A Review of Soybean Oil Reversion Flavor

THOMAS H. SMOUSE, Manager of Lipid Sciences, Ralston Purina Co.,
Venture Management 3RN, Checkerboard Square, St. Louis, MO 63188

ABSTRACT

Crude soybean oil has a characteristic "green-beany" flavor, which during refining, bleaching and deodorization is eliminated to produce a bland tasting, light colored oil. However, flavor returns during storage and has been characteristically called the "reversion flavor" of soybean oil. This deleterious characteristic flavor has influenced the utilization of soybean oil and its fatty acids. Several theories for the cause of reversion flavor include: (a) oxidation of linolenic acid; (b) oxidation of isolinoleic acid of the 9,15-diene structure; (c) phosphatide reactions; (d) unsaponifiables; and (e) oxidative polymers. References are presented that support or contradict these theories. Recent publications concerning the isolation and characterization of the components of reversion flavor indicate slight oxidation of the fatty acids is the major cause. Techniques that are effective in increasing the flavor stability of soybean oil are presented.

INTRODUCTION

Records show that prior to 2000 BC (1), soybeans were considered an important cultivated legume and were classified as one of the five sacred grains with the others being wheat, rice, barley, and millet. Soybeans were not introduced to the American farmer until the early 1920s as a crop to help reduce the surpluses of wheat and cotton. Although soybeans were slow to be accepted initially, production increased rapidly each year to the position of being the most important oilseed crop in the United States (2). Soybean oil and its fatty acids are utilized in both industrial and edible products.

Crude, degummed soybean oil is normally produced in the United States by the processes shown in Figure 1. After cleaning the beans, they are adjusted to 10% moisture and cracked into 6-8 pieces. The hulls are removed by air classification and the cracked cotyledons are tempered with steam to soften the pieces. They are rolled into flakes having a thickness of ca. 0.015 in. Oil is extracted with solvent to produce a mixture known as micella. After extraction, the solvent is removed from the micella by heated falling film evaporators. The final traces of solvent are removed by steaming. The phosphatides are removed from the crude soybean oil by hydration with water, a process referred to as degumming. The hydrated gums are removed by centrifugation which are later dehydrated to produce crude soybean "lecithin." The supernatant from the centrifugation process is crude, degummed soybean oil.

This oil is normally processed by the methods shown in Figure 2 to produce refined, bleached, and deodorized soybean oil commonly referred to as RBD SBO. The crude oil is first treated with alkali to remove the free fatty acids. Refined oil may or may not be bleached with activated earths. When bleached with activated earth to remove pigment material and traces of soap, a product known as refined and bleached soybean oil (RBD SBO) is produced. The next processing step may be hydrogenation if it is desired to "harden" the oil, or it may be deodorized by a high vacuum, high temperature steam treatment to remove traces of odoriferous materials to produce a light colored, bland tasting salad oil (RBD SBO). The product at this stage of processing will normally have the physical and chemical characteristics shown in Table I.

However, the "green-beany" flavor of crude oil may return in a refined, bleached and deodorized oil upon aging and has been referred to as the "reversion flavor" of soybean oil. The term "reversion" is a misnomer since the flavor formed upon aging is not exactly the same as the raw "green beany" flavor typical of crude oil before processing into a finished salad oil. Also, the "reversion flavor" is not that of a rancid oil which generally has a "painty" characteristic. Descriptive terms of "reversion flavor" of soybean oil are "green-beany," "weedy," "hay," "melon," and "fishy." Very initial stages of reversion are sometimes "buttery."

This deleterious flavor has influenced the utilization of

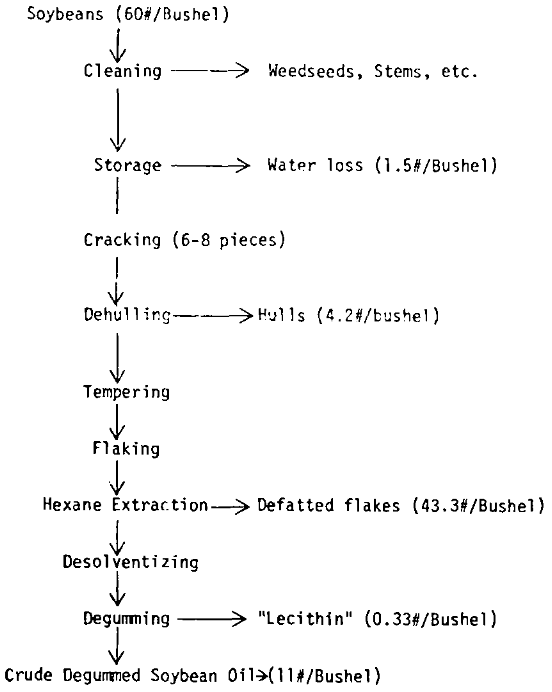


FIG. 1. Unit processing steps for making crude, degummed soybean oil from whole soybeans.

