

Role of Lipids in Flavors

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The best known contribution of lipids to flavor is as precursors. The compounds formed may be readily volatile and have appreciable odors—*e.g.*, lower molecular weight aliphatic aldehydes, ketones, and fatty acids. The intact lipid or low volatile breakdown products of lipids contribute to flavor largely

through mouth stimulation. The taste of such compounds as well as their effects on the rheological properties of foods will be discussed. In addition, lipids may modify the flavor of other compounds, particularly those of low polarity.

The word flavor will be used to indicate the over-all sensual response to food taken into the mouth. This comprises odor, taste, and other mouth sensations. The term taste will be used in its narrow sense as largely a chemical tongue sensation producing one or more of the four sensations described as acid, bitter, sweet, or salty. Odor, aroma, and smell are synonymous terms and their use will be avoided.

Of the three main classes of foodstuffs, proteins, carbohydrates, and lipids, it might be thought that lipids are the most important as sources of flavor compounds but the least important for their own taste and flavor. The former statement could be debated since many important flavor compounds are derived from proteins and carbohydrates. The purpose of this paper is to show that not only are lipids important precursors of many volatile flavors, but they also contribute to other flavors.

Most lipids are hydrophobic, nonpolar materials which exist naturally as liquids (oils) or solids (fats), whereas most proteins and carbohydrates which are solid in the pure state are insoluble in organic solvents, but are soluble or dispersible in water. Lipids may be regarded as material of biological origin consisting of one or more of the following classes: free fatty acids, mono-, di-, and triglycerides, phospholipids, sterols, plasmalogens, and lipoproteins. Of these classes, all but the last can be distilled.

The first part of this paper will be devoted to a brief account of the role of lipids as flavor precursors. In most cases, the volatile flavor compounds are produced by changes occurring in free or esterified fatty acids which may contain double bonds or hydroxy or keto groups. Since the main purpose of this symposium is to consider the nonvolatile aspects of flavor, the greater part of this paper will be devoted to the role of lipids in taste; the effects of lipids in mouth feel; and the ways in which lipids modify the taste and flavor of other compounds in both homogeneous and heterogeneous systems.

ROLE OF LIPIDS AS FLAVOR PRECURSORS

Free fatty acids are generally formed by hydrolysis of the lipid through action of bacterial enzymes, and may contribute to desirable flavors, such as in cheese, or to undesirable flavors, such as in milk.

Aldehydes belonging to the three groups, C_{1-10} *n*-alkanals, the C_{3-12} *n*-2-alkanals, and the C_{5-12} *n*-2,4-alkadienals, are formed from oxidized unsaturated fatty acids, particularly oleic, linoleic, linolenic, and arachidonic, and are mainly

responsible for oxidized flavors described as tallowy, painty, oily, or cardboardy. Thus, methyl linoleate forms three monohydroperoxides which decompose to 2,4-decadienal, 2-octenal, and *n*-hexanal.

During the last 10 years, a number of other carbonyl compounds with intense and characteristic flavors such as *cis*-4-heptenal and *trans*-2,*cis*-6-nonadienal have been isolated from oxidized lipid materials. Since formation of these compounds from oleic, linoleic, linolenic, or arachidonic acids can be explained only through complex pathways, it has been suggested that these flavor compounds resulted from the oxidation of other C_{18} unsaturated fatty acids occurring in trace amounts.

Only a small number of ketones derived from oxidized lipid are important in flavors. 1-Octen-3-one is largely responsible for metallic flavor and 1-penten-3-one (Stark *et al.*, 1967) has an oily flavor. Methyl ketones (2-alkanones) play a major role in the flavor of Blue cheese and can be produced through the action of filamentous fungi such as *Penicillium sp.* and *Aspergillus sp.*, and molds on fatty acids. Methyl ketones may also be formed by the thermal decarboxylation of 3-ketoacids occurring in triglycerides.

