INTRODUCTION

RANCIDITY RESULTING from the oxidation of lipids is a primary concern during storage of fats and fat-containing foods. Objective instrumental techniques to measure rancidity would be useful when sensory evaluation panels are not available; some instrumental methods have been published for determining fat deterioration and quality. Nawar and Fagerson (1962), Scholz and Ptak (1966), Hartman et al. (1970), Jarvi et al. (1969, 1971), and Fioriti et al. (1973) developed gas chromatographic (GC) techniques to evaluate the quality of ground beef, cheese and edible oils. Measuring decomposition products could indicate the degree of rancidity of a food.

Findings by Horvat et al. (1964) with methyl linoleate and by Selke et al. (1970) with soybean oil show that saturated hydrocarbons arise early during autoxidation when aldehydes are either absent or not detectable. Evans et al. (1967) reported that pentane is the predominant short-chain hydrocarbon to arise through thermal decomposition. Correlations of flavor scores and pentane formation have been used to determine rancidity of oils after directly injecting the oils on a GC column (Evans et al., 1969; Jarvi et al., 1971). But deterioration studies of solid foods require analysis of headspace gases. We have found significant correlations between the amount of pentane detected in headspace by GC and the rancidity described by a trained panel for both aged vegetable oils and potato chips.

Indicators of the potential stability of oils and fat-containing foods would be helpful to food processors. Fuller et al. (1971) found that potato chips fried in oleic safflower oil, which had an iodine value of 90, were as stable toward rancidity during accelerated storage as were chips fried in hydrogenated vegetable oil. Linoleic acid derivatives have a much faster rate of oxidation than oleic compounds (Fuller et al., 1971). Since methyl linoleate is the major oxidizable fatty acid in foods (Labuza et al., 1969), the linoleate content of oils could possibly indicate the stability of fats and fat-containing foods. Our flavor studies on pentane formation in foods have shown that it is possible to correlate linoleate content and iodine value with the induction period for pentane formation in oils and potato chips.

EXPERIMENTAL

Materials and storage conditions

Edible vegetable oils included soybean (salad), corn, cottonseed, sunflower (laboratory deodorized), hydrogenated winterized soybean, safflower and high-oleic safflower (redeodorized at the Northern Laboratory). All samples were commercially refined, bleached and deodorized unless specified otherwise. The only sample to contain additives was the hydrogenated winterized soybean oil, which had butylated hydroxytoluene and butylated hydroxy anisole as preservatives and methyl silicone. The safflower and high-oleic safflower oils were combined to give mixtures of the following ratios: 100:0, 75:25, 50:50, 25:75 and 0:100. Potato chips were either purchased locally or provided from experimental runs by the Red River Valley Potato Processing Laboratory, East Grand Forks, MN 56721. These chips had been fried in corn oil, hydrogenated vegetable oil with preservatives or a 70% cottonseed oil/30% corn oil mixture. The linoleate content of the oils and of oil extracted from the potato chips was measured by standard GC methods (Cowan et al., 1971). Their iodine values were then calculated from GC data.

The oil and chip samples were stored in 16-oz wide mouth glass jars. Lids were fitted with rubber serum caps to facilitate headspace sampling. The samples were stored at 60°C in a forced draft oven and were tested periodically for pentane in the headspace. In each jar 60g of chips were placed for storage and taste panel evaluation. Oils were stored in two ways. For oils to be tasted in addition to pentane measurement, 150g of oil were placed in each jar. During storage, the jars were shaken twice a day. For oils which were tested for pentane development only, 50g were placed in each jar along with six strips of 7 in. x 1 in. filter paper folded accordion style. Jars were shaken to saturate the paper at the beginning of storage.

Headspace vapor analyses

Analyses were made with an F&M 1609 GC equipped with a flame ionization detector. The column was a 4 ft x 1/4 in. aluminum tube packed with 80/100 mesh Microtek alumina as described by List et al. (1965). Standards of 1 ppm of pentane in nitrogen were run on the column before and after each day's samples were run. The amount of pentane in the headspace (ppm) was calculated from the sample's peak height in proportion to the height of the standard. The detection limit for pentane by this method is about 0.02 ppm. For each sampling, 1 ml of headspace gas was injected onto the column.