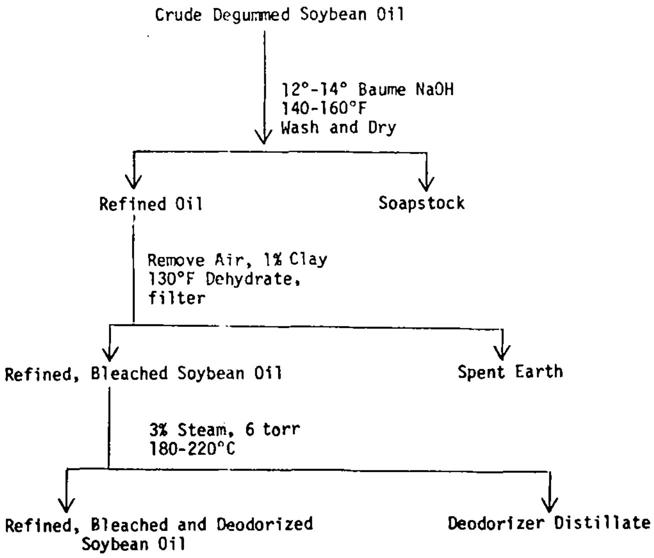


FIG. 2. Unit processing steps for making refined bleached, and deodorized soybean oil from crude, degummed soybean oil.

soybean oil and its fatty acids. When the problem of reversion flavor is solved, the oil and its fatty acids will have better acceptance and its commercial importance should be greater.

THEORIES

Scientists have suggested several theories for the cause of flavor reversion. It has been found that reversion flavors generally occur in vegetable oils or fish oils that contain fatty acids with more than two double bonds such as linolenic or arachidonic acids. It is believed the precursor to the reversion flavor of soybean oil is present in freshly refined oil, and upon aging decomposes to flavor components responsible for reversion flavor. Theories have been proposed to the structure of these precursors and how they decompose to the responsible flavor components. These theories are reviewed in the following pages.

Linolenic Acid Theory

Durkee (3) was one of the first to suggest the linolenic acid theory. He observed that soybean oil normally contained 8-9% linolenic acid, while oils like cottonseed or peanut contain little or none. He also observed that soybean oil would develop reversion flavors while cottonseed and peanut oils would not, thus concluded reversion flavor must be related to the linolenic acid content. Sanders (4) confirmed Durkee's observation. He added 10 parts of linolenic acid obtained from linseed oil to 90 parts of cottonseed fatty acids, esterified the mixture to a finished oil, and observed that its flavor characteristic was very similar to soybean oil. Golumbic (5) also made a synthetic soybean-type oil by using purified stearic and palmitic acids, combined with oleic acid from olive oil, linoleic acid from cottonseed oil and linolenic acid from linseed oil. He concluded that the synthetic soybean-type oil, after being light-reverted, had a poorer flavor quality than cottonseed oil, but was better than soybean oil. The synthetic oil did not have "grassy-haylike" flavor that normal soybean oil develops. Dutton et al. (6,7) and Schwab et al. (8) published several papers in the early 1950s that support the linolenic acid theory. They prepared a soybean-type oil with linolenic acid content of 2-3% by furfural extraction of soybean oil and found the low linolenic soybean oil developed less reversion flavor than normal soybean oil. They also demonstrated that when 7.5% linolenic acid was incorporated into cottonseed oil by interesterification, a panel identified the modified cottonseed oil as reverted soybean oil.

Although much of the research reported since the 1950s confirms that linolenic plays a primary role in flavor reversion, there are earlier research publications that contradict this theory. Dollear et al. (9) obtained soybean oil from Dunfield soybeans which had an unusually low iodine number (106.6) and a linolenic acid content of 2.9%. From the research presented in the previous references, this soybean oil should have superior flavor stability. Contrary to the expectations, it was found to be no better than normal soybean oil.