Delta- and gamma-lactones play important roles in flavor, the former in dairy products such as butter, the latter in fruits such as peaches and apricots. Such lactones may be formed from the corresponding hydroxyalkanoic acids or the corresponding triglyceride by heat—*e.g.*, 130° C. for 1 hour in vacuum.

While saturated alcohols have been isolated from oxidized lipids, they play only a minor role in flavor. However, the unsaturated carbinol 1-octen-3-ol is an important flavor constituent of mushrooms and occurs in oxidized lipids, and 1-penten-3-ol isolated from milk fat and meat has an oily, grassy flavor.

Aliphatic hydrocarbons have been isolated from irradiated and oxidized lipids but generally have weak flavors, flavors which, in some cases, are due to mercaptans, or, as in our studies of the C_3 aliphatic hydrocarbons with unsaturation in the 1-position, to traces of 1-octen-3-ol. While amines are generally derived from proteins and amino acids, Lea (1957) has referred to a fishy flavor in evaporated milk caused by bacterial liberation of trimethylamine, probably from the lecithin. Many other flavor compounds in foods, although they are derived from nonlipid materials, are found predominantly in the lipid phase. This brief account of the flavor compounds derived from lipids is taken from the paper by Forss (1967) on the "Origin of Flavors in Lipids."

Possibly the first example of a sterol contributing to a

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flavor was reported recently (Patterson, 1968). The compound primarily responsible for the sweaty sex-odor of boar fat was identified as 5 α -androst-16-en-3-one.

TASTE OF LIPIDS

Lipids of low volatility are tasteless in terms of sour, sweet, bitter, and salty, partly because they are insoluble in water. 1-Octen-3-one, a compound responsible for a metallic flavor in many fatty foods, may be responsible for a fifth taste, the metallic taste discussed by Moncrieff (1964), which he attributed to the presence of inorganic salts of iron and copper. These metals often catalyze lipid breakdown and may be responsible for lipid oxidation in the mouth and the formation of 1-octen-3-one. Formic, acetic, and propionic acids taste acid and sour, but these characters decrease as the chain length increases. The peppery taste of Blue cheese has been attributed to butyric, hexanoic, and octanoic acids (Day, 1967). Because the lower fatty acids are volatile, it is probable that most taste measurements are really over-all flavor measurements involving olfaction and mouth feel as well. Fatty acids of low volatility (above C₁₀) do not taste acid or sour, nor do they have much flavor. Their flavor has been described as candlelike. Glycerol results from hydrolysis of lipids and has a sweet taste.

Pangborn (1963) used a highly trained panel to establish the concentration of lactic, tartaric, and acetic acids equivalent in sourness to that of citric acid at threshold and suprathreshold concentrations. There was no relation between pH, total acidity, and relative sourness. The taste intensity was not a constant but was materially affected by the absolute concentration chosen for comparison. Pangborn recognized that acetic acid was the only acid of those tested having an odor, and that more reliable data would have been obtained if the nose had been blocked off during evaluation. The buffering action of the saliva must also affect taste and flavor threshold measurements of acids.

ORAL PERCEPTION APART FROM TASTE

Sense organs in the mouth apart from those responsible for taste affect our appreciation of food. These organs respond to pain, temperature, texture, and what might be regarded as chemical hotness and coldness. For example, menthol has a cooling effect in the mouth, whereas certain spices produce the opposite effect. Just how far we regard these sensations as part of the flavor of a food is a matter of definition. For example, Kramer (1968) acknowledges that mouth feel is regarded by many people as a contribution to flavor but suggests a more restrictive definition. He feels that such attributes of mouth feel as chewiness, fibrousness, grittiness, mealiness, stickiness, and oiliness are essentially sensed by the muscular forces applied in the process of mastication. Therefore, they should be considered part of texture and only such sensations as heat, cold, or pain should be included in the flavor category. The author has adopted the wider definition of mouth feel as part of flavor.

