The Flavors of Dairy Fats — A Review[1]

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Abstract

Literature for the three years to August 1970 dealing with the role of dairy lipids in flavors is reviewed. Subjects covered include reviews and conferences, techniques, flavor chemicals in heterogeneous media, desirable flavors and off flavors. All dairy products whose flavor is affected by or derived from lipids are included. These include low fat products such as skim milk and fermented products such as cheese.

Introduction

In June 1968, five papers were presented at a symposium on the "Flavor of Milk and Dairy Products." One dealt with the flavor of butter, Cheddar cheese and several low fat dairy products (1). The period since then is covered in this paper, with emphasis on flavors derived from milk lipids and those occurring in dairy products containing lipids. Actually, this definition includes almost all dairy flavors because flavors derived from lipids occur in oxidized skim milk (fat content below 0.1%) and many flavors derived from non lipids, e.g., from reactions between amino acids and sugars, occur in dairy products high in fat, such as heated butter (99% fat on a dry salt-free basis). Papers on the role of microorganisms in producing flavors are illustrative and were not reviewed extensively. Tastes such as bitter were not considerd.

Topics will be discussed under the following headings: Reviews and Conferences; Techniques; Flavor Chemicals in Heterogeneous Media; Desirable Flavors (milk and cream, butter, fermented products and cheese); and Off Flavors (nonoxidative and oxidative).

Reviews and Conferences

Several excellent reviews have appeared during the last three years. One, "The Flavor Chemistry of Milk Lipids" from Cornell University (2, 3), deals mainly with off flavors. It contains 11 tables and 5 figures and presents a great deal of information in a concise and useful form. A paper (4) from the National Dairying Research Centre in Ireland covers research during the last 30 years on normal and off flavors in milk. Much of the information relates to the production and marketing of liquid milk.

The presence of δ-lactones in dairy products and their roles in both desirable and undesirable flavors has been discussed in the dairy literature for almost 20 years. Much of this information is included in a review from The Pennsylvania State University on the occurrence and biochemical origin of aliphatic lactones in milk fat (5).

The role of lipids, particularly dairy lipids, in flavors was reviewed during a 2½ day "Symposium on the Importance of Nonvolatile Compounds in Flavor." One paper was entitled "Role of Lipids in Flavors." While the best known contribution of lipids to flavors is as precursors of volatile components, other roles are important. These include their actual taste, their effects on oral perception apart from taste, and their effects on the perception of flavor chemicals (6). Other papers dealing with dairy flavors presented at this symposium are discussed later.

One of the seven sessions at the New Zealand Dairy Science Association Conference in June 1969 was devoted to flavor chemistry. Titles of papers were "Cheddar Cheese Flavor Evaluation," "A case(in) History" and "Quantitative Flavour Evaluation" (7).

Techniques

Better methods for characterizing volatile flavor compounds are needed, particularly for compounds with potent flavors occurring at very low levels. Also, there is a desire for more rapid analyses on smaller amounts of materials. Isolation of typical Cheddar cheese flavor is a difficult task, possibly because of the importance of trace amounts of unstable sulfur compounds. Two recent methods permit the rapid analysis of volatile compounds from very small amounts of cheese but could be applied equally well to any material with an appreciable fat content. In one method (8) acetonitrile was used to extract flavor components from cheese and milk fat. Unique advantages of this method are that it does not extract fat and the first drops of the extract are sufficiently concentrated to permit gas chromatography without solvent evaporation. In the other method (9), oil obtained by centrifugation of cheese at room temperature was injected directly into a gas chromatograph. The method required only 1–3 g of cheese, took about 15 min and gave semiquantitative data. Furthermore, there seemed to be less chance for contamination or for any physical or chemical change to occur in the flavor mixture. This may be so but other changes might occur in the heated inlet of the gas chromatograph.

The loss of flavor components during gas chromatography was reported in a joint Canadian-English study (10). A Cheddar cheese distillate lost its typical character on passage through either Carbowax or Porapak Q columns. Of those tested, the only columns from which material with a cheese-like aroma could be recovered were packed with Teflon or a silanized support coated with Apiezon.

Some new derivatives of volatile flavor compounds were reported. Ethylenethioketal derivatives of methyl ketones and ethylenethioacetal derivatives of alkanals isolated from sprayed dried Cheddar cheese were analyzed by gas chromatography (11). Derivatization of aldehydes stops the oxidation which may occur readily with the free compounds.

In solid foods the flavor of surface material is often different from that of the interior. Thin layer chromatography on silica gel was used to separate lipids obtained from three zones (crust, internal yellow zone and internal white zone) of Camembert cheese. Five fractions were obtained: tri-, di- and mono-glycerides, free fatty acids and polar lipids. The flavor of these zones and fractions was studied (12).

Free fatty acids, and to a lesser extent lactones, do not separate well on common gas chromatographic stationary phases. Furthermore, the removal of these acidic materials from a flavor concentrate creates a

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simpler picture of the remaining volatile compounds. A method for separating volatile compound from steam-deodorized milk fat into lactones, free fatty acids and nonacidic compounds was based on their solubility in sodium carbonate solutions. The technique was applied to the volatile compounds obtained from stale milk fat (13).

Fatty acids above hexanoic are usually converted to methyl esters prior to gas chromatography. The preparation of milk fat methyl esters by alcoholysis in an essentially nonalcoholic solution involved the treatment of a 10% solution of milk fat in light petroleum with either 2 N methanolic potassium hydroxide or sodium methoxide at room temperature. Methyl esters of glyceride fatty acids were formed almost instantaneously, and the solution could be analyzed by gas chromatography at once (14).