If the reversion is due to the oxidative decomposition of linolenic acid, then storage of soybean oil under inert gases or vacuum should improve the flavor stability. Robinson (10) found that soybean oil aged under inert gases developed reversion flavor and Bickford (11) made the same conclusions by storing soybean oil under a high vacuum. Sims (12) hydrogenated soybean oil and converted the linolenic acid to various contents ranging from 8-0% and found no correlation between flavor stability and linoleic acid content. These discrepancies may be explained by poor flavor panel data, lack of agreement between laboratories on describing reversion flavor, or other problems associated with reverting the oil. Evidence has been published that linolenic acid, per se', may not be the sole cause of reversion flavor.

TABLE I

The Physical and Chemical Characteristics of a Typical Refined, Bleached, and Deodorized Soybean Oil

Flavor	–	Bland to slightly nutty (+8.0)
Color	–	2.OR/2OY
Active Oxygen Method (AOM)	–	12+ hours
Peroxide Value (PV)	–	0.5
Free Fatty Acids (FFA)	–	0.05%
Anisidine Value (AV)	–	2.0
Oxidation Value (OV)	–	3.0
Iodine Value (IV)	–	132
Iron (Fe)	–	0.1 PPM
Copper (Cu)	–	0.01 PPM
FAC C_{16}	–	10.6%
C_{18}	–	4.6%
$C_{18:1}$	–	25.4%
$C_{18:2}$	–	52.9%
$C_{18:3}$	–	8.3%

Isolinoleic Acid Theory

During World War II, a group of Canadian scientists were investigating the use of hydrogenated linseed oil for edible applications. Several of the published experiments indicated that hydrogenated linolenic acid does develop reversion flavor and that it may be due to isolinoleic acid rather than linolenic acid.

When the unsaturated fatty acids are hydrogenated, many reactions occur at different rates as shown in Figure 3. This figure gives the calculated changes in the levels of trienes, dienes, monoenes, and saturates of linseed oil as it is hydrogenated nonselectively (13). The effect of hydrogenation upon the fatty acid composition of soybean oil gives a similar plot except there are less trienes, less isodienes, and more linoleic and oleic than found in linseed oil (14).

Armstrong and McFarlane (15) found that if linseed oil is separated into saponifiable and unsaponifiable fractions, and both fractions were independently added to sunflowerseed oil, the unsaponifiable fraction did not develop reversion flavor but the re-esterified fatty acids reverted after the mixture was deodorized. These results, plus the fact that hydrogenated ethyl linolenate and sunflowerseed oil mixture would develop reversion flavor but the unhydrogenated mixture would not, suggest that linolenic acid would cause reversion flavor only after it was hydrogenated.

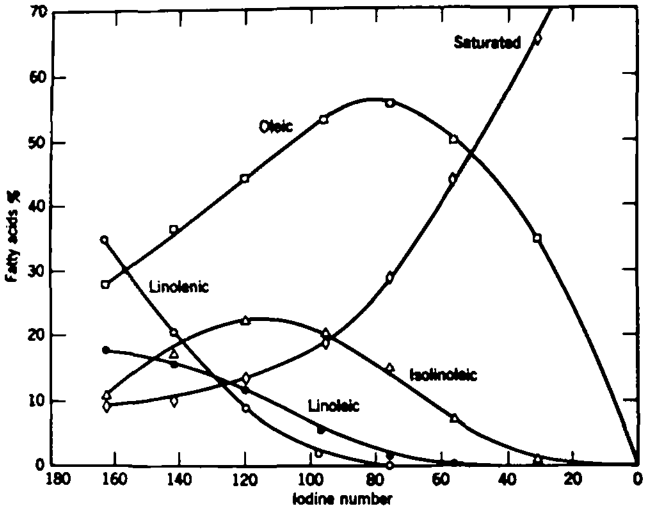


FIG. 3. The changes in composition of linseed oil during hydrogenation.

Lemon (16,17) proposed that a single isomer was preferentially produced by hydrogenating the 12,13 double bond of linolenic and referred to this isomer as isolinoleic. From reports by Daubert (18) and Mattel (19), many other isomers are formed during the hydrogenation of linolenic acid glycerides. Thompson et al. (20) found two types of isolinoleic acid; the Type I isomer is formed when the 12,13 double bond of linolenic is reduced and the 9,10 or 15,16 double bonds do not migrate, while the Type II isomer is formed when migration occurs.

