Flavor Problems in the Usage of Soybean Oil and Meal

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LIPIDS AS A SOURCE OF FLAVOR
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Flavor Problems in the Usage of Soybean Oil and Meal

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Oil and meal flavors in soybeans appear to present a bifurcated subject. But as we shall see, the problems of the meal are in part problems of the oil. Since residual lipids of soybean flakes constitute the precursors for odors and flavors, knowledge of the deteriorative reactions of fats is basic to the understanding of flavor development in soybean meal products. In this review the emphasis has been placed on lipid-derived flavors and their precursors, degradative reactions, separations, analyses, and psychometric evaluations.

To set the discussion of soybean oil flavor in proper perspective, one might first turn to the recent statistics on the disposition of soybean oil. Margarine and shortening comprise large outlets for soybean oil. Cooking and salad oils have been taking an increasing proportion of the "pie" probably because of the relationship of polyunsaturation to blood cholesterol lowering. With this magnitude of consumption of soybean oil the question must inevitably raise in the reader's mind, "What is the importance of the flavor problem?" (Figure 1)

In the early 1940's soybean oil was considered neither a good industrial paint oil, it was slow to dry, nor a good edible oil. In those days soybean oil flavor was considered the "Number One Problem of the Soybean Industry." Only under the exigencies of World War II was it added to margarines—and then to the absolute limit of 30%! The history of soybean oil is a story of progress from a minor edible oil of dubious value in the 1940's to a major edible oil proudly labeled on premium products of the 1970's. It is a story of cooperation between government research on the one hand and industrial implementations of research findings on the other.

Trivial as it may seem at this time, the first significant milestone in research was the development of a more objective method of assessing flavor and odor (1). With this procedure, numerical values for flavor intensity from a taste panel in one plant could be reproduced quite easily by a panel in another company or research institution. Equally important perhaps,
research finally had a reliable way of comparing samples and assessing more reliably the benefit of a given processing treatment rather than relying on the judgment of a single "expert."

With this new tool for evaluation, trace metals were identified as having special significance in the flavor stability of soybean oil compared to other edible fats and oils; whereas, cottonseed oil can tolerate copper and iron in the parts per million (ppm) range, soybean oil is ruined by as little as 0.3 ppm of iron and 0.01 ppm of copper (2). What followed the discovery of the deleterious effect of trace metals, especially in soybean oil, was removal of brass valves in oil refineries and conversion from cold rolled steel deodorizers to stainless-steel and even to nickel.

Strange as it may seem in retrospect, scientists had to establish that "soybean flavor reversion," as it was incorrectly called, was an oxidative process. When we sharpened up our analytical tools, the relation of peroxidation to off-flavor became unmistakable. The response of industry to the conclusion that "reversion is oxidation" was to blanket oils with inert gas at all critical high-temperature steps, including final packaging.

The next milestone has the aspects of a cloak-and-dagger story. At the close of World War II, Mr. Warren H. Goss, a chemical engineer at Northern Regional Research Center (NRRC), was commissioned a major in the Army with special assignment to follow Patton's advancing tanks through Germany and to investigate the German oilseed industry. As the troops advanced, he kept hearing about a recipe to cure soybean "reversion," but not until he reached Hamburg did he learn exact details. It was a strange formula involving many washings...such as contacting oil with

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Table I
Milestones in Improving Flavor Stability of Soybean Oil

