Chemical and Organoleptic Properties of Oxidized Fats[1]

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ABSTRACT

Various commercial fats were oxidized at elevated temperatures, and the extent of off-flavor development was evaluated organoleptically. Objective test methods also were applied to these oxidized fats, and correlations were established between the data and flavor panel results. Good to excellent correlations were obtained with pentane values, oxygen absorption values, peroxide values, and the average flavor scores. Results with the benzidine and thiobarbituric acid spectrophotometric methods were unsatisfactory. The octanoic acid method was found to be too insensitive to be of value. An exception to the above observations was lard, in which case all of the objective test methods gave good correlations with the flavor panel data.

INTRODUCTION

In an article dealing with the flavor evaluation of fats, Evans remarked that taste and smell are the only two human senses which have not been relegated to a secondary position by modern processing operations (1). Since that time significant progress has been made in the analysis and detection of volatile flavor components. But in spite of these advances, this statement, made nearly 20 years ago is essentially correct today. Quantitation of the reversion and rancidification processes is still largely an unsolved problem.

During the past two decades, many researchers have contributed to an understanding of these complex flavor phenomena. Notable among them are Evans and his colleagues at the Northern Regional Research Laboratory (1-5), Chang and coworkers (6,7), the Unilever researchers (8,9), and the workers at the Institute of Fats and Oils (10).

Recently, Smouse reported on the use of quantitative methods to measure the flavor stability of various soybean oils having different histories (11). This work has been expanded and reported elsewhere with similar results (12). These authors indicate that while some tests, particularly the benzidine and the thiobarbituric acid values, are good indicators of past oil history, they are inadequate in predicting oil flavor stability. In the present study we have applied a number of objective test methods to several fats and oils during the autoxidation process and have attempted to correlate the data obtained with flavor panel scores.

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EXPERIMENTAL PROCEDURES

Materials

The various fats and oils used are described in Table I. Beef tallow was obtained from Roberts Food Corp., New York, N.Y.; lard was from Charles Miller and Co., North Bergen, N.J.; high oleic safflower oil (HOSO) came from Anderson Clayton Foods, Dallas, Tex.; and the corn oil was obtained from Best Foods, Englewood Cliffs, N.J. The hydrogenated soybean oil (HSBO) was from Archer Daniels Midland Co., Decatur, Ill. In the table are shown relative percentages of unsaturated fatty acids (by gas liquid chromatography [GLC]), the initial peroxide values as received, and the various additives which were included by the suppliers. Since none of these fats was completely bland and odorless, each was steam, vacuum deodorized for 4 hr at 200 C in all glass laboratory equipment. They then were stored under nitrogen at 5 C until tested for stability as described below.

Methods

In the initial test 1.6 kg of each fat was stored at 37.8 C in a capped gal jar for 12 weeks. Aliquots (200 ml) were removed at intervals for flavor evaluation and for various objective measurements.

In a subsequent test, 20 portions (50 g) of each fat were incubated for up to 16 days at 60 C. Storage was carried out in brown pint glass bottles which were stoppered with rubber septa. Because of its high resistance to oxidation, the HSBO was stored at 75 C. Oxygen absorption was monitored by GLC as described below. On each day of flavor panel evaluation, the contents of two of the bottles, having nearly identical O_2 absorption levels, were combined and used for organoleptic and objective test measurements.

Flavor Panel Evaluation

The panel consisted of 15 people only one of whom had prior experience in oil tasting. Members were instructed in oil evaluation procedures using six oils ranging in flavor intensity from bland to rancid. Samples were scored on a

TABLE I

Properties of Samples Used[a]

Name	Additive[b]	Peroxide value	Percent unsaturated fatty acid		
			Mono-	Di-	Tri-
Beef tallow	PG	0.1	49.4	1.5	0.6
Lard	BHA, PG Citric acid	0.4	47.3	12.5	Ca. 0.8
Hydrogenated soybean oil	Citric acid	4.4	74.8	1.6	Trace
High oleic safflower oil	Tenox 6	2.4	75.5	15.9	0.4
Corn oil	Isopropyl citrate Methyl Silicone	1.6	25.4	59.8	1.0

[a]Prior to deodorization. See text for details.