The Type I isomer has six carbons between the double bonds and has been found to produce a beany flavor when added to cottonseed oil. The Type II isomer has only four or five carbons between the double bonds and has not been shown to form beany off flavors with aging.

Consistent with the case for linolenic acid not being the sole precursor to reversion flavor, reports have been published that suggest isolinoleic may not be the cause. Lips et al. (21) observed that reversion flavor can occur in hydrogenated oils that are hydrogenated to iodine values considerably below those where isolinoleic would be present. They also demonstrated no improvement in flavor stability with decreasing concentrations of isolinoleic acid. In fact, they noticed poorer stability at the lower iodine values. Thus, they have concluded isolinoleic acid is not the only cause of reversion flavor.

Phosphatide Theory

The German oil technologists have predicated their oil processing on the theory that phosphatides are the precursors to reversion (22). They remove all lecithin by two hot water washings followed with the addition of citric acid to "inactivate" lecithin that is not removed. Extensive research conducted at the Northern Regional Research Laboratory reported in a review article by Cowan (23) indicates that the addition of citric acid is more important than the two hot water washes. Citric acid will chelate metals such as iron and copper rather than "inactivate" the lecithin. The Germans steam for 90 seconds to "inactivate" the lecithin. The steaming is really inactivating biological enzyme systems within the bean. Recent research has shown that steaming the beans results in an improved crude oil and from this a better soybean salad oil can be manufactured (24).

Davies and Gill (25) found that nitrogen could enter into a linolenic acid oil by holding the oil and lecithin together for a period of time. Similar observations have been made with trimethylamine oxide. The theory is that lecithin provides the trimethylamine oxide which, in the presence of hydroperoxides from autoxidation, forms formaldehyde and dimethyl amine. Dimethyl amine may have a fishy odor. Data reported by Bickford (11) supports that of Davies and Gill in that linolenic acid will release formaldehyde from trimethylamine oxide. Chang et al. (26) found nitrogen is present in the flavor extracts of reverted soybean oil. Chang et al. (27) also observed a gas chromatographic effluent that possesses a "fishy" odor from their studies of soybean oil reversion. There has been little data presented showing that phosphatides are not the precursor to reversion flavor. Research at the Northern Regional Research Laboratory has shown that addition of 0.02% soybean phosphatides to soybean oil would improve the oxidative stability and not change the flavor stability.

Unsaponifiable Matter Theory

Mattel (28) was the first to suggest that the unsaponifiables of soybean oil could be responsible for reversion flavor. He found a typical reversion flavor developed when this fraction was isolated from soybean oil and added to cottonseed oil. When this experiment was repeated with the unsaponifiables from linseed oil, no reversion flavor was produced. An excellent review by Kochar and Meara (29) gives data that show unsaponifiables like squalene in soybean oil, carotene in palm oil, and tocopherol in lard are related to the flavor stability of these products. However, the contribution of the unsaponifiables to the reversion flavor of soybean oil is only of minor significance.

Oxidative Polymer Theory

This theory was suggested by S.S. Chang (30,31). Chang and Kummerow (32) found in working with oxidized ethyl linolenate polymers that these polymers could decompose under nitrogen to yield flavor components that are identical to those isolated from reverted soybean oil. They also found that these oxidative polymers contained 9.25% more oxygen than a RBD soybean oil and would not need oxygen to form oxygenated flavor components like carbonyls. These polymers were also found to decompose under high vacuums or inert atmospheres. Holm et al. (33) have shown that high-molecular-weight unsaturated compounds isolated from oxidized rapeseed oil had no distinctive flavor, but when they were heated, intense flavors developed. They also found that hydrogenation would not completely reduce these compounds, and poor flavor stability was caused in hardened fats. Evans et al. (34) published data that show soybean oil, oxidized to 10 PV prior to deodorization, causes no changes in the flavor stability. However, when oxidation prior to deodorization is greater than 10 PV, then the RBD soybean oil has a poorer flavor stability. A similar study was conducted in my own laboratory and reported at the 45th Fall AOCS Meeting held in Atlantic City (35) and again at the 11th World Congress of ISF held in Goteborg, Sweden (36). Soybean oil oxidized to ca. 25 PV and then redeodorized was found to have better flavor stability than a sample that was oxidized to100 PV. To date, there is no data that contradict this theory, and the oxidative polymers of soybean oil would have the following precursor characteristics: (a) they are present in soybean oil and not in cottonseed oil;(b) they are not easily removed by present soybean oil processing methods; (c) they have little or no flavor themselves; and (d) they decompose to reversion flavor and are not inhibited by antioxidants or inert gas storage conditions.

