Edible Oil Quality as Measured by Thermal Release of Pentane[1]

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Abstract

As part of their thermal decomposition products, fatty hydroperoxides produce normal hydrocarbons. The extent of hydrocarbon formation can be measured and associated with the quality and potential stability of an oil. Edible oils containing linoleic acid develop 13-hydroperoxy-9,11-octadecadienoic acid as one product of autoxidation. On thermal decomposition this hydroperoxide yields pentane; the amount released has been correlated with the flavor scores of fresh and aged soybean and cottonseed oils and with the peroxide values of these oils. The quantity of pentane released has an inverse linear relationship to flavor score and a direct linear relationship to peroxide values. Edible oils exposed to light exhibit a different relationship between flavor score and thermally derived pentane than do the same oils when autoxidized in the dark.

Introduction

Edible oil quality and stability are measured and expressed by some means related either to the degree of oxidation of the oil or to the resistance of the sample to oxidation. It is generally accepted that the first product of fat oxidation is a fatty hydroperoxide (1,8). Rates of hydroperoxide formation have been studied under widely varying conditions and for many different fats and fatty acids. The stability of fatty hydroperoxides has not been investigated to the same extent. Little is known about the mechanism of decomposition of a simple fatty acid hydroperoxide. Little is known on how to influence the course of the decomposition and the yield of any particular end product. Indeed, postulations far exceed facts.

We have proposed that each fatty hydroperoxide of known structure will yield a specific hydrocarbon as one of its thermal decomposition products (6). Thus ethane is derived from oxidized linolenic acid, pentane from linoleic acid and octane from oleic acid. A myriad of other products appear along with the hydrocarbons, and a gas liquid chromatographic flavor profile is extremely complex even when limited to the more volatile constituents. The complexity, variability and lack of resolution make the total profile technique of limited value for routine evaluations of flavor. The correlation of taste panel scores with an analytical determination of one or two prominent flavor components has given highly acceptable results and usable techniques (2,17,18,20).

A gas solid chromatographic technique that uses alumina as the adsorbent for separating hydrocarbons and selectively retains oxygenated polar compounds, proved ideal for determining short chain hydrocarbons resulting from the autoxidation of fats (12). Edible oils containing linoleic acid develop 13-hydroperoxy-9,11-octadecadienoate as one product of autoxidation (4,6). This particular hydroperoxide yields pentane on thermal decomposition, and the amount of pentane released correlates with the flavor scores of both soybean and cottonseed oils. This paper reports on the methodology used and on the correlation of flavor scores of both autoxidized and light-struck soybean and cottonseed oils with the amount of pentane released upon thermal treatment of the oils.

Experimental Procedures

Edible oils used in this study came from various commercial sources. Samples of soybean and cottonseed salad oils (nonhydrogenated) were subdivided for the various storage experiments and were used as received. Other samples were obtained as commercially refined and bleached, undeodorized soybean and cottonseed oils. These oils were deodorized (210 C, 1 mm, 3 hr, 6% steam) in all glass equipment in the laboratory immediately before they were placed in storage. No antioxidants or metal scavengers were added to the oils during processing. Aging of the oils was conducted at 60 C in a thermostatically controlled forced draft air oven. Other samples were exposed to light as described by Moser et al. (16). All samples were stored in clear glass bottles stoppered with cellophane-covered corks. The headspace in each bottle was air, and since all sample transfers were conducted in air, it is assumed that the oils were at equilibrium with dissolved air when placed in storage.