[b]PG = propyl gallate and BHA = butylated hydroxyanisole.

FLAVOR PANEL BALLOT

SCORING SYSTEM

10 BLAND
8 SLIGHT FLAVOR (NOT UNPLEASANT)
6 OFF-FLAVOR
4 STRONG OFF-FLAVOR
2 RANCID

NOTE: TASTE a FIRST

SAMPLE #		FLAVOR SCORE	COMMENT
I CONTROL	a		
OXIDIZED	b		
II CONTROL	a		
OXIDIZED	b		
III CONTROL	a		
OXIDIZED	b		
IV CONTROL	a		
OXIDIZED	b		
V CONTROL	a		
OXIDIZED	b		

FIG. 1. Flavor panel ballot.

10-2 scale as indicated in Figure 1. During the actual taste session each panelist evaluated 10 samples kept at 60 C. Five of these samples were the unoxidized controls which had been stored under nitrogen at 5 C. Each oxidized sample was compared to its control oil which was tasted first. Panel members were allowed to assign odd number scores between the ratings shown on the ballot. In obtaining an average flavor score (AFS) for each sample, those judgments which differed from the mean by more than two units were discarded. In each case, this procedure eliminated at most 3 scores, so that each AFS represented an average of at least 12 judgments.

Objective Test Methods

Peroxide values (PV) were determined by AOCS Official Method Cd 8-53 (13). Benzidine values (BV) were obtained as described by Holm, et al. (14). Thiobarbituric acid values (TBA) were run by a modification of the procedures as described by Jacobson, et al. (15). Samples (0.12 g) were dissolved in 2 ml 50% (v/v) absolute alcohol in 2,2,4-trimethylpentane to facilitate multiple analysis. To the solution in 25 x 150 mm culture tubes with teflon lined caps was added 5.0 ml trimethyl pentane and 3.0 ml thiobarbituric acid solution (0.33 g TBA in 10 ml H_2O and 90 ml isopropyl alcohol). The capped tubes were shaken

TABLE II

Correlation of Flavor Scores with Thiobarbituric Acid Values

Temperature, C	Sample	R^2 Values 452mμ	532mμ
37.8	Beef tallow	<0.40	<0.40
	Lard	0.89	0.88
	Hydrogenated soybean oil	<0.40	<0.40
	High oleic safflower oil	0.41	0.60
	Corn oil	0.45	0.74
60	Beef tallow	<0.40	<0.40
	Lard	0.96	0.99
	High oleic safflower oil	0.87	0.95
	Corn oil	0.71	0.94
75	Hydrogenated soybean oil	<0.40	0.56

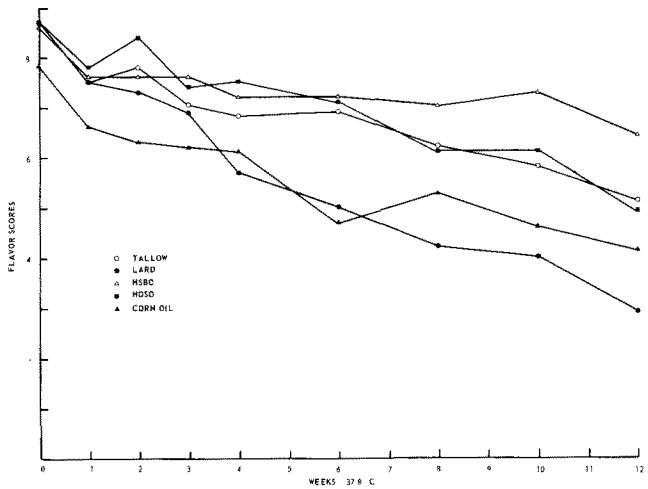

FIG. 2. Change of average flavor scores with storage time. ○ = Tallow, ● = lard, △ = hydrogenated soybean oil, ■ = high oleic safflower oil, and ▲ = corn oil.