Perhaps the only role of lipids in mouth feel is in their effect on texture. This is an important factor, but an attractive property of butter is its pleasant cooling effect on the tongue, while the attractiveness of dairy cream is largely due to the globular structure of the fat particles. The major flavor sensation of milk is ascribed to its tactile effect, and its pleasant mouth feel is attributed to its

emulsion and colloidal structure. The mixed triglycerides which make up 98 to 99% of milk fats are quite bland in taste but impart smoothness and palatability to fat-containing dairy products (Kinsella *et al.*, 1967). The swallowing of oils as such is a nauseating experience.

The important role of lipids in texture is recognized in the food industry. Boekenooogen and Taylor (1966) of the Unilever Research Laboratorium at Vlaardingen, The Netherlands, went so far as to say, "Texture happens to be the most fascinating aspect of fat research. In the long term, it is a matter of understanding crystal nucleation, ripening and growth of crystals under controlled conditions, regenerative (thixotropic) and unregenerative forces, which operate between fat crystals and determine the physical characteristics of them *en masse*, and the rheological properties of mixed crystalline/liquid fat systems which are subject to mixed regenerative and unregenerative forces." They commented further on the broad role of lipids in mouth feel. "For domestic use of fats, the governing factors are an ability to spread and a favorable oral response in terms of quickness in melting, cooling on melting, and thinness of the melted material on the tongue. Research has been directed, on the one hand, towards the development of instrumental analogues which give precision to these factors and enables strict comparison of the experimental material to be made, and on the other, towards modification in plant and processes which lead to more desirable properties."

Butter is composed of a continuous phase of butterfat enclosing drops of aqueous solution and globules of lipid material. Crystals or agglomerates of solid fatty substances may also be present. Plastic properties of butter and other fat products such as margarine, lard, and shortening are the result of the presence of a three dimensional network of fat crystals. In addition to the important effect of the solid-liquid fat ratio in these products, major changes in consistency may be brought about by mechanical treatment (Matz, 1962). The structure of continuously-made butter resembled that of margarine and contained fat crystals of larger size and more irregular shape than those in conventional butter (deMan and Wood, 1959).

The solid fat content of plastic fats is very dependent on temperature, but at any particular temperature the solid fat content will depend on the temperature history of the product (Vasic and deMan, 1965). Between 40° and -40° C., milk fat is a mixture of solid (crystalline) and liquid constituents, the ratio of which may be determined by measuring the plasticity of the fat (Vasic and deMan, 1966).

The chemical composition of the lipid is a major factor in the rheological behavior of high fat foods. Thus, in spite of much research, butter has poor spreadability compared with margarines. However, Gerson and Escher (1966) reported that the addition of as little as 1% butterfat monoglycerides to cream prior to churning improved the spreadability of the resulting butter by approximately 30%. Similarly, the addition of 0.15% monoglyceride to Neufchatel and 0.20% monoglyceride to cream cheese imparted a smooth, spreadable body to the cheese. The softness of the finished cheese varied mostly with the degree of unsaturation of the added monoglycerides (Miller *et al.*, 1965).

Through judicious choice of processing procedures, the crystalline characteristics of food products can be controlled to obtain the desired performance in specific

applications. Procedures such as blending, hydrogenation, interesterification, and fractionation markedly alter the molecular composition and configuration, while rotating and tempering practices directly affect the crystal structure of the product (Hoerr, 1967).

Free fatty acids may affect the flavor indirectly through changes in texture. King *et al.* (1962) have shown that small concentrations of linoleic and linolenic acids rapidly reduce the solubility of cod actomyosin, which suggests that the accumulation of free fatty acids occurring in the muscle of fish during frozen storage may perhaps be one cause of the denaturation that spoils its texture.

Oily flavor in sweet cream butter, though similar to the defect of stored acid butter, develops under very different conditions. It is characteristically a defect of fresh butter, usually appearing within a few days of manufacture. It may occur in the output of a large factory spasmodically or it may affect a large proportion of the butter with varying intensity over a long period (Pont and Rogers, 1967). It is not clear whether the defect is due to volatile organic compounds or whether it is an example of mouth feel.