FLAVOR CHARACTERIZATION

From the diversity of the data presented and the contradictions that have been given, it appears that soybean oil reversion flavor may be a combination of several flavor components coming from several precursors. Research completed since the 1960s has been successful in isolating and identifying some of the chemicals that are responsible for "reversion flavor." G. Hoffmann found in the early 60s several key flavor ingredients (37-39). The "green bean" flavor was caused by *cis*-3-hexenal which would be formed by the autoxidation of linolenic acid. He also found *trans, cis* and *trans, trans* 2,4-heptadienals and 2,4-decadienals. It is believed the precursors for these dienals would be linolenic and linoleic acids, respectively. Another compound that could be identified as having a musty odor is 1-octen-3-ol, commonly known as "mushroom alcohol." It is proposed that this material is formed from the oxidation of linoleic acid and has been confirmed to be present in reverted soybean oil (40). Other key components identified were ethyl vinyl ketone (41) and diacetyl (42). Both of these flavor components may be formed from the oxidation of linolenic acid. Ethyl vinyl ketone has been described as a metallic flavor when tasted in milk but in the presence of pentanal, its flavor is similar to the early stages of soybean oil reversion. Levels of ethyl vinyl ketone and pentanal at ca. 10 PPB appeared to be most suggestive of early reversion flavor. It has been proposed that diacetyl is responsible for the buttery flavor characteristic that sometimes appears in the early stages of reversion flavor development before the green-grassy flavor notes form that are characteristic of reversion flavor.

Much of the research that has been published concerning the isolation and identification of flavor components responsible for reversion flavor used highly oxidized soybean oil. However, reversion flavor appears in soybean oil at very early stages of autoxidation before hydroperoxides increase to levels responsible for rancidity. Smouse (40,43) identified 76 compounds in reverted, but not rancid, soybean oil by using a high vacuum, countercurrent, steam deodorization technique previously described by Chang et al. (26). Flavor was isolated from 65 gallons of reverted soybean oil and characterized by gas liquid chromatography, infrared, mass, and nuclear magnetic resonance spectrometries. Short chain organic acids were found to be responsible for much of the reversion flavor. Twenty-six were identified by removing them from the total reversion flavor by sodium carbonate extraction followed by the separation of their methyl esters by gas chromatography. The nonacidic fraction of reversion flavor consisted of the green-beany flavor notes and was found to consist of aldehydes, enals, dienals, ketones, alcohols, lactones, 2-pentyl furan, several aromatics and hydrocarbons.

Later studies of 2-pentyl furan (44,45) have shown it is one of the compounds responsible for reversion flavor. When added at 5 ppm to other vegetable oils, it will cause them to have the characteristic soybean oil reversion flavor. However, it is believed that 2-pentyl furan is formed from the oxidation of linoleic acid. This led Ho et al. (46) to theorize that *cis* and *trans* 2-(1-pentenyl) furans may be responsible for reversion flavor and would be formed from slightly oxidized linolenic. Likewise, Smagula et al. (47) suggested that *cis* and *trans* 2-(2-pentenyl) furans may also be produced by a similar oxidation pathway. These compounds have been synthesized (45,47) and found to contribute reversion flavor notes to sunflower seed oil when added at levels of a few parts per million. Recently, Smagula et al. (48) reported the isolation and identification of 2(*cis* and *trans* -1- pentenyl) furans as being responsible for the reversion flavor of soybean oil. The 2(*cis* and *trans* 2-pentenyl) furans have not been identified in reversion flavor, but their flavor characteristics suggest they may be present. A similar flavor note has been associated with 5(pentenyl)-2-furaldehyde which has been postulated to arise from the 9-hydroperoxide of linolenic acid. It has been found in oxidized soy phospholipids (49), but its contribution to the flavor of soybean protein or soybean oil has not been ascertained.