<table>
<thead>
<tr>
<th>Date</th>
<th>NRRC Research</th>
<th>Industry Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>1945</td>
<td>Standardized taste test</td>
<td>Worldwide acceptance</td>
</tr>
<tr>
<td>1945</td>
<td>Trace metals</td>
<td>Brass valves, sheet steel out</td>
</tr>
<tr>
<td>1948</td>
<td>Metal deactivators</td>
<td>&quot;Nary a lb without citric acid&quot;</td>
</tr>
<tr>
<td>1948</td>
<td>Flavor is oxidation</td>
<td>Inert gas blanketing</td>
</tr>
<tr>
<td>1951</td>
<td>Precursor--linolenic</td>
<td>Homozygous (it can't be done)</td>
</tr>
<tr>
<td></td>
<td>--breed it out</td>
<td>Practiced but now obsolete</td>
</tr>
<tr>
<td></td>
<td>--extract it out</td>
<td>&quot;Specially processed soybean oil&quot;</td>
</tr>
<tr>
<td>1966</td>
<td>Recognition of room odor problem</td>
<td>Commercial production of cooking oils by copper catalysts</td>
</tr>
<tr>
<td>1974</td>
<td>Copper catalysts</td>
<td></td>
</tr>
</tbody>
</table>
water glass; but weird or not, when tested at NRRC it worked. It worked, as we were to learn, not because of the unusual washing treatments, but because citric acid was added to the deodorizer (3). Citric acid, we were to learn at NRRC, functioned by binding or complexing the deleterious traces of prooxidant metals. Based upon this discovery came the surge of metal deactivators--i.e., sorbitol, phosphoric acid, lecithin, polycarboxy acids, and starch phosphates. The immediate response of industry was to adopt metal deactivation, and I suspect that today there is not a pound of soybean oil product not protected by citric acid or some other metal deactivator.

These palliative steps, important as they were, still begged the question as to what causes off-flavor to develop--i.e., what are their unstable precursors? Unsaponifibles, i.e., sterols, were suspect. Circumstantial evidence pointed to the 7% content of linolenic acid, which draws its name from linseed oil where this trienoic fatty acid amounts to ca. 50%.

In what is now a classic experiment, 9% linolenic acid was interesterified into the glyceride structure of a nonreverting nonlinolenic acid oil; namely, cottonseed oil. The taste panel identified cottonseed oil interesterified with linolenic acid as soybean oil! (4)

Armed with this new basic information, what could be done? Three alternatives suggest themselves with regard to linolenic acid removal: (1) Breed it out; (2) extract it out; or (3) react it out.

Of the three alternatives listed, reacting out linolenic acid was chosen as the most practical research approach--and thereupon began a long search for selective hydrogenation catalysts--those that would react with linolenic acid but not attack the desired, essential polyunsaturated fatty acid--linoleic acid.

Fortunately, at this time our basic researches of catalyst selectivity bore fruit. NRRC's scientists found that among many metals active as hydrogenation catalysts, copper behaved with almost enzymatic specificity, hydrogenating linolenic acid some 15 to 20 times more rapidly than linoleic acid (5). It meant that not 3 to 4% linolenic acid in salad oils characteristic of nickel hydrogenation of soybean oil but "zero" percent linolenic oils could be produced, with little attack on the essential linoleic acid and with concomitantly low winterization losses. Room odor studies, conducted by our taste-odor panel, could scarcely detect the fishy odors characteristic of unhydrogenated soybean oil or of soybean oil partially hydrogenated by conventional nickel catalysts (6).

Now, it can be reported that in the United States a new plant has been built and has come on stream using copper catalysts. A large producer in Europe was observed to be test marketing three brands of copper-hydrogenated soybean oil in France, and a major French oil processor has a plant operating with copper catalysts.
The special interest in copper-hydrogenated soybean oil in France stems in part from the quadrupling in price of peanut oil coming from Africa. (Aflatoxin in the meal lowers its feed value and therefore raises oil prices.) A French law permits soybean oil with less than 2% linolenic acid to be sold as a salad or cooking oil. The copper-hydrogenation soybean oil may rank as one of the important developments in edible oil production in recent years.

Although samples of copper-hydrogenated soybean oil produced abroad have appeared to our taste panel to be of the same quality as that which is successful in the United States, the French housewife, not the taste expert, determines the consumer acceptance. Because the copper-hydrogenated soybean oil when stored or heated does not have the odor or flavor of the familiar peanut oil, there is some question as to whether the copper-hydrogenated soybean oil can replace it. Likewise, in the Mediterranean region where olive oil is the traditionally used deep-fat frying fat, the future of edible soybean oil will be determined by its acceptability in odor and flavor upon cooking. If soybean oil is to find new markets in France and in the Mediterranean region, it must meet this remaining problem of room odor.