Organoleptic evaluation of the oils was made by a 16-member taste panel (15). The amount of pentane obtainable from each oil was determined by gas solid chromatography (GSC). Aluminium oxide was used as the analytical adsorbent column (12). Experimental work shows that pentane added to soybean oil is recoverable under the conditions employed. A linear relationship exists between the amount of pentane added to the oil and height (or area) of the pentane peak as determined by GSC. One microliter of oil was injected directly into the column of a gas chromatograph (F & M Model 1609). Since the column extended through an injection heater, the temperature of the forepart of the column could be controlled independently of the column oven temperature. An injection port temperature of 260 C was maintained and the ¼ in. × 4 ft column packed with 60/80 mesh alumina, was operated at 250 C to obtain hydroperoxide breakdown rapidly and to elute the pentane. A hydrogen flame detector was operated with nitrogen, 50 ml/min as the carrier gas, at sufficiently high sensitivities to give most pentane peak heights of 50% of the chart width. At the highest sensitivities (range 1, attenuation 2) a freshly deodorized oil showed a pentane peak approximately 10–20 mm high.

Results

Previous work had indicated that hydroperoxide breakdown is rapid at temperatures above 180 C (3). Immediate release of pentane from the sample is needed for gas chromatographic determinations. Low injection-port temperatures gave low and variable amounts of pentane. Figure 1 shows the amount of pentane released at various temperatures when a microliter sample of cottonseed oil with a peroxide

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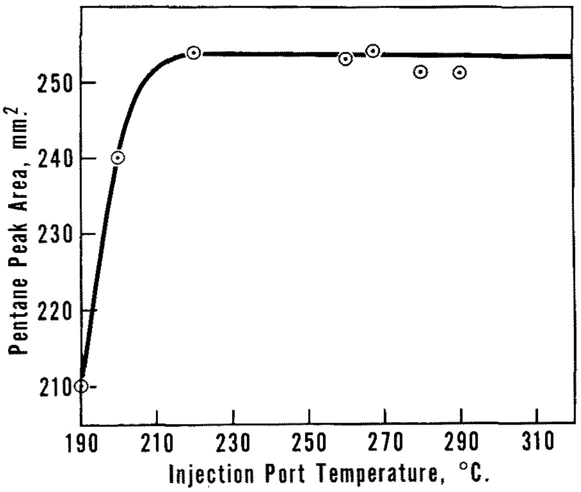

FIG. 1. Temperature effect on yield of pentane thermally derived from autoxidized cottonseed oil (PV 28).

value of 28 is injected directly into the heated column. The flatness of the curve above an injection-port temperature of 220 C indicates that the hydroperoxide breakdown is rapid and complete. All pentane determinations were made under the same gas chromatographic conditions and since all samples were 1 μliter in size, the pentane peak height was used as a measure of pentane content. Soybean oil containing added pentane showed a constant ratio of 2.8 mm in peak height per parts per million of pentane (range 1, attenuation 2 for a 1 μliter sample). Twenty replicate 1 μliter injections of an oxidized soybean oil (PV = 40.8) gave a peak height mean of 134.2 mm (attenuation 1 × 8) and a standard deviation of 11.1.

High correlations above 0.94 were obtained between peroxide values of the autoxidized soybean and cottonseed oils aged at 60 C and amount of pentane thermally derived from these oils (SBO correl. coef. $r = 0.98$ reg. coef. $b = 0.087$ $\sigma xy = \pm 0.99$; CSO correl. coef. $r = 0.94$ reg. coef. $b = 0.085$ and $\sigma xy = \pm 3.35$). The regression line calculation changes 9.92 mm in peak height per unit change in peroxide value and 0.082 peroxide value units per millimeter change in pentane peak height. The use of an internal standard, as was done by Scholz and Ptak (20), might give a better relationship at high peroxide levels, since the problem is primarily one of injecting a uniform size sample.

Figure 2 shows the association of peroxide values with the amount of thermally derived pentane obtained from soybean oil aged at room temperature and periodically sampled over an interval of 13 weeks. Statistical coefficients for pentane-peroxide relationships on the 10 samples, pentane determined in triplicate, are correl. coef. $r = 0.98$, reg. coef. $b = 0.083$ and $\sigma xy = \pm 2.48$. The equation for the regression line, obtained with 1 μliter sample size and an attenuation of 1 × 2 is, $PV = 0.22 + 0.083 \times$ peak height. Similar relationships were obtained for 60 C aged soybean and cottonseed seed oil samples.