Flavor compounds boiling below 100 C usually require special methods for their isolation and identification. Such methods were described (15).

Flavor Chemicals in Heterogeneous Media

Many new flavor chemicals have been isolated from dairy products during the last two years and will be discussed later. Of great importance is recent research on the effects on flavor of such factors as pH and the distribution of flavor chemicals in heterogeneous systems. The work on fatty acids is a good example.

Ten years ago a symposium on lipid flavors might have been dominated by discussions on the roles of alkanals, 2-alkenals and alkadienals. During the last five years the importance of fatty acids has been recognized. Formerly, fatty acids were regarded as being important primarily for their role in off flavors caused by bacterial lipases (hydrolytic rancidity). Now fatty acids are being appreciated for their part in desirable dairy flavors, not only in those products formed by microorganisms, such as cheese and yogurt, but also in nonfermented products such as sweet cream butter and milk.

Work at Oregon State University has done much to clarify the role of fatty acids in such foods. It has been shown that in the nonhomogeneous conditions existing in most dairy products, the distribution of the fatty acid between fat, membrane and aqueous phase has a marked effect on the flavor. This distribution is very dependent on the pH of the aqueous phase (16). The rancid flavor of whole milk was shown to be due to acids from butyric to lauric but no single acid in this series was of predominant importance. In butter the additive flavor interaction of certain acids was demonstrated. When average flavor threshold values of fatty acids were related to the amounts present, it was found that butyric and caproic acid contributed much more to butter flavor than did caprylic acid although the last was present in considerably greater quantity. Duplication of Blue or Swiss cheese flavor based on analytical data was achieved only when the level of short chain acids was reduced one third to one half and acids with chain lengths longer than caprylic acid were completely omitted. Because analytical methods do not discriminate between the various forms in which the anion may appear (i.e., protonated, dissociated, insoluble salt) and because the flavors of these forms vary so widely, it is impossible to gain much more than a qualitative appreciation of their role. Even knowing the actual distribution of a fatty acid between the serum, the membrane and the fat globule in milk may not be sufficient to determine its flavor contribution.

Any compound affected by pH will behave in a similar way. Such classes of compounds occurring in dairy products or derived from them include lactones, phenols and pyrazines. The behavior of carbonyl compounds such as 2-alkanones and aliphatic aldehydes is more easily predicted (6). In either case, quantitative data should be treated with caution.

Desirable Flavors

Milk and Cream

While smelling and tasting are probably the most rapid and definitive ways of evaluating milk, there has always been a desire for objective tests. A Swedish paper on the evaluation of the odor of milk and milk products discusses the chemical basis of odor and describes the use of gas chromatography for such evaluations (17). Another objective test for determining the quality of raw refrigerated milks involved the addition of hydrogen peroxide and the later addition of potassium iodide. There was good agreement between bacteriological and hydrogen peroxide tests, and between hydrogen peroxide tests and flavor tests (18).

To obtain a better understanding of the contribution of milk fat to the flavor of milk, a series of beverages containing 1–3% milk fat or vegetable fat, was prepared with skim milk. Untreated milk fat in whole milk concentrate and partially deodorized milk fat were the only fats which improved the flavor of skim milk. The data indicated that the desirable flavor characteristics of milk fat are attributable partly to nonvolatile compounds which are probably unique to milk fat (19, 20).

In Russia, cows receiving large amounts of clover haylage had milk with better flavor (21). On the other hand, studies in Finland on the production of milk from an odorless, protein-free (urea) diet showed that the taste and smell of this so-called "zero milk" was very similar to that of normal milk. There were differences in some trace constituents. Total lactones, particularly odd carbon number δ-lactones and *trans*-4-methyl-δ-hexalactone, were higher than in normal milk due to increased fatty acid biosynthesis in the rumen, but indole and skatole contents were lower, showing that these compounds originate from the fodder (22).

Free fatty acids, δ-lactones and methyl ketones are being increasingly implicated in dairy flavors where the product has been heated. Because of their relatively high flavor thresholds, methyl ketones only play a secondary flavor role. The following compounds were formed by heating milk at 82 C for 30 min followed by heating at 146 C for 4 sec: $C_{3,4,5,7,9,11,13}$ methyl ketones, the $C_{8,10,12}$ δ-lactones, benzaldehyde, furfural, phenylacetaldehyde, vanillin, 1-octen-3-ol, 1-heptanol, 2-butoxyethanol, maltol, acetophenone, benzonitrile, benzothiazole, and diacetyl. Diacetyl appeared to be a key flavor component. The amount of diacetyl in raw milk was 5 ppb, while the amount in the heated milk was 38 ppb, which is above the average flavor threshold for diacetyl in milk. It was suggested that diacetyl contributes to the rich or heated note in the flavor of heated milk (23).

Concentrations of free fatty acids, γ- and δ-lactones, and methyl ketones in sterile concentrated milk were determined during storage. Free fatty acids increased, but contrary to previous reports, the C_{10} and C_{12}-δ-lactones decreased at all storage temperatures. γ-

Dodecalactone increased at all storage temperatures. The $C_{7,9,11,13}$ methyl ketones increased but were below flavor thresholds (24).

In another investigation of stored, sterilized, concentrated milk, in addition to those compounds already mentioned, 2-furfural, 2-furfurol, hydroxymethylfurfural, and *o*-aminoacetophenone were isolated. Heat degradation of thiamine was studied as a possible source of flavor compounds such as benzothiazole. Volatile compounds identified included hydrogen sulfide, 2-methyl furan, 2-methyl thiophene and possibly a dihydro-2-methyl thiophene (25). Thiamine occurs in dairy products and thiophenes might therefore be expected to occur in them.