Two recent reviews (50,51) have covered the flavor components isolated and identified from soybean products other than oil. Many of the compounds are the same except for the sulfur and nitrogen-containing compounds which are undoubtedly derived from other than oil sources. Nevertheless, many of the flavor components are lipid derived, and it has been stated (52) that the flavor problem of soybean products such as flakes, flours, concentrates, and isolates is connected with fat decomposition products from the small amounts of residual fats in these products.

From the flavor components that have been identified in reverted soybean oil, all are believed to have fatty acids as their precursors. Not all are derived from linolenic, and in fact several of the important components of reversion flavor are believed to be derived from linoleic. Therefore, reversion flavor must be caused by trace amounts of oxidation of its fatty acids at extremely low levels of hydroperoxide formation. Linolenic acid, which is the most unstable fatty acid in soybean oil, may initiate autoxidation and thus catalyze the oxidation of linoleic acid which is present in much larger quantities, thus producing a total reversion flavor that is not caused by any one compound but due to a combination of several flavor components. The methods given in Table II have been found to improve the flavor stability of soybean oil. Although none of the methods prevent reversion flavor alone, when several are used in combination with one another, a high quality salad oil can be manufactured from soybeans.

TABLE II

Methods to Improve the Flavor Stability of Soybean Oil

1. Steam whole beans to inactivate lipoxygenase.
2. Store oil in crude form.
3. Process crude oil with minimum amount of oxidation.
4. Use good quality whole beans that are not burnt, cracked, moldy, or field damaged.
5. Remove all phosphatides, soaps and metals during the manufacturing of a soybean salad oil.
6. Hydrogenate to low levels of linolenic acid.
7. Use a chelation agent to bind iron and copper that is not removed during processing.
8. Prevent oxidation by storing under nitrogen, in the absence of light, and at reduced temperatures.

REFERENCES

1. Encyclopedia Americana, Vol. 25, Rand McNally and Company, Washington, DC, 1963, p. 320.
2. Waggle, D.H., and C.W. Kolar, "Soy Protein and Human Nutrition," Academic Press, New York, 1979, p. 20.
3. Durkee, M.M., Ind. Eng. Chem. 28:898 (1936).
4. Sanders, J.H., First Conference on Flavor Stability of Soybean Oil, Chicago, IL, 1946.
5. Golumbic, C., A.I. Schepartz, and B.F. Daubert, Oil Soap 23:380 (1946).
6. Dutton, J.H., C.R. Lancaster, C.D. Evans, and J.C. Cowan, JAOCS 28:115 (1951).
7. Dutton, A.J. C.D. Evans, and J.C. Cowan, "Status of Research on the Flavor Problem of Soybean Oil at the Northern Regional Research Laboratories," AACC Trans, Vol. 11:116 (1953).
8. Schwab, A.W., H.A. Moser, P.M. Cooney, and C.D. Evans, JAOCS 27:314 (1950).
9. Dollear, F.G., P. Krauczunas, and K.S. Markley, Oil Soap 15:263 (1938).
10. Robinson, H.E., and H.C. Black, Ind. Eng. Chem. 37:217 (1945).
11. Bickford, W.G., Oil Soap 18:95 (1941).
12. Sims, R.J., JAOCS 29:347 (1952).
13. "Bailey's Industrial Oil and Fat Products," Edited by D. Severn, Interscience, 1964, p. 820.
14. Bodman, J.W., E.M. James and S.J. Rini, "Soybeans and Soybean Products," Edited by K.S. Markley, Interscience 1951, p. 704.
15. Armstrong, J.G., and W.D. McFarlane, Oil Soap 21:322 (1944).
16. Lemon, H.W., Lips, A., and W.H. White, Can. J. Res. 23F:295 (1945).
17. Lemon, H.W., Ibid. 25F:34 (1947).
18. Daubert, B.F., and L.J. Filer, Oil Soap 22:299 (1945).
19. Mattel, K.F., Oil Soap 22:213 (1945).
20. Thompson, S.W., W.G. Taylor, and A.R. Gudheim, Second Conference on Flavor Stability of Soybean Oil, Chicago, IL, October 1946.
21. Lips, H.J., H.W. Lemon, and G.A. Grant, Can. J. Res. 25F:44 (1947).
22. Goss, W.H., Oil Soap 23:241 (1946).
23. Cowan, J.C., JAOCS 300A-320A (1966).
24. Rice, R.D., Lipoxyidase Inactivation in The Whole Soybean and Its Effect on Extracted Oil and Meal Quality, Ph.D. Thesis, University of Illinois at Urbana-Champaign, IL, 1971.
25. Davies, W.L., and E. Gill, J. Soc. Chem. Ind. 55:141 (1936).
26. Chang, S.S., K.M. Brobst, H. Tai, and C.E. Ireland, JAOCS 38:671 (1961).
27. Chang, S.S., Y. Masuda, and B.D. Mookherjee, Chem. Ind. (London) 1023-1024 (1962).
28. Mattel, K.F., JAOCS 24:243 (1947).
29. Kochar, S.P., and M.L. Meara, A Review of The Role of Unsaponifiable Matter on the Flavor Stability of Edible Oils, Scientific and Technical Survey No. 98 from Leatherhead Food, R.A. Leatherhead, Surrey, England, 1977.
30. Chang, S.S., and F.A. Kummerow, JAOCS 30:251 (1953).
31. Johnson, O.C., S.S. Chang, and F.A. Kummerow, JAOCS 30:317 (1953).
32. Chang, S.S., and F.A. Kummerow, JAOCS 31:324 (1954).
33. Holm, U., K. Ekbom, and G. Wode, JAOCS, 34:606 (1957).
34. Evans, C.D., E.N. Frankel, P.M. Cooney, and H.A. Moser, JAOCS 37:452 (1960).
35. Smouse, T.H., J.E. Covey, and J.K. Maines, The Correlation of