The odor principles that cause the residual odor from deep-fat frying fats then assume practical importance. One method of studying them is the gas chromatograph-mass spectrometer system combined with "nose in the computer loop" as shown in Figure 2. In what has been dubbed a "micro frying pan" either the oil or individual purified constituents of oil are heated to deep-fat frying temperatures, while air is passed over the surface and then through a needle downward into a gas chromatographic column. The volatile odors are frozen out in the first few inches of this column at dry ice temperatures. After 5 minutes of collection of the odors, the gas chromatograph is returned to its usual source of gas pressure, and the chromatograph is programmed. The effluent from the column is split in three ways. The flame ionization detector, of course, provides us with the information on how many compounds and how much of each. The second split goes to the mass spectrometer-computer system which answers the question as to what the component is. And finally, a third part is sent for sniffing by the human nose and for its owner's recording the intensity of the odor sensation by means by a voltage dividing potentiometer and recorder. Thus, he simultaneously prepares and draws his intensiogram at the same time the gas chromatograph is recording the chromatogram. Whereas a flame ionization detector tells how many compounds and how much, the mass spectrometer tells what they are, the human nose tells how significant is the odor.

An example of the application of this technique to the room odor and the volatiles of heated soybean oil is given in Figure 3. The lower part is the usual gas chromatogram and the upper section is that of an intensiogram as drawn by the human observer (7). As
Figure 1. Disposition of U.S. soybean oil—1976

Figure 2. A nose in the GC-computer loop
would be expected, there are large peaks on the gas chromatogram that have small odor response and, contrariwise, there are minimal peaks in the gas chromatogram that give a large olfactory response. At the present time we are not only able to identify most of the peaks of this chromatogram chemically, but we have also made similar measurements upon the purified components that comprise soybean oil and are thus able to associate individual peaks of this curve as having their precursor of oleic, linoleic, linolenic, or saturated acids.

Unfortunately, it is widely understood but rarely acknowledged that the total volatiles collected at the exit port of a gas chromatograph should not differ from the odor of the mixture injected. Specifically, the whole should be equal to the sum of its parts. Because of the heat lability of odor principles with which we deal and the necessary temperatures for their volatilization in the gas chromatograph, this criterion unfortunately cannot be met. We are reminded of some work conducted in 1952 in which separation was performed by liquid upon silica gel and the rancid components of reverted soybean oil were separated from the painty components (8). It would be hoped with the modern developments of high-pressure liquid chromatography (HPLC), and with the developments of new phases, that it will be possible to separate unchanged the sensitive mixture of odor components. The current problem of this approach is that of interfacing the high-pressure liquid chromatograph to the mass spectrometer. It is a problem of separating the volatile odor materials from a frequently equally volatile developing solvent. At the present time the advances in our scientific knowledge are being limited by needed advances in technique.

The disposition of U.S. soybean meal as shown in Figure 4 differs markedly from that of the oil. From this chart and the relative dollar value of oil and meal components of the soybean, it may be inferred that the soybean crop is raised primarily for its protein content and for its outlet in the animal feeding economy. It is of interest that the nonfeed uses of soybean meal, which include 2% for human food, amount to only 5% of the total disposition. There is a need worldwide by protein-starved nations for just this kind of high-quality, low-cost protein which soybeans provide. This statement then begs the question of why there is not more volume of edible soy products, particularly in the light of many commercially available products in the United States which contain soybean meal or constitute food-grade soybean meal for mixing purposes.

Some of the critical factors that restrict the use of soy meal in foods are legalistic—about which research has little to say. There are, however, problems of functional properties and of form. There are problems of making available maximal nutritional values by processing treatments. For example, a soybean meal that is designed for minimal denaturation and maximum solubility may have anti-metabolites or its amino acids may be less available
Figure 3. (Top) odor intensiogram or odor intensity of peaks corresponding to the chromatogram of volatiles (bottom) collected for 10 min immediately after soybean oil reached 193°C.

Figure 4. Disposition of U.S. soybean meal—1976
than if it were heat treated. However, this very process of
toasting will reduce the solubility characteristics; thus, there
must be a trade-off or compromise between solubility and its
nutritional value.