vigorously for 30 sec and then immersed in a water bath at 60 C for 30 min. The cooled solution then was scanned from 400-600 mμ in a Cary 14 recording spectrophotometer. Peaks at 452 and 532 mμ were used to compute TBA values by the formula:

$$\text{TBA value} = \frac{(\text{optical density sample} - \text{optical density blank})\ 10}{\text{wt of sample (g)}}$$

The rate of oxygen absorption was measured following the method of Bishov and Henick (16). Sample (5 g) in a 100 ml serum bottle sealed with a rubber septum was stored at 60 C and analyzed at regular intervals; 0.20 ml of headspace gas was injected into an Aerograph model A-90-P gas chromatograph equipped with a thermal conductivity detector. The column was a 6 ft x 3/8 in. outside diameter aluminum coil packed with 50-60 mesh 13x molecular sieves. At room temperature and a 50-60 ml/min helium flow rate, oxygen and nitrogen are separated and emerge in less than 2 min. The relative percent oxygen in the headspace was obtained by electrical integration using an Infotronics CRS-104 integrator.

Pentane values were obtained by the method of Evans et al. (17) using a Perkin Elmer model 900 gas chromatograph having a 6 ft x 1/8 in. outside diameter stainless steel column packed with 80-100 mesh alumina (MicroTek F-20). The injection port and column were at 250 C, the flame ionization detector at 300 C. A 5 μliter sample was injected. In the first experiment, isooctane was used as an internal standard (11); but this was found to be unnecessary since the reproducibility of determinations was within ±5%.

The octanoic acid values (OAV) were measured by a modification of the procedure outlined by Smouse, et al. (11). To 200 mg of oil in a 25 ml teflon-lined screw cap vial, was added 1.0 ml 0.4N $KOCH_3$ in methanol. The sample was heated to 60-65 C and shaken until all the oil dissolved (usually ca. 5 min). This transmethylation step was followed by the addition of 1 ml 0.1% nonanoic acid in methanol and 2.0 ml 14% (W/V) BF_3-CH_3OH. The contents of the vial were mixed, heated to 60 C for 5 min, and cooled. Addition of 10 ml saturated NaCl solution and 4.0 ml CS_2 was followed by 1 min of vigorous hand shaking. The organic phase (20-40 μliter) was injected into a Hewlett-Packard 5750 gas chromatograph. The column was 10 ft x 1/8 in. outside diameter packed with 10% EGSS-X on 100-120 mesh Gas Chrom Q (Applied Science Lab., State College, Pa.). The column was held at 100 C for 10 min and then programed to 220 C at 10 C/min. To

TABLE III

Summary of Flavor Score Correlations

Temperature, C	Sample	R^2 Values: Peroxide values	Pentane values	Oxygen absorption
37.8	Beef tallow	0.93	0.95	---
	Lard	0.94	0.97	---
	Hydrogenated soybean oil	0.80	0.71	---
	High oleic safflower oil	0.95	0.91	---
	Corn oil	0.84	0.78	---
60	Beef tallow	0.99	0.96	0.99
	Lard	0.90	0.94	0.84
	High oleic safflower oil	0.97	0.97	0.98
	Corn oil	0.96	0.97	0.98
75	Hydrogenated soybean oil	0.42	0.51	0.33

improve separation and extend the column life, the metal liner of the injection port was filled with column packing material achieving, in effect, on-column injection.