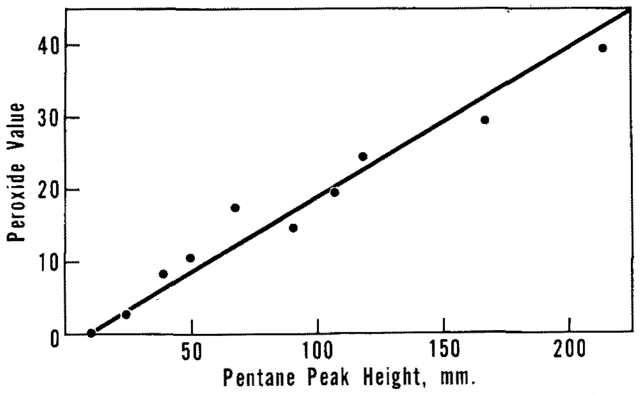

FIG. 2. Effect of level of autoxidation of soybean oil on yield of thermally derived pentane (1.0 μliter sample size and 1 × 2 attenuation).

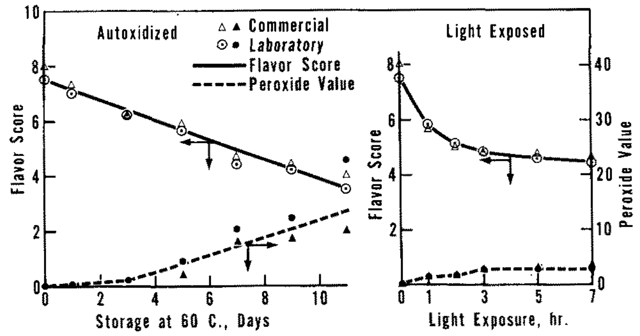

FIG. 3. Change in flavor score of soybean oils after autoxidation at 60 C and fluorescent light exposure.

The influence of storage conditions, time and rate of peroxide development on the flavor change in soybean oil is shown in Figure 3. Data are presented for a commercial salad oil, and a laboratory-deodorized oil, both of which were autoxidized under Schaal-oven storage conditions and under fluorescent light. Flavor scores dropped with aging at 60 C, whereas peroxide values increased, and no difference in stability is apparent between the two lots of soybeans oils being investigated.

Aging under light markedly accelerates the rate of flavor deterioration and forms some peroxides. Both soybean and cottonseed oils behaved similarly and show an extremely rapid drop in flavor score within 3 hr of fluorescent light exposure.

Figure 4 illustrates the relationship of flavor score to the height of the pentane peak derived from the same soybean oils for which flavor and oxidative data were plotted in Figure 3. The linear relationship between flavor and evolved pentane is expected for the 60 C autoxidized oils because of the direct linear relationship of these two measurements with the peroxide value. Curves in Figures 3 and 4 show the rapid loss of flavor on exposure to light and indicate that light deterioration does not allow the accumulation of a large amount of thermally releasable pentane. Under light exposure the loss in flavor was at the same rapid rate for both lots of soybean oil. However under autoxidation conditions at 60 C, the relation of flavor score to thermally derived pentane is different for the two oils. Uncatalyzed oxidation rates vary with each lot of oil; consequently, regression lines with individual slopes would be expected for each oil. The relationship of flavor to thermally derived pentane is complex and is a partial function of the rate of hydroperoxide formation and decomposition. These interdependent relationships are further developed and discussed later.