A problem sometimes encountered in soybean protein use is
that of gas production or flatus. Research has established that
the galactoside type of tri- and tetrasaccharides, which are
present in soybean meal to the extent of 10%, are indicted in
flatus (9).

Certainly the most important factor that restricts the wide-
spread food use of soybean meal at the present time is its flavor.
It is well known that this is a critical factor and that starving
populations will not eat nutritious materials if the flavor is not
acceptable to them. In some bland products where it is used as an
extender, soybean meal is limited by flavor to ca. 30% addition.
Therefore, it is in this area of reduction of flavor that the
greatest effort of research should be concentrated.

Given in Table II is a listing of flavor scores recorded by
the taste panel for commercial products, for the concentrates and
for the isolates. A score of 10 is indication of a bland product.
In most instances the alcohol treatment to produce the concentrate
or the precipitation to produce the isolate gives an improved
flavor, as well as improved flatus characteristics, to the
product (10).

Table II
Odor and Flavor Scores of Hexane-Defatted Soy Flours

<table>
<thead>
<tr>
<th>Sample</th>
<th>Odor scores</th>
<th>Flavor scores</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial flours, A-G</td>
<td>5.8-7.5</td>
<td>4.2-6.6</td>
</tr>
<tr>
<td>Raw flour</td>
<td>5.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Azeotrope-extracted</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexane:methanol</td>
<td>6.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Hexane:ethanol</td>
<td>7.9</td>
<td>7.2</td>
</tr>
<tr>
<td>Hexane:2-propanol</td>
<td>5.9</td>
<td>5.1</td>
</tr>
</tbody>
</table>

The flavor of soybean meal comes from two general sources:
first, it is indigenous to the bean itself and, secondly, it may
be formed upon storage. As shown in Table III, the flavor inten-
sity values for the beany characteristic of maturing soybeans
remained relatively constant during the maturation process (11).
However, the bitter principle increased rather sharply as the
soybeans matured. Many of the compounds contributing to the green
flavors of raw soybeans are known, and some of the principal ones
are listed in Table IV (12).
Table III
Flavor Intensity Values (FIV) of Maturing Soybeans

<table>
<thead>
<tr>
<th>Days After Flowering</th>
<th>Beany</th>
<th>Bitter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>¥a</td>
<td>¥b</td>
</tr>
<tr>
<td>28</td>
<td>100</td>
<td>2.0</td>
</tr>
<tr>
<td>34</td>
<td>90</td>
<td>2.3</td>
</tr>
<tr>
<td>49</td>
<td>100</td>
<td>2.5</td>
</tr>
<tr>
<td>56</td>
<td>100</td>
<td>2.2</td>
</tr>
<tr>
<td>63</td>
<td>100</td>
<td>2.7</td>
</tr>
<tr>
<td>66</td>
<td>92</td>
<td>2.5</td>
</tr>
</tbody>
</table>

a. Percentage of panelists giving a positive response.
b. Based on score 1 = weak to 3 = strong.

Table IV
Key Compounds Contributing to Green Flavors of Raw Soybeans and Peas

<table>
<thead>
<tr>
<th>Compound</th>
<th>Flavor description</th>
<th>Threshold (ppm in oil) Odor</th>
<th>Taste</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Hexanal</td>
<td>Green grassy</td>
<td>0.32</td>
<td>0.15</td>
</tr>
<tr>
<td>3-cis-Hexenal</td>
<td>Green beany</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>n-Pentylfuran</td>
<td>Beany</td>
<td>2</td>
<td>1-10</td>
</tr>
<tr>
<td>Ethyl vinyl ketone</td>
<td>Green beany</td>
<td>5 (milk)</td>
<td></td>
</tr>
</tbody>
</table>

The flavors mentioned can also arise from deteriorative reactions either in the processing or storage of the soybean meal. These reactions may be of an enzyme-catalyzed nature as for example by lipoxygenase or they may come about by antioxidation in a manner not greatly dissimilar to that in the oil (13). In any case, the hydroperoxides thus formed may undergo decomposition to form the keto or hydroxy type of functional groups as postulated in Figure 5, or even the epoxide type of compound as is shown in Figure 6.