β-Keto acids, the precursors of methyl ketones, were measured in the fat of cultured cream, cream, cows' milk, goats' milk, ewes' milk and ewes' colostral (26).

Flavor threshold values may indicate the importance of individual compounds in a particular flavor. Three lots of concentrated milk (ultra high temperature, high temperature short time, and conventionally sterilized) were stored at 42 C and 37 C for eight months. Of the many volatile compounds measured, only methyl sulfide occurred at a concentration greater than its flavor threshold value (27). In similar experiments in another laboratory, after 13 weeks storage at 27 C methyl ketones and *o*-aminoacetophenone were present in sufficient quantities to contribute significantly to the flavor of concentrated milk (28).

Further evidence of the marginal flavor role of methyl ketones in dairy products not formed by enzymes is reported. A method for determining the concentration of the C_5 through C_{15} odd carbon-numbered methyl ketones in fluid milks was based on the free C_{13} methyl ketone content and the methyl ketone potential remaining in the fat phase of the products. Application of the procedure to samples of commercial evaporated milk led to the conclusion that the role of methyl ketones in the off flavor of this product was dependent on the total methyl ketone potential of the milk fat, composition of the methyl ketone potential (especially the 2-heptanone potential), and the degree of hydrolysis and decarboxylation of β-keto acids as determined by heat treatment and storage conditions (29).

Cooked flavor is a serious flavor defect in whipping cream. Tests on whipping cream have been carried out at Wolfpassung, Austria over a 10-year period. Tests for the period 1965–68 showed an improvement in flavor and a decrease in samples with a mild cooked flavor. Flat taste was the predominant flavor defect (30). U.S. Patent 3,468,671 describes a process for the production of a whippable, sterilized cream with no cooked flavor defect (31).

Butter

Butter is a water (below 16%) in oil emulsion of milk fat. Small amounts of protein and lactose are present and sodium chloride may have been added. Butter oil, the product of commerce, is mainly the triglyceride part of milk fat. Ghee is a type of dehydrated butter prepared by removal of the water usually at atmospheric pressure. Changes occurring in the fat, protein and lactose during heating are responsible for the development of the characteristic flavor of ghee. Likewise, sweet cream butter may be dehydrated at atmospheric pressure to produce certain desirable flavors.

The neutralization of cream prior to buttermaking deadens the flavor but improves the keeping quality of the butter. If the copper content can be kept low, neutralization may be avoided. Work from Australia supports this hypothesis. Butter made from unneutralized factory-separated cream was investigated under commercial conditions. The butter had serum pH values in the range 6.46 to 6.63, had very good keeping quality and had the advantage over neutralized cream butter of a much brighter flavor. All butter had copper contents of less than 0.05 ppm (32).

Chilling milk to 6 C for some hours before separation prevented subsequent development of cooked flavor and reduced the copper contents of cream and butter due to increased passage of copper and a labile constituent from the fat globule membrane into the skim milk (33).

One way of assessing the importance of various flavor compounds in a particular food is to determine the actual amounts present. The neutral, volatile fraction of fresh sweet cream butter was analyzed semiquantitatively by capillary gas liquid chromatography. Butter concentrations for 49 compounds ranged from approximately 5 ppm for δ-dodecalactone to 5×10^{-4} ppm for benzene. Compounds included odd number methyl ketones, alkanals, δ-lactones, γ-lactones, diacetyl, ethyl esters and aromatic compounds (34). The presence of many compounds below their flavor threshold values indicates their synergistic role in butter flavor. Other experiments support this thesis.

A new approach to the determination of the contribution of individual fatty acids (C_4-C_{12} even-numbered) to the flavor of sweet cream butter was carried out at Oregon State University. This approach can be applied only to compounds present in subthreshold amounts. The amount of each individual fatty acid which had to be added to butter to reach the threshold value of that acid was determined. This value was then combined with the endogenous level of the acid in the butter to give a total threshold value. The syngergistic flavor interaction of free fatty acids was also studied. Butyric acid had the lowest threshold value. A soapy after taste was observed with decanoic and dodecanoic acids. Evidence showed that fatty acids at subthreshold concentration interact to contribute to desirable butter flavor. Butters with total levels of fatty acids above threshold had inferior flavors (35).

Similar conclusions were reached in another study at the same university. Taste thresholds of 31 volatile compounds found in butter were measured in deodorized butter oil and 7 were measured in fresh butter. Among the thresholds measured, several were lower than their reported concentration in butter, and thus might contribute to sweet cream butter flavor. Compounds that fell into this group were diacetyl, butyric and caproic acids, hexanal, acetaldehyde, methyl sulfide and possibly δ-decalactone. Levels of 2-heptanone and 2-nonanone were high enough to influence flavor due to synergistic interaction. It was concluded that the aroma and flavor of fresh cream butter depend on a concentration balance of low threshold compounds (plus possibly some volatiles not as yet identified in butter), with little contribution to flavor by high threshold compounds. Synergistic interactions exhibited by mixtures probably play an important role in giving butter its unique flavor and aroma (36). Unfortunately, only seven of 31 volatile compounds studied had their flavor thresholds measured in butter. As already indicated, compounds can have quite different flavors and flavor thresholds in butter and butter oil.

Three types of precursors of carbonyl compounds (bound aldehydes, total ketoglycerides and β-ketoglycerides) were measured in milk fat from a cow fed normally and from another on a synthetic diet ("zero milk"). The values for the latter were normal in all cases (37). Bound aldehydes have high molecular weights and contribute little to flavor. β-Ketoglycerides are the precursors of methyl ketones. Twenty-eight carbonyl compounds were isolated from the volatiles of butter fat obtained from "zero milk" and 37 from butter fat obtained from normally fed cows. Missing in the synthetic butter fat were 10 2-alkenals. The former butter fat contained one carbonyl compound not present in the latter. Both butter fats contained a class of carbonyl compounds not previously reported (38). In spite of the differences, the milks had similar flavors (22).