The dryness in high quality ice cream is due primarily to the extent and kind of agglomeration of finely dispersed fat globules. Apart from conditions of stirring in the freezer, a proper selection of emulsifier is one of the main factors contributing to this agglomeration (Ludwig and Gakenheimer, 1967).

The short plastic range of cocoa butter contributes to the good handling properties of chocolate at room temperature and the prompt liquefaction of the substance in the mouth. This property is due not to the restricted melting range of the fat (32–5° C.) but to a special crystal form assumed by the glycerides. Texture of the finished chocolate is highly dependent upon the condition under which solidification occurs. Improper storage conditions lead to the development of "bloom," a texture defect characterized by crumbly or gritty structure (Matz, 1962) and surface whitening.

EFFECTS OF LIPIDS ON FLAVOR PERCEPTION

Lipids modify the taste and flavor of other compounds in foods. They also influence the physical state of the food, which affects the movement of compounds to the taste and odor receptors. Taste and odor perception might be expected to be more rapid from liquid foods than solid foods.

The sense of taste involves the solution of the material in water. The presence of lipids will modify taste sensation. Many workers have compared the taste of various compounds in water with those in oils. Mackey (1958) observed that the taste of caffeine, quinine, and saccharin was more easily detected in water than in mineral oil.

The physical nature of the medium in which compounds are dispersed affects their perceptible flavor concentration. Generally, flavor potential is much stronger in an aqueous (lipophobic) than in an oily (lipophilic) medium. This may also depend on the polarity of the particular flavor compounds (Kinsella *et al.*, 1967). Thus, substances of low polarity (long chain fatty acids) have low flavor thresholds in aqueous medium and high thresholds in oil, whereas more polar substances (short chain fatty acids) have lower flavor thresholds in oils and higher thresholds in water. Volatility of the stimulus is essential for olfactory perception. Bonding to solvent molecules

apparently tends to reduce volatilization of polar components from water in much the same manner that oils "fix" nonpolar odorants. This thesis is supported by the data shown in Figure 1, which shows graphs of the flavor thresholds of fatty acids in water and a vegetable oil. The high threshold value for acetic acid may be due to its strong tendency to form hydrogen bonds with water and to dimerize.

The situation is simpler with the flavor thresholds of aliphatic aldehydes (*n*-alkanals) in which the molecular weight has less effect on polarity. The data of Lea and Swoboda (1958) for *n*-alkanals show that flavor thresholds are much lower in water than in paraffin or vegetable oil (Figure 2), and that thresholds were similar for the higher aldehydes (C_{4-10}) in vegetable and paraffin oils. The data of Meijboom (1964) for these aldehydes in paraffin oil show great variation in flavor thresholds between aldehydes differing by one carbon atom, such as the C_3 , C_4 , and C_5 *n*-alkanals. Similarly, great differences in flavor thresholds were observed by Lillard *et al.* (1962) for the C_4 , C_5 , and C_8 *n*-alkanals in milk. The gross amount of lipid in a food influences both its taste and flavor. When an oil is taken into the mouth, mixing of the oil with