Cottonseed salad oil flavor scores associated with extended autoxidation, light-catalyzed autoxidation and thermally derived pentane are presented in Figures 5 and 6 for commercial and laboratory-deodorized oils. Stability data for cottonseed oil aged at 60 C are in agreement with the known greater flavor stability of this oil. Under Schaal-oven aging

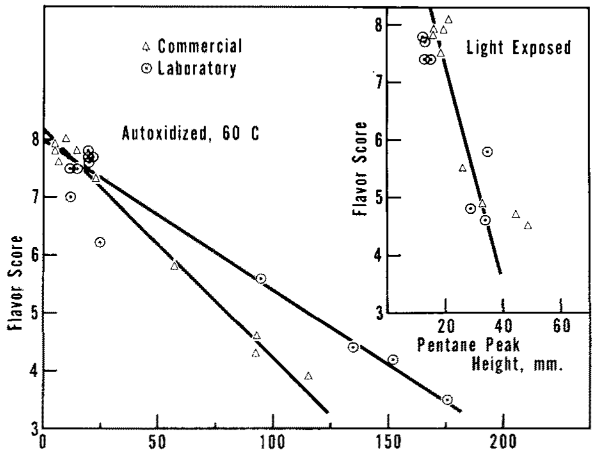

FIG. 4. Pentane peak height relationship to flavor scores of autoxidized 60 C and fluorescent light-exposed soybean oils.

conditions, cottonseed oil had a higher rate of peroxide development but a slower loss of flavor score than soybean oil. Exposure to light was about equally detrimental to both cottonseed oil and to soybean oil. The absence of peroxide buildup on continued exposure is typical for light-struck oils, and the low level of peroxides in the light-struck cottonseed oils accounts for the small amount of thermally cleaved pentane obtained from these samples. The amount of pentane released after light exposure is only twice that of the blank. For 60 C autoxidation of cottonseed oil the pentane increased 10- to 15-fold. Extreme changes in flavor occur with light-struck oils but with only minor increases in thermally derived pentane. Although the curve depicted for light-struck cottonseed oils is linear, it may be only a segment of an exponential curve.

Like soybean oil, each sample of cottonseed oil autoxidized in the dark at 60 C exhibited its individual relationship between the flavor score and the amount of thermally derived pentane. The data also show that the degree of deterioration in light exposed oil is not readily ascertained by a peroxide or pentane determination.

Discussion

Reproducibility and reliability of the pentane determination offer no problem, even though the pentane concentration in the oil is only a few parts per million. Likewise, the linear relationship between thermally derived pentane and the hydroperoxide content of the sample aged in the dark at 60 C presents no question about the close association of these two quantities. However, the enigma that must be explained is the close relationship of the flavor of an edible oil to the amount of pentane which can be thermally derived from a flavorless hydroperoxide component.

Reportedly, hydroperoxides have no flavor (10), yet soybean oils having only slight peroxide levels may have a low flavor score (5). The presence of any peroxides is indicative that the oil has been exposed to oxidizing conditions, and it is on this premise that some manufacturers of salad dressings have written specifications requiring oils to have an extremely low peroxide value. The history of an oil and knowledge of its behavior under test conditions are needed before a peroxide value has flavor significance beyond merely indicating that an oil has been exposed to oxygen. Peroxides present in an oil at the time of titration are not a measure of the total amount of oxidation.

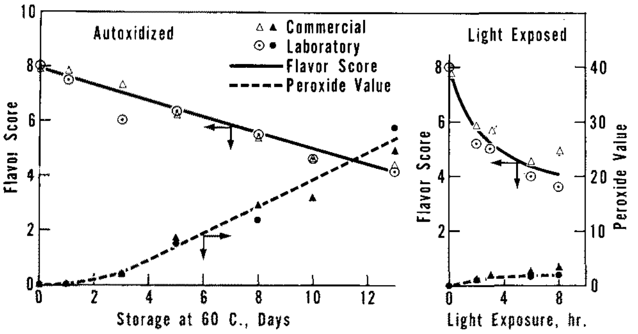

FIG. 5. Change in flavor score of cottonseed oils after autoxidation at 60 C and fluorescent light exposure.

The true degree of oxidation of a fat is not readily ascertained, and the instability of the various fatty hydroperoxides is a major factor affecting flavor. Each fatty hydroperoxide isomer has its own stability that varies with structure and with the particular environment to which it is exposed. To correlate flavor, which an oil system presents after mild storage conditions, to a few parts per million of pentane, is not readily apparent unless it is realized that the slow but continuous decomposition of fatty hydroperoxides constantly generates many flavor materials (13).