In 1966 three lactones with a double bond outside the ring were reported by chemists from Unilevers to be in butter fat. They were δ-9-tetradecenolactone, δ-9-dodecenolactone and γ-6-dodecenolactone (39). Workers in Japan prepared the lactones of the $C_{5,6,8,10,12}$ 5-hydroxy-2-alkenoic acids as well as 5-hydroxy-8-methyl-2-nonenoic acid, 6-ethyl-5-hydroxy-2-octenoic acid, 5-hydroxy-5,6,6-trimethyl-2-heptenoic acid, 5-hydroxy-5-methyl-2-nonenoic acid, 5-hydroxy-2-decenoic acid and 5-hydroxy-8-methyl-2-nonenoic acid. The lactones of 5-hydroxy-2-decenoic acid and 5-hydroxy-8-methyl-2-nonenoic acid were shown to have the best butter or butter cake flavor (40). Homologous 4- and 5-substituted 5-hydroxy-2-alkenoic acid lactones were also prepared and their flavor investigated. The best butter flavor was obtained when the 4-substitution was as short as possible, when an *n*-pentyl group was on the 5 position and when the total carbon number was 10. The best compound in this comparison was the lactone of 5-hydroxy-2-decenoic acid (41). In a third comparison, δ-2,4-decadienolactone, δ-2,4-octadienolactone and δ-4-decenolactone were prepared. Compounds with the best butter flavor were δ-2-alkenolactones with the double bond in the 2 position of the lactone ring, and δ-alkadienones with double bonds in the 2 and 4 positions. The flavor of δ-4-decenolactone was the worst (42). So far these unsaturated lactones have not been found in dairy products.

Vacuum steam distillation at 210 C of butter oil and various creams yielded over 120 volatile compounds, 34 of which had not been reported previously in dairy products. All products studied contained the odd carbon number methyl ketones from C_3 to C_{15}, hexanal, acetaldehyde, benzene and toluene. Other compounds identified included 2-furfural, 5-methyl-2-furfural, diethyl-acetals and hydrocarbons including terpenes (43). Some of these compounds were undoubtedly produced because of the high temperature used in the distillation. Results from such experiments require careful interpretation.

Measurement of the concentration of certain flavor compounds over a period of time may indicate their origin or method of formation. A quantitative study of the effects of various environmental and physiological factors on heat-treated bovine milk fat showed that the mono-carbonyls underwent a seasonal trend, being higher in the winter than in the summer. Furthermore, there was a highly significant positive correlation between the monocarbonyls and methyl ketones, and the δ-lactones and short chain fatty acids (4:0–14:1) over the season. No significant difference in total monocarbonyl potential from fats of different breeds, fat production and milk from ketotic animals could be shown. The experiments indicated the dependence of the formation of such nonoxidative compounds on the availability of acetate during the biosynthesis of fatty acids (44).

Changes in polyunsaturated fatty acids such as linoleic during storage are mainly responsible for the production of volatile carbonyl compounds which cause various oxidized flavors. A stable butter oil was obtained by a process of trace hydrogenation. The product was free from off flavors such as hydrogenation flavor, and deodorization was not necessary. Some desirable butter flavor was retained (45). From the nutritional standpoint, the removal of linoleic and related acids might be undesirable.

In hot climates, butter made from buffaloes' milk had a better flavor in confectionary fillings than that made from cows' milk. This was attributed to greater percentages of saturated fats and higher melting triglycerides in the buffalo butter (46).

In small quantities, ascorbic acid retards oxidation in butter. At higher levels it is prooxidant. Storage studies on sweet cream butters containing added ascorbic acid, ascorbic acid and yeasts, and yeasts alone showed that the flavor of the butters containing yeasts alone was best and the butter with ascorbic acid and yeasts was second best. The control sample had the worst flavor (47). The yeast apparently retarded oxidation of the ascorbic acid.

Much oxidation in butter occurs at the surface, due to ready availability of oxygen and to contact with catalytic materials such as copper in the wrapping material. In an extensive survey of bulk and packaged butter in Denmark, the bulk butter received slightly better ratings for appearance, consistency, and taste and odor. The superior flavor of the bulked butter was probably due to its smaller surface area. The percentage of individual flavor defects are listed (48).

Adding a 50% aqueous solution of citric acid to cream at a 0.3% level before churning adversely affected the flavor and keeping quality of the butter (49). The effect may be simply one of decreased pH accelerating oxidation, or the releasing of fatty acids. On the other hand, citric acid is often used to increase the effectiveness of antioxidants.

Very desirable flavors are formed when butter is heated at high temperatures. Volatile compounds isolated from butter heated at 145–150 C included several lower fatty acids. Caproic, caprylic and capric were present in amounts 0.5–1.0 mg/kg, approximately 20–50 times greater than those of unheated butter. Butyric acid was present in traces and maltol was present in relatively large amount 5–15 mg/kg. While the typical aroma of heated butter was not fully reproduced by a mixture of these substances experiments showed that the acids were essential. Maltol, devoid in the pure state of the aroma it possessed when isolated from strongly heated butter, was thought to be a carrier for traces of as yet unidentified aroma compounds (50). In similar experiments (Forss, unpublished work) with butter heated to 135 C, relatively large amounts of acetic acid were also isolated.