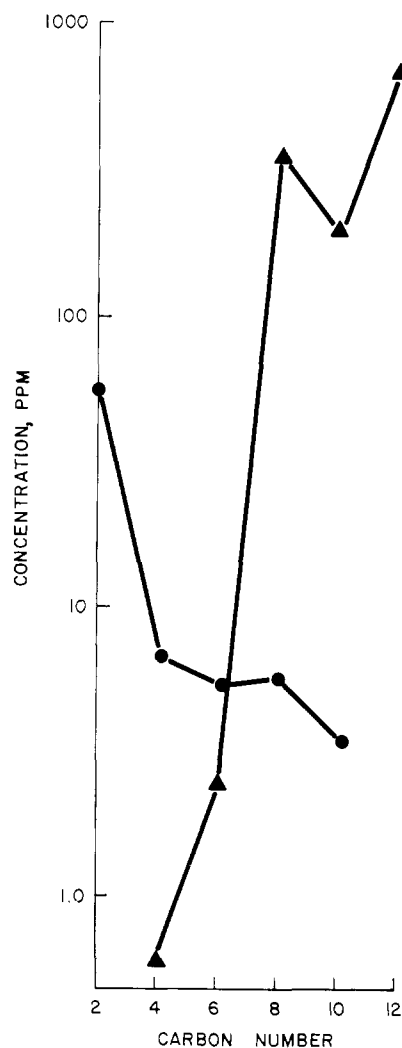


Figure 1. Flavor thresholds of fatty acids

▲—▲ in vegetable oil (Feron & Govignon, 1961)
●—● in water (Patton, 1964)

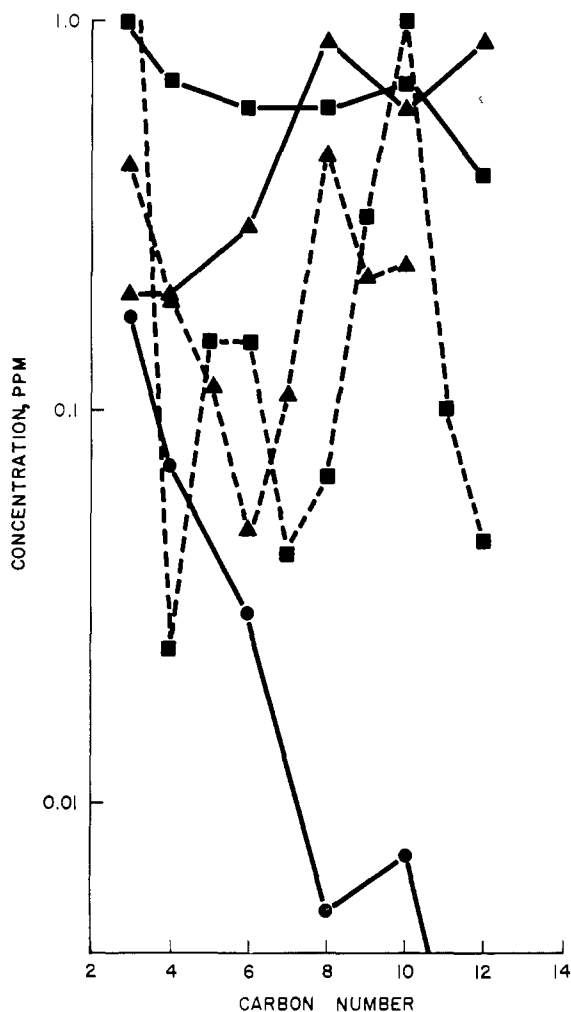
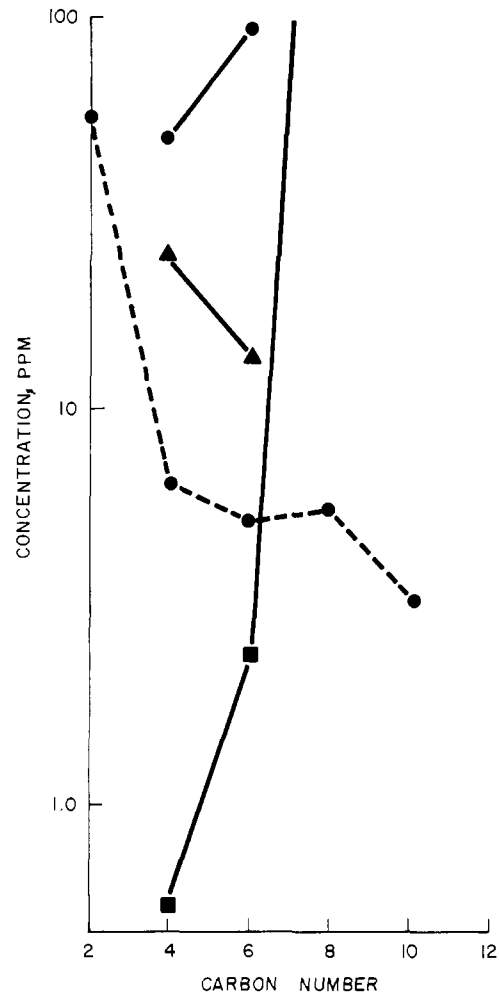