RESULTS AND DISCUSSION

Flavor Panel Data

The various commercial fats selected for study were all of good quality, but each had a significant level of flavor and odor. Laboratory steam, vacuum deodorization effectively removed almost all of the remaining flavor components which might otherwise have interfered with the panel evaluation of oxidized flavors as they were developed. The samples chosen—beef tallow, lard, HSBO, HOSO, and corn oil—are considered to be representative of the types of oxidizable fats found in most processed foods.

Storage tests were run at elevated temperatures (37.8 and 60 C, 75 C with HSBO) to accelerate development of off-flavors. It is recognized that, as Hoffmann (9) points out, the results obtained may not be strictly comparable to those which might have been found at room temperature. However, to obtain meaningful data within a reasonable period, acceleration of these changes was required.

It also is recognized that evaluation of 10 samples at a single session may cause fatigue. However, AFS were found to be reproducible within one unit using this procedure. Since the panel compared each oxidized sample to a bland control there was a built in bias in flavor of the control amounting to ca. one AFS unit, i.e. when a control identified as oxidized was tested against itself it scored one AFS unit lower.

The panel data obtained at 37.8 C are summarized in Figure 2. As might be expected, there is a downward trend in flavor scores with storage time. The HSBO had the best stability; beef tallow and high oleic safflower oil were intermediate, while corn oil and lard showed the most rapid deterioration.

Oxygen Absorption

During the first study (37.8 C), the oxidizing fats were analyzed for rate of oxygen absorption. This gives data somewhat comparable to that obtained by the active oxygen method (AOM) (18). Results with high oleic safflower oil are shown in Figure 3. As expected, the rate of oxygen absorption increases during storage. Arbitrarily, an oxygen absorption value of 70 meq/kg was selected as the approximate point of rancidity. The data inserted in Figure 3 indicate the decrease in OV_{70} value with the increase of PV. This same pattern was observed with lard and corn oil. In the case of lard, the OV_{70} dropped from 14 days to 1 day during 12 weeks. Corn oil showed a similar drop from 12 to 4 days during this period. As in the case of AOM, the OV_{70} can be used as an index of stability. However, with beef tallow and HSBO, this change in OV_{70} was much slower and quite erratic. Because of this limitation and the time involved in carrying out these tests, oxygen absorption was not used in the subsequent higher temperature studies.

Benzidine Test

With soybean oil, Smouse (11,12) found that the benzidine test was an excellent indicator of past oxidative

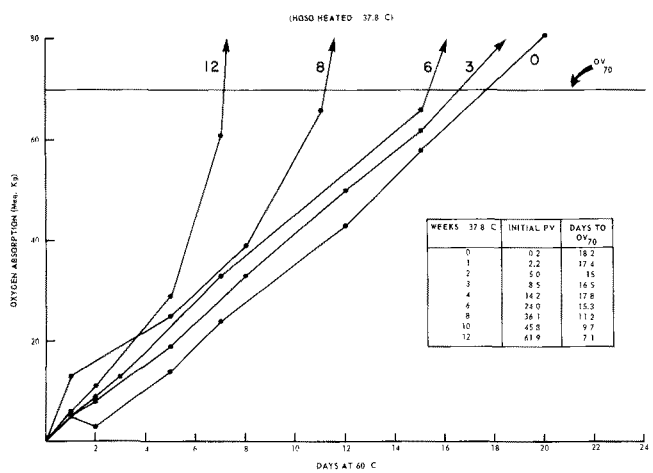

FIG. 3. Effect of the state of oxidation of high oleic safflower oil upon oxygen absorption.