Seven volatile carbonyl compounds were isolated from Indian ghee and four characterized as 2,4-dinitrophenylhydrazones. They were acetaldehyde, butanal (or formaldehyde), acetone and butanone. None of these compounds would be expected to contribute greatly to ghee flavor. However, when the carbonyl compounds were regenerated from the mixture of all 2,4-dinitrophenylhydrazones and added to deodorized ghee, the flavor resembled that of ghee (51). Important compounds in ghee flavor were, therefore, isolated but not identified.

Fermented Dairy Products

Enzymes derived from milk itself, animals, bacteria, yeasts and molds are responsible for many of the compounds contributing to the flavor of fermented dairy products. An important substrate is triglyceride fat, but enzymes may also act on protein and carbohydrate and on simple molecules such as secondary alcohols. Many of the flavor compounds encountered (fatty acids, ketones, diacetyl) are also formed nonenzymically. In some cases the characteristic flavor is due to a certain class of compounds such as the methyl ketones in Blue cheese. In other cases (e.g., Cheddar cheese) compounds such as fatty acids provide a background flavor, and trace amounts of sulfur and other compounds are responsible for the unique flavor.

The flavors of yogurt and sour cream are mainly due to enzymic reactions. Twenty-one volatile compounds were isolated from fresh yogurt. Results were tabulated and graphically presented for the following acids: acetic and formic, propionic, butyric, isovaleric, caproic, caprylic and capric (52). Yogurt with a titratable acidity of 51–65° SH and an acetaldehyde content of 23–41 ppm had the best flavor. Diacetyl appeared only in traces (53).

The effect of incubation temperature on volatile substances in cream culture was determined by a gas chromatographic headspace technique (54). Porapak Q preceded by a short column of Porapak R was used for the quantitative analysis of acetaldehyde, methyl sulfide, acetic acid, diacetyl and propylene glycol in synthetic culture flavor concentrates (55). The method appears applicable to other foods.

In a campus survey, age, sex, like or dislike for sour cream, use or nonuse of sour cream and smoking were factors included in a study of consumer responses to levels of diacetyl, acetic acid and associated flavor compounds in sour cream (56). In another evaluation triangular and paired preference tests were used to compare commercial sour cream (18–20% fat), cream acidified to pH 4.6–4.8 with glucono-γ-lactone alone or together with either lactic acid or citric acid, cultured acidified cream, and acidified cream containing also acetic acid and a flavor concentrate (diacetyl, acetaldehyde and methyl sulfide) (57).

Partially hydrolyzed milk fat is used in milk chocolate and other foods. A study showed that to some extent the nature of flavor depended on the agent used, e.g., lactic acid bacteria (58). This is consistent with the desire to release lower fatty acids. English workers have compared the pattern of release of the fatty acids from milk fat under the action of intrinsic and added (including porcine pancreatic) lipases (59).

A patent describes a dried product having a butter aroma, for use in ice cream, chocolate and confectionery which was prepared from condensed milk treated with yeast lipase (60). Another patent describes a butter flavor, for use in margarine prepared by heating at 130–195 C skim milk or whole milk or fat-enriched skim milk, each containing cultured milk (61).

A Japanese review of the literature on cheese flavors and their components contains a short chapter on flavor of unripened cheese, followed by a substantial chapter on ripened cheese (62). Studies on the volatile flavor components of Cheddar cheese are discussed in the 1968 Research Report of the Food Research Institute, Ottawa (63).

Fatty acids are very important in Cheddar and probably all cheese flavors. Fat, preferably milk fat, seems essential for development of cheese flavor. Work on lactic starters has confirmed the importance of acetic acid itself and its relation to other free fatty acids in Cheddar cheese flavor. Cheddar cheese was made with mixed lactic starter without *Streptococcus diacetilactis* and with milk of different fat contents. The cheese with the finest flavor had a concentration of free fatty acids and acetate of 12–28 μ moles/g cheese solids or a ratio of free fatty acids to acetic acid of 0.55–1.0. Analysis by GLC showed that all cheese contained C_4 to C_{18} fatty acids from the first day of manufacture. Cheese with rancid, fruity or fermented flavors had two to three times the concentration of C_{10}, C_{12} and C_{14} acids than that found in cheese of fine flavor. Cheese from skim milk did not develop Cheddar flavor. Only cheese containing greater than 50% fat in dry matter developed typical flavor. As the fat in the cheese decreased, the concentration of fatty acids decreased, but the acetate increased and the ratio between free fatty acids-acetate became undesirable. Typical Cheddar flavor did not develop when fat hydrolysis was either low or excessive (64).

The importance of milk fat is unclear. In one experiment milk fat was not considered necessary for the production of cheese flavor. Vegetable dairy cream cheese looked and tasted like the natural product and cost 10 cents less per pound (65). In another experiment cheese made from skim milk and vegetable fat was low in volatile fatty acids, acetic acid being the major one present. Polypeptides were absent and the level of amino acids was low (66). No comment was made on the flavor.

Reference has already been made to two methods for the isolation of cheese flavors. Similar methods were compared with reduced pressure distillation. Direct injection of the oil, low temperature vacuum distillation, and extraction of the cheese oil with methanol were used to isolate the volatiles from Cheddar cheese and Cheddar cheese powder prior to gas chromatography and mass spectrometry. Compounds identified included ketones, aldehydes, alcohols, acids, esters, lactones, terpenes, alkanes, alkenes, alkylbenzenes and some chlorinated compounds (67). Of these compounds, only the acids were believed to be important in Cheddar flavor.