Some of the major volatile compounds derived from linoleic acid by lipoxygenase and analyzed in headspace are shown in Table V. These chemical compounds are readily rationalized by the oxidative mechanisms of breakdown of hydroperoxides of linoleic acid (14).
Figure 5. Postulated decomposition of unsaturated fatty acid hydroperoxides

1) \(\text{ROOH} + \text{R} = \text{ROH} + \text{R}^*\)

2) \(\text{OOH} \rightarrow \text{O}^* \rightarrow \text{R}^* \rightarrow \text{OH}\)

Figure 6. Postulated formation of epoxides from fatty acid hydroperoxides
Table V

Major Volatile Compounds Generated from Linoleic Acid Hydroperoxides (LCHP) by Pea and Soybean Lipoxygenases

<table>
<thead>
<tr>
<th>Compound</th>
<th>Quantity in headspace, GLC peak height&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Pea</th>
<th>Soybean</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butanal</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>n-Pentanal</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>n-Hexanal</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>n-Heptanal</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>n-Hept-trans-2-enal</td>
<td>+++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>2-n-Pentyl furan</td>
<td>+</td>
<td>+++</td>
<td>+++</td>
</tr>
</tbody>
</table>

<sup>a</sup> See Ref. 15.

<sup>b</sup> 5-10 mm; 11-50 mm; >50 mm. GLC = gas liquid chromatography.

For soybean meal as compared to other vegetable meals, the linolenic acid is an unusual component of the residual fat. When the linoleate hydroperoxides were tasted by our taste panel, rancidity was listed as one of the most frequent responses. By contrast, when linolenic acid was so treated, rancidity was a less prominent response. The grassy-beany flavors, which may be assumed to include paintiness as well, were the most important response in the linolenate hydroperoxides (13).

Although it has not been established, it would appear that oxidized soybean phosphatidylcholine contributes to the bitterness of the soybean meal. This has been studied by oxidizing purified phosphatidylcholine and submitting to the taste panel at various levels. It has also been indicated by fractionation studies in which the bitter principle from hexane-extracted soy flour was found to be concentrated in the purified soybean phosphatidylcholine fraction (15). While all of this basic type of research is being conducted on the flavor of the soybean meal, industry has been implementing some of the research results generated 30 years ago. At that time, it was established that ethanol extraction of the flakes had a particular merit in removing bitter principles from soybean meal (16). Illustrated in Table II, the hexane-ethanol azeotropic solvent was capable of removing the residual lipids and the bitter flavor. It was noted that washing with diethyl ether by itself did not remove bitter flavor, but not until the hot ethanol treatment was given were the bound lipids removed which contained the highly flavored principles. As shown in the Table, many of the commercial flours had odor and flavor scores not greatly different from raw soybean flour. Upon extraction by the azeotropic alcohol mixtures the flavor was improved, but of those investigated the hexane-ethanol seemed to
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have a peculiarly beneficial effect in improving the flavor. In fact, the combination of toasting and azeotropic extraction in the laboratory appears to have raised the flavor score for odor and flavor to that equivalent to wheat flour. The flavor intensities of the grassy-beany and the bitter flavor were reduced. It has been inferred that alcohol treatment may be responsible for some of the improved flavor of soybean meal products now being produced.

In summary, then, the flavor stability of soybean oil which was regarded as the number one problem of the soybean industry three decades ago has now, at least in part, been solved; but the flavor of the meal is today held as the major deterrent to the increase of soybean protein in human food products. Since residual lipids of the soybean flakes constitute the precursors for odors and flavors, knowledge of deteriorative factors of fats is basic to the understanding of flavor development in both soybean meal and oil products. Highly sophisticated gas chromatographic-mass spectrometric systems and HPLC are being used for analysis of odors of oil and meal products, and these techniques are particularly effective where the human nose is included in the computer loop. Meanwhile current applications of past research on the processing of soybean oil and meal appear to have made a significant contribution in solving the respective problems for the food industry.

Literature Cited


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