Figure 3. Flavor thresholds of fatty acids

- in butter (McDaniel *et al.*, 1969)
- in vegetable oil (Feron and Govignon, 1961)
- ▲—▲ in milk (Patton, 1964)
- in water (Patton, 1964)



saliva results in a distribution of any flavor compounds present between the oil and aqueous saliva. The coating of the tongue with the oil may decrease or prevent perception of water-soluble taste compounds. Many foods consist of emulsions of either oil in water or water in oil, and often the globules are coated with a membrane which affects further the distribution of flavor compounds within the food. The distribution of added flavor compounds in such media is difficult to measure and one may be concerned about the validity of threshold measurements based on the addition of single chemical compounds to such heterogeneous media.

Butyric and hexanoic acids, which have a profound effect on the flavor of many foods, are more readily perceived in vegetable oil than in water (Figure 3). Since both cases deal with homogeneous systems, supposedly bonding of the fatty acids to the solvent molecules is stronger in the aqueous system. Since butter and milk are emulsions of oil and water, intermediate flavor threshold values might be anticipated. This was not so, partly because of the uneven distribution of the free fatty acids between the oil and water, but mainly because much of the free fatty acids in the milk and butter are present as their salts. The importance of salt formation is shown (Figure 2) by the threshold values of aldehydes (which do not form salts), which in milk are intermediate between those for water and oils, using the data of Lea and Swoboda (1958).

The differences between flavor thresholds of the higher fatty acids in vegetable oil and butter are less marked than for butyric and hexanoic acids (Figure 4). This may be

due to the fact that most of the higher fatty acids in butter are in the fat phase of a water in oil emulsion. The effect of the partition between oil and water would be expected to be more marked in milk, which is an oil in water emulsion. An interesting effect is observed with the flavor thresholds of decanoic and dodecanoic acids in butter, where the values decrease. This is partly due to salt or soap formation where the soap has a lower flavor threshold than the corresponding fatty acid. These acids taste soapy in butter (McDaniel *et al.*, 1969).

Kintner and Day (1965) found that most of the free fatty acids of milk were distributed in the fat and the fat globule membrane. Milk serum free of lipid material contained less than 10% of the total free fatty acids. Heating of milk had a pronounced effect on the quantity of free fatty acid in the serum; extended heat treatments resulted in decrease of total free fatty acids. On the other hand, induced lipolysis caused a marked increase in free fatty acids. In general, the free fatty acid composition of the milk, regardless of treatment, was comparable to the fatty acid composition of milk glycerides. At the normal pH of milk, the small quantity of fatty acid in the serum exists in the salt-to-free-acid ratio of approximately 60 to 1 according to the Henderson-Hasselbalch equation for an ideal aqueous phase. Hence, in normal flavored milk, although the total quantities of free acids are large, the quantity available in the serum is quite small. The remainder is in the fat phase or present as salts or soaps. The fat globule membrane may serve as a barrier which affects the equilibrium of the free acids and salts between