Certain bacteria are required for the development of Cheddar cheese flavor. Analysis of the neutral volatiles in Cheddar cheese made aseptically with and without starter bacteria showed that methyl disulfide and methyl sulfide were the only compounds consistently found in higher concentrations in the cheese made with starter than in the cheese made without starter. However, these authors demonstrated that important flavor compounds were lost during gas chromatography (10). There was no significant difference in flavor of Cheddar cheese containing a heat stable bacterial lipase until the ninth month of storage in spite of marked changes in the acids compared with controls (68).

Several investigations of the volatile components of dried cheese have been reported. In a gas chromatographic study of the volatile flavor components of dried Cheddar cheese, it was found that injection of nitrogen into cheese slurries prior to atomization contributed to puffing and greater retention of flavor volatiles. Cheese powders produced by conventional spray-drying contained less volatile material and exhibited poorer flavor quality than equivalent powder produced by foam spray-drying. This was attributed partly to the formation of larger particles during foam spray-drying. In addition, the injected nitrogen caused an increase in surface area without an increase in particle weight. Therefore, evaporation occurred at a faster rate, and the particles presumably remained cooler during the falling rate drying period (69).

GLC was used to measure methyl ketones and alkanals in experiments on spray-drying Cheddar cheese. Heating the emulsion prior to spray-drying had an adverse effect on the flavor of the dried product and was found to be unnecessary (11). The presence of either methyl ketones or alkanals in above normal amount was indicative of effects of heating and of oxidation, respectively.

Cheddar cheese is usually cured for several months. Experiments have been carried out to produce cheese-flavored products in a few days. More flavor was achieved when 100 ppm reduced glutathione was added to Cheddar cheese slurries and when conditions included incubation at 30 to 35 C, NaCl concentration of 3%, daily agitation, and the incorporation of sodium citrate, manganese, riboflavin or cobalt (70).

TLC was used to study lipolysis in Camembert cheese. Pronounced lipolysis was found in the external zone preferentially towards the unsaturated triglycerides (12). Apparently, the organism required oxygen. Flavor differences in different zones were therefore anticipated.

While probably unimportant in Cheddar flavor, higher free fatty acids are important in the flavor of several European cheeses. For this reason methyl esters of higher free fatty acids in Danish Blue, a ewes' cheese milk (Manchego), and Herreruela and Asturian goats' milk cheese were analyzed by gas chromatography (71). Limburger cheese made with whole milk had the best flavor. Cheese made from milk containing 0.08% and 1.5% fat did not develop the typical flavor. Hydrolysis of the fat to a certain level of free fatty acids was necessary; 10–20 μ moles/g cheese solids was the optimum flavor level. Isovaleric acid was an essential flavor component (72).

The major volatile components of Norwegian Blue cheese were 2-pentanone, 2-heptanone, 2-nonanone, 2-pentanol and 2-nonanol (73). These are common components of Blue cheese, but an unsaturated ketone, 7-nonen-(1,2)-one, was also identified.

The predominating free fatty acids in ewes' milk cheese were palmitic, butyric, caproic, caprylic and capric. The lower acids were formed in the course of lactose fermentation and deamination of amino acids. The higher fatty acids were products of fat hydrolysis (74).

Nonoxidative Off Flavors

In the dairy industry, the term rancidity is used to describe hydrolytic flavor changes in lipids usually caused by bacterial lipases. In the edible oil industry, rancidity generally relates to oxidative changes in lipids. To avoid ambiguity it is well to refer to either hydrolytic rancidity or oxidative rancidity. Reference has already been made to desirable lipolytic changes deliberately induced in dairy products such as cheese and yogurt. The first part of this section deals with undesirable flavor changes caused by lipases.

Lipolytic Flavors

With the widespread use of pasteurization, unwanted flavors caused by bacteria and other microorganisms, usually lipolytic in nature, are becoming relatively rare. Nevertheless, even in the Western world (Norway), there is still interest in lipase activity in raw milk stored over a long period (75). In studies of hydrolytic changes in lipids under cold storage conducted in Texas, rancidity was induced in raw whole milk by homogenization, freeze-thawing and momentary heating at 32 C (76). Hydrolytic rancidity in milk is often due to faulty installation of pipeline-type milking machines. The lipolysis is caused by the effects of agitation on the fat-globule membrane and thermal shock on refrigeration. Ways to minimize these effects are listed (77). Milk with a high lipase activity was the cause of objectionable flavors in ice cream. Rapid cooling of the milk in the bulk vat was responsible (78).

In milk from individual cows and in those from herds there was a significant correlation between lipase taint and total free fatty acid concentration both before and after aeration storage. Increase in the free fatty acid concentration was mainly in butyric acid (79). More rapid, objective tests for measuring souring in milk are desired. A simple test using Rhodamine B showed excellent correlation with acid degree values (80). In a survey of German butters, mostly made from ripened cream and by the batch and continuous processes, the flavor defects most frequently encountered were cheesy, stale and oily. Here, lipolytic and oxidative changes must have occurred (81). Rancid flavor in cheese was shown to be due to lipases produced by gram negative bacteria which grew when the milk was stored above 40 C for 48 hr. Immediate pasteurization of the milk destroyed most of these bacteria and their lipases (82). Such storage conditions are unusual.

Though formed by the action of *Streptococcus lactis* var. *maltigenes* on leucine, 3-methylbutanal is responsible for a malty flavor in several fat-containing dairy products (83).

A seminar in Ireland on "Methods of Assessing Oxidative and Hydrolytic Off Flavors in Dairy Products" dealt with the effect of such factors as light, heat, copper, iron, transport, packaging and food additives (84).

Weed Flavors

Approximately 20% of butter produced in Queensland, Australia is tainted by weeds. The weeds responsible, their importance and their geographical distribution are discussed (85).