Sensory evaluation

An 18-member trained panel evaluated both chips and oils. Samples were tasted immediately after pentane measurement. Oils were scored on a 10-point scale with 10 as excellent or bland and 1 as bad or as having a strongly deteriorated flavor. Chips were scored on a similar scale with 10 as excellent or as having a good potato chip flavor and 1 as having a strongly deteriorated flavor. The number of rancid descriptions for both the chips and oils is expressed as a percentage of the total number of panel members giving this response.

Moisture content of potato chips

The effect of moisture content of potato chips on pentane formation was tested. A desiccator with 30% relative humidity and a...
Table 1—Flavor scores, percentage of taste panel giving rancid descriptions and ppm of pentane in safflower oils

<table>
<thead>
<tr>
<th>Days storage at 60°C</th>
<th>Flavor score</th>
<th>Rancid descriptions (%)</th>
<th>Pentane (ppm)</th>
<th>Flavor score</th>
<th>Rancid descriptions (%)</th>
<th>Pentane (ppm)</th>
<th>Flavor score</th>
<th>Rancid descriptions (%)</th>
<th>Pentane (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>7.4</td>
<td>7</td>
<td>0</td>
<td>7.6</td>
<td>7</td>
<td>0</td>
<td>7.9</td>
<td>7</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>3.6</td>
<td>86</td>
<td>0.08</td>
<td>7.5</td>
<td>28</td>
<td>Trace</td>
<td>5.7</td>
<td>64</td>
<td>0.04</td>
</tr>
<tr>
<td>4</td>
<td>4.3</td>
<td>87</td>
<td>0.08</td>
<td>6.4</td>
<td>47</td>
<td>0.02</td>
<td>6.0</td>
<td>47</td>
<td>0.05</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>4.3</td>
<td>92</td>
<td>0.18</td>
<td>5.9</td>
<td>54</td>
<td>0.05</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td></td>
<td>4.7</td>
<td>92</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RESULTS & DISCUSSION

Pentane formation and rancidity of oils

Flavor evaluations and pentane formation of mixtures of safflower and high-oleic safflower oils are given in Table 1. A linear correlation of 0.79 (significant at the 99% level) was calculated for the percentage of rancid descriptions given by the panel at various levels of pentane in the headspace of the oils. The correlation coefficient is 0.95 if results are omitted for the mixture of 50% safflower/50% high-oleic safflower oils stored 6 days at 60°C. Figure 1 shows the data with this day’s results omitted. Pentane formation was unusually fast for this sample in comparison with the others.

Evans et al. (1969) and Jarvi et al. (1971) found correlations between pentane and flavor scores and between pentane and peroxide values. These oils were directly injected on a GC column. Headspace sampling has advantages over injecting the sample directly onto the column, where heat deterioration occurs, because composition of headspace gases is a measure of the actual oil quality. Besides headspace gas analysis is a more direct and simpler method. Correlating rancid descriptions with pentane formation provides a more specific index in determining rancidity than do flavor scores or peroxide values. For fresh oils in which no pentane was detected, 7% of the panel gave rancid descriptions. This 7% represents a minimum bias of the panel since the same individuals do not report rancidity in all samples. Rancidity is easily confused with staleness, and in the terminology of a few tasters, the samples were either fresh or rancid.

Samples with as little pentane as 0.08 ppm were described as rancid by 90% of the panel. More than 0.08 ppm of pentane neither increased the number of rancid descriptions significantly nor decreased the flavor score much further. In the oils studied, 0.02 ppm of pentane in the headspace is enough to decrease the flavor score significantly and to have 50% of the panel describe the sample as rancid. If samples have at least 0.1 ppm of pentane, there is no doubt that the oil is rancid.

Significant correlations between rancid descriptions and ppm of pentane point more specifically to pentane as an index of product quality for stored samples than flavor score which includes poor quality characteristics other than rancidity.

