progress to peroxide values of 38. As shown in Table IV, glyceride rearrangement had no appreciable effect on the total carbonyl content and little on the proportions of unsaturated and saturated total carbonyl compounds. However the interesterification increased the free volatile monocarbonyl compounds and, of much more significance, changed the proportions of the classes of the volatile monocarbonyl com-

TABLE V
Effect of Glyceride Rearrangement Process on Monocarbonyl Patterns in Lard Samples Stored to PV 38 at 60C with 0.01% BHA Added

	Control lard	Randomized lard
Saturated		
C_6	++++	+++
C_7	–	–
C_8	–	–
C_9	++	++
C_{10}	+	+
C_{11}	–	–
2-Enals		
C_7	+	+
C_8	++	++
C_9	++	++
C_{10}	+	+
C_{11}	++	++
2,4-Dienals		
C_7	++	++
C_9	++	++
C_{10}	++	++
C_{11}	+	+

+ Represents about 15% compound in each class.

pounds. This consisted in higher proportions of alk-2-enal and alk-2,4-dienal classes.

As indicated in Table V, there were no qualitative differences in the individual aldehydes. There was however, a clear quantitative change in the pattern of the alkanals. The rearranged lard had 15% lower proportions of alkanal and a much smaller proportion of the C_6 alkanal. This compound represented about 70% of the alkanal in the parent lard but only about 50% in interesterified lard. Such an observation may indicate some selective action involving the formation or breakdown of C_6 alkanal precursors which is related to position in the glyceride.

It is not considered that these findings solve or complete this phase of the investigation. Further study of the carbonyl oxidation products under other autoxidative conditions seems advisable.

Indicated Means of Improvement in Interesterification. The two commercial interesterified lard samples were processed in the presence of air. Lard commercially randomized under such conditions is a crude product which must be bleached, deodorized, and fortified with antioxidants for edible use. The full extent of commercial practice in protection from air is not known. This work indicates that such precautions have considerable advantage. Interesterification in the absence of air produced an odorless and colorless product with stability similar to the parent lard. No traces of animal fat flavor could be detected in the product. Lard so processed might contain a trace of methyl fatty acid esters, which could be removed by a mild deodorization process.

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Supplement

Shortly after this manuscript was received from the reviewer, we became aware of the paper by K. G. Reghuveer and E. G. Hammond entitled, "Influence of Glyceride Structure on the Rate of Autoxidation," in the Journal of the American Oil Chemists' Society, *44*, 239 (1967). The abstract of this paper contained the statement: "The concentration of unsaturated fatty acids in 2-position of glycerol should stabilize a fat toward oxidation. This was confirmed on natural fats."

Since our paper offers a contrary conclusion, the following comments are offered. The higher rate of oxidation of simple unsaturated triglycerides, dissolved at low concentrations in saturated triglycerides as compared with randomized blends, might merely be attributable to a better chance of radical chain reaction when three susceptible acids are esterified in one GU_3 type than when dispersed mainly as GUS_2 in viscous media. This interpretation seems to be supported by the finding of little difference when 10% trilenolein was used in a mixture which was interesterified. There was an increase in the induction period but virtually no difference in the rate of autoxidation of the randomized sample. Experiments showed in some cases a slower initial rate of oxidation in rearranged samples.

The Raghuveer and Hammond presentation did not include measurement of the degree of randomization attained by various treatments with the alkaline catalyst. A huge increase in stability was reported with a short interesterification treatment of 1.5% trilinolein in tridecanoin. Such a process, which is termed crystal modification, involves little randomization.

As shown in the current paper, results obtained with natural fat cannot be interpreted unless natural antioxidants are removed. Raghuveer and Hammond did not describe such an evaluation or removal treatment on the natural fats they studied.

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