The taints arising in milk and butter through the ingestion by dairy cattle of *Lepidium* spp. (peppercresses) were studied over 20 years ago in Australia and the U.S.A. In a reinvestigation of these taints in Australia 0.5 ppm skatole and 0.3 ppm indole were isolated from butter fat. Flavor evaluations showed that skatole was principally responsible for the flavor defect, somewhat modifying the conclusions of earlier investigations (86).

Over the last 25 years in Australia and New Zealand, attempts have been made to determine the compounds responsible for the taints observed in dairy products due to cows eating the cruciferous weed, *Coronopus didymus*. Recent research in Australia showed that unheated *Coronopus*-tainted milk yielded butter fat from which benzyl methyl sulfide, benzyl isothiocyanate, benzyl cyanide, indole and skatole were isolated. Evidence suggested that benzyl methyl sulfide was the principal contributor to this flavor defect. Other compounds, particularly benzyl mercaptan, are probably involved in commercial weed-tainted butter made from pasteurized cream (87).

A paper from New Zealand reviews the research on *Coronopus didymus* and the taints it causes in dairy products. Similar conclusions were reached. There are at least two distinct off flavors. Benzyl methyl sulfide may be the key flavor compound in cream and butter not heated above 50 C, and benzyl mercaptan is possibly the key compound in cream and butter heated above 80 C (88). Removal of *Coronopus didymus* taint in cream by conventional methods such as Vacreation has been largely unsuccessful. More extreme measures for taint removal are described in a paper from New Zealand (89).

Stale and Gluey Flavors

Stale flavors in dairy products are difficult to describe and may be due to several causes. Sometimes loss of desirable flavor components is sufficient to give a stale impression. In other cases changes in the physical state of the product due to variations in processing may cause a different mouth feel often described as oily or stale. Sometimes lipid oxidation is responsible. An important component contributing to stale flavor in dried skim milk, *o*-aminoacetophenone (90) is probably derived from tryptophane.

Diffusion dialysis and ion exchange chromatography were used to isolate the stale flavor principle from concentrated milk. There was a correlation between the stale flavor intensity and the acid ferricyanide reducing substances in the diffusate. A 1-amino-1-deoxy-2-ketose formed by a Maillard reaction was postulated as the key compound (91).

Gas chromatograms of the steam volatiles from stale milk fat were correlated with taste panel evaluations. Several types of reduced pressure steam distillation were compared. In all cases, the distillates when added back to fresh milk reproduced qualitatively the flavor characteristics of the stale fat. Distillation at 75 C or higher produced artifacts undesirable for following the formation of stale flavor compounds during storage (92).

The sale of edible casein is limited by the presence of an off flavor often called gluey. Two papers from Australia deal with gluey flavors. The range of compounds identified in stored gluey casein suggested that there are at least two degradative processes operating during storage: lipid oxidation and nonenzymic browning. The acids, alkanals, 2-alkanones and alkanols are all common products of lipid oxidation and are likely to result from the degradation of the small amounts (1–2%) of milk fat remaining in commercial casein. The steam distillate from gluey casein contained 25–30 μg of volatile components per gram of casein of which 20 μg consisted of acids (93). However, it was concluded that the presence or absence of fat plays only a minor role in off flavor development and that greatest improvement in flavor was achieved by removal of some other component, probably lactose during preparation (94). Many of the other flavor compounds identified probably arose through browning reactions.

In a review of aromatic hydrocarbons in foodstuffs, the presence of several in milk fat, Cheddar and Swiss cheese are tabulated (95). Though hydrocarbons such as the alkanes are relatively flavorless, others such as the naphthalenes have distinct flavors, and 1-methyl naphthalene has been approved as a food flavor in the U.S.

Oxidized Flavors

In addition to review papers already discussed, one from Ireland deals with off flavors in dairy products caused by lipid oxidation (96). Another from Norway presented at the 4th Scandinavian Symposium on Fats and Oils discusses oxidized flavors arising in milk during its production (97). Two additional papers by the same author also deal with oxidized flavors (98, 99).

Many carbonyl compounds isolated from oxidized dairy products may have desirable flavors under different circumstances. For example, *cis*-4-heptenal confers a creamy flavor to fudge and *cis*-3-hexenal is important in fruit and vegetable flavors.

Cold storage of milk may delay its oxidation. Studies on milk and its lipids during three days' cold storage showed that fat from fresh milk or milk cold-stored for one day showed a higher rate of peroxide formation on heating at 112 C for 8 hr than fat from samples (whether raw or pasteurized) cold stored for two or three days (100).

Peroxide values and thiobarbituric acid (TBA) tests continue to be related to flavor changes. Unexpectedly, milk fat oxidized at 50, 35, 21, 4, −10 and −27 C had the same flavor at all temperatures. In general, there was a better correlation between chemical tests (peroxide and TBA) and tallowy flavor than with oxidized-metallic flavor (primarily due to 1-octen-3-one). The addition of copper influenced the chemical tests more than the flavor (101).

Workers at the University of California at Davis have been investigating the relationship of copper and ascorbic acid to the TBA test for over 15 years. Recent research is covered in three papers which discuss the role of copper and ascorbic acid in linoleate oxidation. "I. Measurement of Oxidation by Ultraviolet Spectrophotometry and the Thiobarbituric Acid Test" (102). "II. Ascorbic Acid and Copper as Oxidation Catalysts" (103). "III. Catalysts in Combination" (104).