Pentane formation and rancidity of potato chips

Flavor evaluation and pentane meas-

![Fig. 1](image1.png)  ![Fig. 2](image2.png)

Fig. 1—Correlation between percentage of the taste panel giving rancid descriptions and various levels of pentane in headspace gas of mixtures of safflower and high-oleic safflower oils.

Fig. 2—Relationship of percentage of taste panel giving rancid descriptions and of development of pentane with days of storage at 60°C for potato chips in glass jars. Circles denote rancid descriptions, triangles denote pentane concentration.
measurement for aged potato chips fried in corn oil are plotted in Figure 2. At 20 days of storage, 0.03 ppm of pentane was measured in the headspace with 69% of the panel describing the sample as rancid. Three additional days of storage brought the ppm of pentane to 0.08 with 100% of the panel giving the chips rancid descriptions. Chips stored for 24 and 25 days at 60° C were not tasted because of their strong rancid odor, and no doubt all the panel would have described them as rancid. A second series of chips fried in a mixture of 70% cottonseed oil/30% corn oil was evaluated in the same way with similar results. Before pentane developed the chips were described primarily as stale. There was a gradual increase in the number of rancid descriptions given as storage continued. As soon as pentane was detected in the headspace there was a significant increase in the percentage of the panel giving rancid descriptions—from 31 to 69%. The flavor score was significantly lowered—from 5 to 3.7. Once pentane began to form, it accumulated rapidly in the headspace. Because pentane seems to coincide with rancidity of potato chips, its formation could be used to evaluate objectively the flavor quality of stored chips on an experimental basis.

Figure 3 shows the development of pentane in the headspace gas of potato chips stored at 60° C. Only traces of pentane are shown for samples stored from 0 to 22 days. At 23 days a prominent peak for pentane is observed. After 25 days, a strong pentane peak occurs, and well-resolved peaks are also easily discerned for each of the lower hydrocarbon homologs.

Linoleate content and iodine value vs. pentane formation

For this study, oils were saturated on filter paper strips as described previously. The oils developed pentane in the headspace of the jars at a slightly faster rate than did the oils placed in the jars without paper. Increased surface area of the oil to air plus trace amounts of prooxidative contaminants in the paper seem the probable cause.

Pentane formation by various aged oils is shown in Figures 4 and 5. The linoleate content and iodine value of each oil have been plotted against the induction period, which is the number of days of storage at 60° C for a sample to reach an arbitrary pentane level of 0.35 ppm. Samples with this amount of pentane in the headspace are described as definitely rancid by our taste panel. Table 2 contains a list of the linoleate content and iodine value of each oil tested. In the vegetable oil series shown in Figure 4, hydrogenated winterized soybean oil is the most stable to pentane formation followed by corn, cottonseed, soybean, sunflower and safflower...
oils in that order. Hydrogenated winterized soybean oil with a linoleate content of 35% took 38 days of storage at 60°C to reach 0.35 ppm of pentane, whereas the safflower oil with 78% linoleate took only 2 days. The correlation between linoleate content and days of storage to reach 0.35 ppm of pentane was 0.87, which is significant at the 95% level.

In mixtures of safflower and high-oleic safflower oils (Figure 5), the percentage linoleate in each sample was plotted against the induction period. The correlation coefficient (0.98) was significant at the 99% level. Significant correlations were also obtained by plotting the iodine value of the oils against the induction period for the six different vegetable oils and for the safflower/high-oleic safflower oil mixtures.

Apparently the induction period for pentane formation is not affected by linoleate content alone. Any factor that influences oxidation also affects pentane formation. Three of the vegetable oils tested—soybean, cottonseed and corn—have approximately the same linoleate content, but their induction periods range from 8 to 24 days. Such factors as prior oxidation, light, oxygen, metal contamination, tocopheryl, added antioxidants and chelates in the oil all contribute to the stability or instability of an oil. The safflower/high oleic safflower oil series was a more controlled test because it had fewer variables, other than differences in linoleate content, than did the series with the six different vegetable oils.