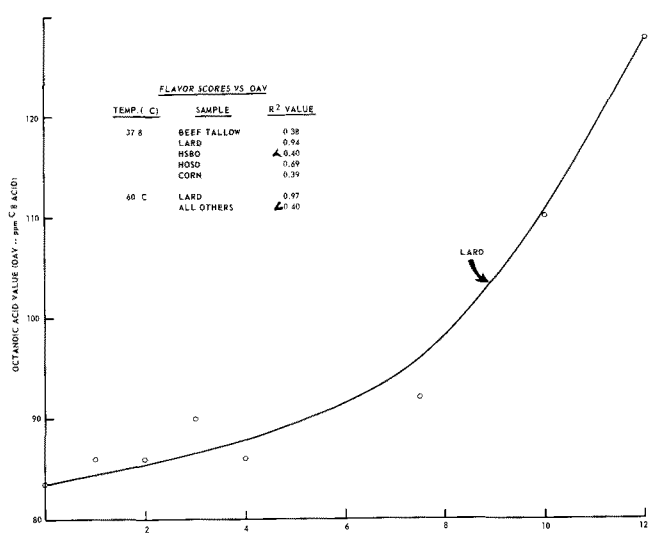

FIG. 4. Octanoic acid value and average flavor scores.

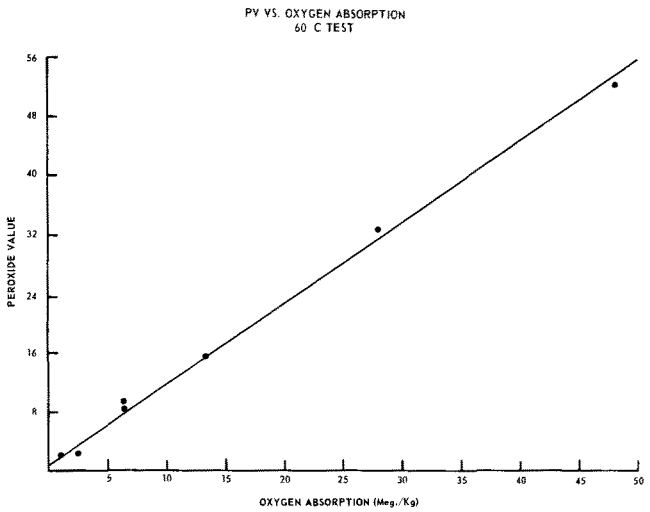

FIG. 5. High oleic safflower oil; rate of peroxide value formation vs. oxygen absorption.

history; but it showed only a fair correlation with flavor scores. In the present study, with the exception of lard, benzidine values gave poor correlation with flavor panel scores. The initial values for tallow, lard, HSBO, HOSO, and corn oil were 2, 1, 4, 14, and 26 units, respectively. With the exception of lard, these values changed only slightly and in an erratic manner during the course of oxidation. It is concluded that the benzidine values are much more characteristic of the type of fat than they are indicative of the degree of oxidation.

TBA Test

The TBA test has been used extensively to measure oil deterioration. As modified by Jacobson and coworkers, TBA reacts with both saturated and monunsaturated aldehydes to give a yellow color absorbing at 452 mμ and with diunsaturated aldehydes to give a pink color absorbing at 532 mμ (15). They found that the yellow color development parallels closely the drop in flavor score during oxidation of beef fat, chicken fat, soybean, and cottonseed oils. The pink color correlated better with flavor deterioration of pork fat. In his studies, Smouse reports that TBA values give a better correlation with the flavor of reverted soybean oil than does any other of the tests used (11,12).

Results obtained in our experiments were subjected to statistical analysis using the least squares regression technique. R is the correlation coefficient and R^2 is the amount of variation in flavor rating that can be explained by fitting the line $Y = b_o + b_1X + b_2X^2$, where X = the average flavor score and Y = a particular analytical measurement. Following the convention set by Evans, et al. (1), the correlation is considered excellent if R^2 = 0.85-1.0, good at 0.70-0.84, fair at 0.60-0.69, and poor if below 0.60.

In Table II, it is evident that TBA values correlate well with flavor scores in the case of lard at both temperatures but rather poorly with other fats. In general, the pink color absorption shows the better correlation even though the values at this wavelength are small and, therefore, subject to greater experimental error. Correlations for beef tallow and HSBO were both poor. Our experience indicates that the modified TBA test is of limited value in measuring the extent of oxidized flavors in fats.