Fatty hydroperoxides have a poorly defined stability (17), and abnormal storage conditions will change the half-life markedly. Under essentially static conditions of low temperature storage some decomposition of peroxides takes place (9). This slow, but apparently continuous, decomposition of peroxides generates flavor components whose concentrations are in proportion to the total peroxides formed in the oil. Thus the flavor of an oil is a function of the amount of peroxide decomposition, and is indirectly related to total oxidation. In our laboratory, soybean oils carefully oxidized in the dark to peroxide values of 10 gave high scores if tasted immediately after oxidation (Evans et al., unpublished data).

The wavelength of light is extremely important as a catalyst in the autoxidation of fats (14). It is assumed that the fat peroxides decompose more rapidly upon exposure to the shorter wavelengths

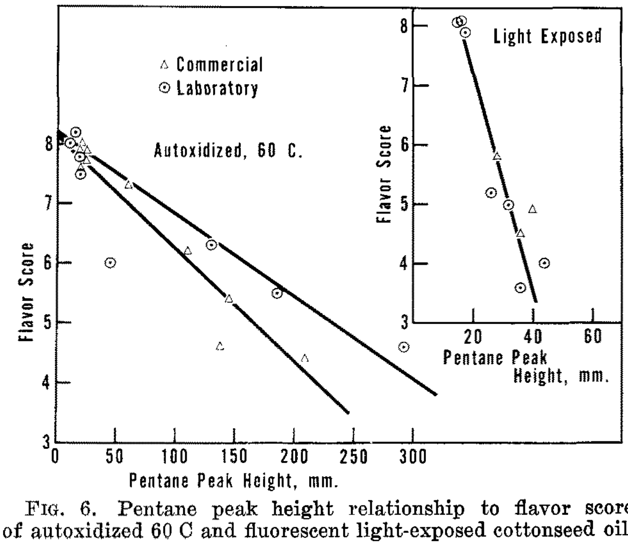

FIG. 6. Pentane peak height relationship to flavor scores of autoxidized 60 C and fluorescent light-exposed cottonseed oils.

(21). Edible oils exposed to direct sunlight or ultraviolet light show immediate flavor deterioration. Storage life of oils or fatty foods is extended through use of dark bottles or colored cellophane containers.

Some evidence has been gained that light and certain metals like copper may influence the type of breakdown to give more unsaturated materials (11). Unsaturated short chain aldehydes and ketones are known to have odor thresholds many times greater than their saturated analogues (8). Thus oxidation conducted under mild conditions and in the dark will attain high peroxide levels before there is sufficient peroxide decomposition and accumulation of volatile decomposition products to impart a detectable odor and taste to the oil. Flavor tests indicate that the type and percentage of volatile decomposition components will be different for light-exposed samples than for the same samples autoxidized in the dark. All light-struck cottonseed and soybean oils show a large change in flavor score for a very small change in peroxide or pentane levels. The development of less flavor in oils exposed to light under vacuum indicate that light-struck flavor is oxidative in nature (Evans et al., unpublished data).

Soybean and cottonseed oils aged in the dark and at a moderate temperature (60 C) exhibit a high correlation between flavor scores and thermally derived pentane. The amount of pentane is a measure of only one of many hydroperoxides that may be formed on autoxidation. Oils high in linoleic acid and which do not contain linolenic acid are characterized as forming, in their later stages of oxidation, typical rancid flavor responses. It is quite possible that the measurement of ethane, a thermal decomposition product of a linolenic acid hydroperoxide, by the gas solid chromatographic technique could also be used as a measure of reversion in linolenic acid-containing edible oils. Quantitative determination of thermally derived hydrocarbons takes into account both the composition and the concentration of the respective fatty acids and therefore is an integrated measure of the ease of oxidation of a fat.

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