Figure 6 relates the linoleate content of the oils to the number of days storage required to develop various amounts of pentane. A general second degree equation was fitted to the data by least squares. The resulting response surface provides predicted levels of pentane based on: Actual amounts of pentane measured in the headspace of the safflower/high oleic safflower oil mixtures, the linoleate content of these oils and the days of storage at 60°C. A multiple correlation coefficient of 0.95 (significant at the 99% level) was found between the observed pentane and the pentane predicted from the equation. The response surface of Figure 5 shows contours of constant pentane level. These contours indicate how much pentane will have formed in a given oil with a certain linoleate content after a specified number of storage days.

For oils with high linoleate content, only a few days are needed to develop pentane, whereas it takes significantly longer for oils with low linoleate. By looking at a given day of storage, the effect of linoleate content on pentane formation can be seen in Figure 6. At 7 days of storage, the predicted amount of pentane to develop in an oil with a linoleate content of 63% is 3.2 ppm, whereas only 0.08 ppm is expected to form in an oil with 17% linoleate. Statistically, an eightfold difference is needed between amounts of pentane formed in two samples before significant variations in pentane accumulation can be seen. For example, the oil with 55% linoleate develops approximately 1.6 ppm of pentane after 7 days of storage, which is significantly faster than the 0.2 ppm produced by the oil with 27% linoleate. The lower the linoleate content the longer the oil is stable to pentane formation. If the percentage linoleate of a product is known, its potential stability in relation to similar foods might be predicted.

### Table 2—Linoleate content and iodine value of seven different vegetable oils and of three safflower/high-oleic safflower oil mixtures

<table>
<thead>
<tr>
<th>Oils</th>
<th>Linoleate content</th>
<th>Iodine value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Safflower</td>
<td>78</td>
<td>146</td>
</tr>
<tr>
<td>Sunflower</td>
<td>73</td>
<td>140</td>
</tr>
<tr>
<td>Soybean</td>
<td>65</td>
<td>135</td>
</tr>
<tr>
<td>Corn</td>
<td>89</td>
<td>125</td>
</tr>
<tr>
<td>Cottonseed</td>
<td>60</td>
<td>114</td>
</tr>
<tr>
<td>Hydrogenated soybean</td>
<td>35</td>
<td>111</td>
</tr>
<tr>
<td>High oleic safflower</td>
<td>17</td>
<td>94</td>
</tr>
<tr>
<td>Safflower/high-oleic safflower oil mixtures</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% Safflower/25% high-oleic safflower</td>
<td>63</td>
<td>133</td>
</tr>
<tr>
<td>50% Safflower/50% high-oleic safflower</td>
<td>48</td>
<td>120</td>
</tr>
<tr>
<td>25% Safflower/75% high-oleic safflower</td>
<td>32</td>
<td>107</td>
</tr>
</tbody>
</table>

### Table 3—Pentane formation of potato chips fried in oils with various linoleate content

<table>
<thead>
<tr>
<th>Frying oil</th>
<th>Linoleate content</th>
<th>Lot</th>
<th>Days of storage at 60°C for 0.02 ppm pentane in headspace of the chips</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogenated vegetable oil&lt;sup&gt;a&lt;/sup&gt; with preservatives</td>
<td>8</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>70% Cottonseed oil/30% corn oil&lt;sup&gt;b&lt;/sup&gt;</td>
<td>57</td>
<td>14&lt;sup&gt;c&lt;/sup&gt;</td>
<td>24&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Corn oil&lt;sup&gt;a&lt;/sup&gt;</td>
<td>58</td>
<td>A</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B</td>
</tr>
</tbody>
</table>

<sup>a</sup> Linoleate content determined from oil extracted from the chips
<sup>b</sup> Linoleate content determined on oil before chips were fried
<sup>c</sup> Stored when fresh
<sup>d</sup> Stored after being held 4 months at −17°C
showed that increasing the moisture content has an inhibitory effect on the oxidation of methyl linoleate. Quast and Karel (1972) found that in early stages of oxidation at low humidities the rate of oxygen uptake is a strong function of relative humidity.

Figure 7 contains results of duplicate tests conducted to determine whether or not chips were affected by different moisture levels. The chips were fried in corn oil. Pentane formation was slower in the sample with 3.8% moisture in comparison with the chips with 0.95% moisture.

REFERENCES


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