Flavor Scores to Chemical Tests for a Series of Soybean Oils of Different Oxidative Histories, Paper 89, AOCS 45th Fall Meeting, Atlantic City, NJ, 1971.
36. Smouse, T.H., J.K. Maines, D.L. Minaldi, and R.R. Allen, Flavor Components of Soybean Oil and Chemical Test that are Utilized to Evaluate Present Quality and Predict Future Quality, Paper No. 155, The 11th World Congress of The International Society for Fat Research, Goteborg, Sweden, 1972.
37. Hoffmann, G., JAOCS 38:31 (1961).
38. Hoffmann, G., Ibid. 31:1 (1961).
39. Hoffman, G., Ibid. 39:439 (1962).
40. Smouse, T.H., Isolation and Identification of Chemical Components in Reversion Flavor of Soybean Oil, Dissertation Abstracts 26:7016 Order No. 66-1205 (1965).
41. Hill, F.D., and E.G. Hammond, JAOCS 42:1148 (1965).
42. Seals, R.G., and E.G. Hammond, Ibid. 43:401 (1966).
43. Smouse, T.H., and S.S. Chang, Ibid. 44:509 (1967).
44. Chang, S.S., T.H. Smouse, R.G. Krishnamurthy, B.D. Mookherjee, and R.B. Reddy, Chem. Ind. (London) 1926-1927 (1966).
45. Krishnamurthy, R.G., T.H. Smouse, B.D. Mookherjee, B.R. Reddy, and S.S. Chang, J. Food Sci. 32:372 (1967).
46. Ho, C.T., M.S. Smagula, and S.S. Chang, JAOCS 55:233 (1978).
47. Smagula, M.S., C.T. Ho, and S.S. Chang, JAOCS 56:516 (1979).
48. Smagula, M.S., C.T. Ho, and S.S. Chang, "Isolation and Identification of 2-Pentenyl Furans as Being Responsible for The Reversion Flavor of Soybean Oil," Paper No. 16, 39th Annual IFT Meeting in St. Louis, MO, 1979.
49. Sessa, D.J., J. Agric. Food Chem. 27:209 (1979).
50. Maga, J.A., Ibid. 21:864 (1973).
51. Cowan, J.C., J.J. Rackis, and W.J. Wolf, JAOCS 50:426A (1973).
52. Fujimaki, M., "Fundamental Investigation of Proteolytic Enzyme Application to Soybean Protein in Relation to Flavor," Final Research Report Conducted Under Grant Authorized by Public Law 480 for the USDA, Oct. 1964 – March 1969, Project No. UR-A11-(40)-8, Grant No. FG-Ja-111.