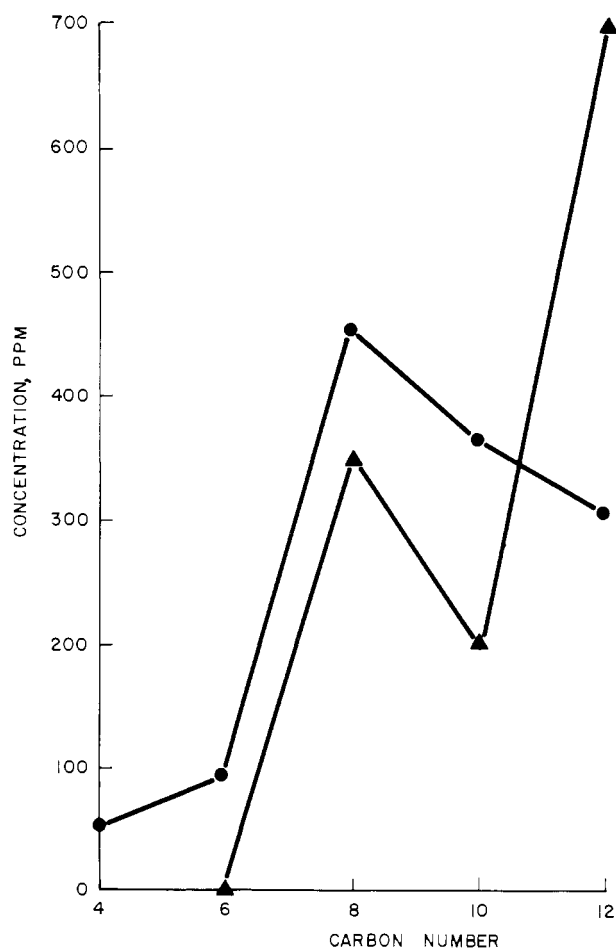


Figure 4. Flavor thresholds of fatty acids

▲—▲ in vegetable oil (Feron and Govignon, 1961)
●—● in butter (McDaniel *et al.*, 1969)

the serum and lipid phases. In the event of lipolysis, which must occur at the interface, the free fatty acids might be expected to redistribute predominantly to the aqueous phase, where they eventually exceed the flavor threshold of rancidity. This hypothesis is supported by the observed effect on flavor when the pH of milk in a normal sample and in a second sample with induced lipolysis was adjusted to the pK_a of the fatty acids. The pH adjustment caused an immediate intensification of rancid odor in the lipolytic sample, whereas no odor change was noticeable in the normal milk. The short chain acids (butyric and hexanoic) were found to partition more to the aqueous phase where the flavor threshold is higher and their flavor is diminished due to salt formation, whereas the longer chain acids partitioned more to the lipid phase where their flavor thresholds are higher. This would account for the relatively large amounts of unesterified fatty acids in normal milk without a noticeable rancid flavor.

On the other hand, when Scanlan *et al.* (1965) added to fresh milk the fatty acids in the quantities reported liberated by lipase, a flavor similar to the flavor of rancid milk was produced. When samples of milk with groups of fatty acids and fatty acids singly omitted from the fatty acid mixture were evaluated for rancidity by a flavor panel, the results indicated that the even-numbered fatty acids from butyric to dodecanoic accounted for the fatty acid contribution to rancid flavor and that the fatty acids above dodecanoic contributed little if any to the rancid flavor. No single fatty acid in the butyric-dodecanoic

acid series exerted a predominating influence as a contributor to rancid flavor.

Quantitative analysis of the volatile compounds in a complex material such as cheese may provide information of very limited flavor value. Both the distribution of the compounds between the fatty and water phases and the relative amounts that are free or chemically bound such as, free fatty acids or salts, affect the flavor. Thus when Langler *et al.* (1967) added a synthetic mixture containing the lower free fatty acids and other volatile components found in Swiss cheese to a synthetic cheese base, the product had a vinegary, acidic flavor. A second flavor mixture was prepared in which the fatty acid concentrations were reduced to one-half the value found in the cheese. This reduced the harshness of the acid but the sample still lacked the desirable Swiss flavor. The pH of this sample was 4.5, which was considerably lower than that found in natural cheese. When the pH of the second sample was adjusted with 2*N* alkali to 5.6 and the flavor re-evaluated, the sample was judged to have a typical Swiss cheese-like character and resembled the flavor of natural cheese.

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