OAV

The OAV originally was proposed by Swoboda to measure the degradation of frying fats (19). The test, as modified by Smouse (11), who used a double esterification technique, measures the free and bound octanoic acid. As

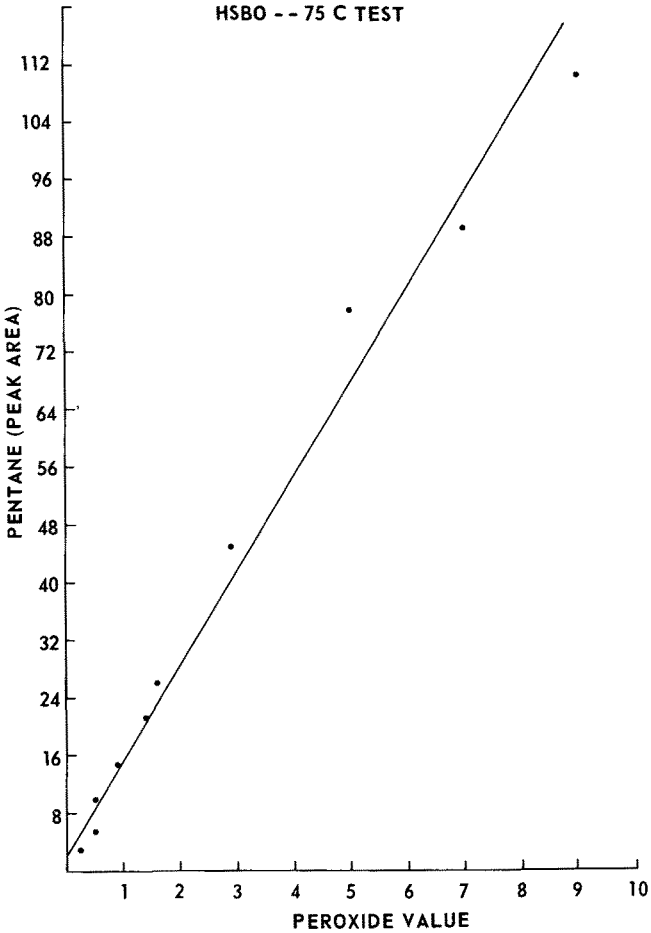

FIG. 6. Hydrogenated soybean oil; rate of peroxide value formation vs. pentane value.

the data in Figure 4 show, all correlations of OAV with flavor scores are poor, with the exception of lard. In the case of the more stable fats, tallow and HSBO, the values at the end of the oxidation period are so close to the initial values as to be within experimental error. With corn oil and HOSO, the values actually decrease toward the end of the studies. These negative features, coupled with the fact that the method is time consuming, suggest that the OAV is of little value in predicting flavor deterioration of oxidizing fats.

Correlation of Flavor Panel Scores with Objective Test Results

In the second experiment (60 C), the oxygen absorbed by each sample was measured prior to running the flavor evaluation. A typical result is shown in Figure 5, where rate of O_2 absorption of HOSO at 60 C is plotted against measured peroxide values. An $R^2 > 0.9$ was obtained with all of the fats, indicating the decomposition of hydroperoxides (if any) is much slower than their formation.

Pentane values also show a high correlation with both peroxide values and oxygen absorption data. With all of the fats there was a linear correlation between peroxide value and level of pentane in the sample. This is illustrated for HSBO in Figure 6. This linear relationship might have been predicted, since the pentane is formed by thermal decomposition of hydroperoxides (17).

Since peroxide values, oxygen absorption values, and pentane values correlate well with each other, all that remains is to demonstrate similar correlations with average flavor scores. The extent of these correlations is shown in Table III. With the exception of HSBO, all correlations with AFS are seen to be good to excellent. Even with HSBO at 37.8 C, the correlation is good; but, at 75 C, it is poor.

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