Esterification and Interesterification

N.O.V. SONNTAG, Technical Director, Southland Corporation Chemical Division,
First Continental Bank Building, Suite 400, 5801 Marvin D. Love Freeway,
Dallas, TX 75237

ABSTRACT

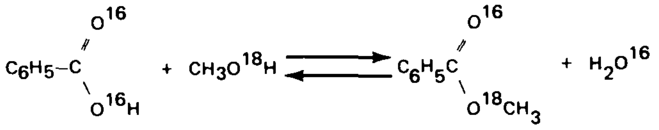
A versatile and large group of fatty acid esters are prepared from monohydroxy alcohols (C_1 to C_{22} members), glycols (ethylene and propylene glycols and others), etherglycols (many polyoxyethylene glycols), triols (glycerol and others), tetraols (pentaerythritol and others), polyglycerols, carbohydrate materials (sorbitol, sorbitan, sucrose and others). The two most important direct esterifications of fatty acids are those done with monohydroxy alcohols (methanol, butanol, etc.) and glycerol itself. Esterifications of these materials are carried out with or without the use of catalysts. For edible ester products, the choice of catalyst is determined by (a) rate of reaction promotion permitted by the use of the catalyst; (b) color of product obtained; (c) ease of removal of catalyst; (d) toxicity of catalyst, and perhaps; (e) other factors including promotion of acrolein formation from glycerol, loss by volatilization at high temperatures, inactivation above certain threshold temperatures, and catalyst corrosivity on the materials of construction of the esterifier. In certain instances the last factor may indeed be the paramount one in a particular catalyst choice for a direct esterification. Industrial production of methyl esters is principally by a process of interesterification called methanolysis. Polyols require conditions for complete esterification that are vigorous and severe. The two most important interesterification methods used in the fatty acid industry are the methanolysis of fats and oils for the production of methyl esters and the glycerolysis of fats and oils for the production of three kinds of so-called "monoglycerides," namely the 40%, 60% and 90% monoglycerides.

Since the original direct esterification in 1844 by Pelouze and Gelis of glycerol with butyric acid (1), both esterification and interesterification have been developed to the state where today they collectively constitute the most widely used methods for the production of fatty acid derivatives. Applications appear to be about equally divided among edible and nonedible industrial products.

The versatile and large group of fatty acid esters are prepared from monohydroxy alcohols (C_1 to C_{22} members), glycols (ethylene and propylene glycols and others), etherglycols (many polyoxyethylene glycols), triols (glycerol and others), tetraols (pentaerythritol and others), polyglycerols, carbohydrate materials (sorbitol, sorbitan, sucrose and others).

Esterification, according to all the textbooks, is the reverse reaction of hydrolysis, and in the case of glycerol it is the reverse reaction of fat splitting. For many years it was recognized that in the reaction the mechanistic course could correspond to one or both of two separate routes.

In short, does the water that is produced arise from the hydroxyl group of the acid or from the hydroxyl group of the alcohol? An examination of the course of the esterification of benzoic acid and methanol with radioactive oxygen atoms (2) proved out this point: the water is formed from the hydroxyl of the acid and the hydrogen of the alcohol:



$$C_6H_5-C(=O^{16})O^{16}H + CH_3O^{18}H \rightleftharpoons C_6H_5C(=O^{16})O^{18}CH_3 + H_2O^{16}$$

Perhaps the most important direct esterifications of fatty acids are those carried out with monohydroxy alcohols (methanol, butanol, etc.) and glycerol itself. By no means does this exhaust the list of important directly esterified products. Esterifications of these alcohols are carried out with or without the use of catalysts. For edible ester products, the choice of catalyst is determined by: (a) rate of reaction promotion permitted by the use of the catalyst; (b) color of product obtained and need, if any, to bleach or decolorize; (c) ease of removal of catalyst; (d) toxicity of catalyst; (e) promotion of acrolein formation (from acidic catalysts with glycerol); (f) loss of catalyst by volatilization above certain temperatures; (g) catalyst inactivation above certain threshold temperatures or in the presence of certain impurities; and (h) catalyst corrosivity on the materials of construction of the esterifier. In certain instances the last factor may indeed be paramount in a particular catalyst choice for a direct esterification.

Industrial production of methyl esters is principally by a process of interesterification called methanolysis. When fatty acids are converted to methyl esters directly, the acids