The rate of lipid oxidation in ultra high temperature creams was measured by the TBA test, a peroxide test and by tasting. Creams manufactured during the summer months were most resistant to oxidation. Creams with no detectable oxidized flavor had TBA values $\leqslant$0.08. TBA values $\geqslant$0.16 and peroxide values $\geqslant$2.0 were associated with pronounced oxidized flavor. Relationships between the chemical and flavor tests were highly significant. Low peroxide levels were not necessarily indicative of good flavor quality. A chalky, grainy texture observed in some creams was attributed to high homogenization pressure.

A cheesy flavor was thought to be caused by protein hydrolysis, presumably by heat stable or reactivated enzymes. The more complete homogenization attainable with summer creams as a result of their higher protein concentration might provide increased protection against oxidation. Alternatively, the increased protein could be responsible for greater amounts of –SH groups. The TBA method was the more useful since it identified creams as possessing either acceptable or unacceptable flavors (105).

Twenty years ago, a common example of light induced off flavors was in milk delivered in glass bottles to front porches. Nowadays, off flavors caused by light occur frequently in supermarket display cases. In a study of orientation of milk constituents, light induced off flavors in milk were shown to be largely due to degradation of low density lipoprotein existing as the innermost layer of the fat globule membrane (106). In experiments in Belgium the intensity of light-induced off flavor in whole milk powder increased with exposure, but the intensity of off flavor in skim-milk powder was constant (107). In similar experiments in Minnesota, although free fat in dried whole milk powder had a higher peroxide value than the total fat, there was no indication that it oxidized at a faster rate upon subsequent storage (108). Light-induced flavors in Gouda cheese may be desirable (107).

Factors influencing photo-oxidation in butter were studied. Both salt and chlorine in the wash water exhibited prooxidant activity which increased with increasing concentration. Washed butters had lower TBA serum values and higher fat peroxide values. The factors studied appeared to operate independently of one another (109). Malonaldehyde, the compound from oxidized fat which reacts with the TBA reagent, is very soluble in water.

Very low levels of UV light promoted oxidation of butter although no flavor change was apparent. At temperatures below 35 C the level of oxidation was very low. When such butter was placed in cold storage little further oxidation occurred (110). The results differ from those of experiments with higher levels of UV light. In Ireland copper levels and light intensity were major factors of off flavor development in packaged butter caused by lipid oxidation. However, other factors such as the age of the butter were important. Microbiological factors were relatively unimportant. High levels of copper (mean value 0.39 ppm) were observed (111).

With the present widespread interest in air pollution, it is likely that many unwanted flavor changes will be traced to contaminants in the air. Foam and conventionally spray-dried milks prepared in the Washington D.C. area during the summer months were shown to have inferior flavors. This was shown to be mainly due to the presence of ozone in the air. Skim milk and whole milk powders manufactured in air containing 32 ppb ozone showed appreciable flavor deterioration compared with those manufactured under a background level of 2 ppb. Foaming heightened the damaging effect of ozone on flavor quality (112). Charcoal filters completely removed the ozone from the air entering the dryer and prevented development of the off flavor. Cellulose dust filters were less effective (113). *trans*-6-Nonenal was shown to be responsible for the off flavor. This aldehyde had a flavor threshold in whole milk of 0.07 ppb and was believed to originate by trace ozonolysis of minor lipid constituents on the surface of the dried product (114).

Several isolinoleic acids isolated from butterfat yielded *cis*-4-heptenal on oxidation (115). Two of these acids (*cis*-11,*cis*-15 and *cis*-10,*cis*-15-octadecadienoic) were synthesized (116). A micromethod using osmium tetroxide was developed for the determination of the position of double bonds in unsaturated fatty acids yielding *cis*-4-heptenal (117). At a level of 1 ppb *cis*-4-heptenal confers a creamy flavor to deodorized butter oil.

Possibly the two most important products of lipid oxidation from a flavor point of view are 1-octen-3-one and malonaldehyde. 1-Octen-3-one has a metallic flavor and is a key component in many oxidized flavors. Malonaldehyde has no flavor itself but its measurement through various TBA tests has been a means of measuring oxidation and oxidized flavors. The value of the TBA test as an index of oxidation has been compared with various (hydro) peroxide tests. A paper from Ireland discusses the formation and importance in oxidized flavors of 1-octen-3-one and malonaldehyde (96).

A paper from the Netherlands lists aroma compounds mostly carbonyl, isolated from or expected to occur in butter with cold storage defects and from autoxidized fatty acids. Several compounds not reported previously are included, e.g., alkatrienals and alkadienones (118).

Antioxidants present in milk were investigated. Oxidized flavor in high fat sterilized cream was retarded by the addition of ascorbic acid. Ascorbic acid decreased at a faster rate in cream without added skim milk solids, than in creams with added solids. The presence or absence of added α-tocopherol made no difference on this effect (119). Control of oxidized flavor by direct addition of emulsified α-tocopherol to milk required less than 1/100th of the amount required by supplementing the ration. Because oxidation commences immediately after the milk is taken from the cows, the addition of tocopherol is most efficiently done at the farm (120).

The effectiveness of antioxidants, though their use is not always permitted, has been studied in dairy products. Antioxidants were added to oxidized milk fat, oxygen was removed, and the samples were incubated in sealed tubes at 40 C. The relative effectiveness of butylated hydroxyanisole, nordihydroguaiaretic acid and α-tocopherol in accelerating peroxide decomposition depended on the concentration of antioxidant and the peroxide level. Synergists such as citric acid and isopropyl citrate decreased the rate of decomposition of peroxides and decreased the accelerating effect of added antioxidants on peroxide decomposition. Although these synergists had a large effect on peroxide decomposition in vacuo, they did not have corresponding effects on the organoleptic stability of milk fat in the presence of oxygen (121). In a later paper (122) the authors stated that deodorization of the milk fat did not affect the results appreciably.

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