

SECTION II
LITERATURE REVIEW

Formatted in Accordance with the *Journal of Agricultural and Food Chemistry Style Guide*.

Chapter 3. Flavors and Off-Flavors of Milk Products

Introduction

A complete overview of flavors associated with milk products is beyond the scope of this literature review. Milk is an extremely complicated entity comprised of lipids, proteins, carbohydrates, and minerals. Over 400 volatile compounds in milk products have been identified (1). This literature review will focus on specific processing and storage induced flavors associated with extended shelf-life fluid milk products. Flavors developed as a result of ultra-high-temperature (UHT) heat processing, storage, autoxidation of lipids, light exposure, and package migration will be addressed specifically.

Flavors Developed During Heat Treatment and Storage of Milk

Introduction

Virtually all milk and milk products are heat processed to some degree and stored for a period of time. The factors and mechanisms responsible for the formation of off-flavors in heat-processed milk have been thoroughly investigated by previous researchers. Milk is a complex entity and contains many components that may be precursors of off-flavor chemicals (proteins, fat, lactose, etc.). Reactions occurring between milk components during the heating or storage of milk products result in off-flavors. Table (1) illustrates the differences in the concentration of volatile compounds present in pasteurized milk subjected to a mild heat treatment, (13 sec at 75°C), versus milk subjected to a more severe heat treatment, (4.6 sec at 142°C).

Ketones

Diketones, cyclic ketones, and methyl ketones are formed in heat processed milk and are the major contributors to their cooked and stale flavors (2-25). Shibamoto (22) identified the diketone compounds; 2,3-butanedione (diacetyl) and 2,3-pentanedione, contributed significantly to the heated, burnt, and fermented notes in heated milk. Hodge (26) proposed a formation mechanism for diacetyl in a nonenzymatic browning reaction. Hodge suggested that diacetyl is formed from methyl α -dicarbonyl, an intermediate compound formed during nonenzymatic browning reactions. Alternatively, Heyns et al. (27) proposed that diacetyl is formed from the reaction of methyl glyoxal and glycine or its derivatives. Jenness and Patton (28) reported that

methyl glyoxal is produced by heating lactose and trace amounts of free amino acids and compliments Heyne's theory. A small amount of diacetyl (3-5 ppb) are found in raw milk, but at a concentration below its flavor threshold in milk (10-19 ppb) (29-31).

The cyclic ketones, cyclopentanone and 2-methyl-tetrahydrofuran-3-one, also contribute to the heated, burnt, and fermented notes in heated milk (22). However, the mechanism by which these compounds are formed in heated milk is not well documented. Ferretti and Flanagan (32) have reported that cyclopentanone and 2-methyl-tetrahydrofuran-3-one are found in a casein-lactose browning system, but no other reports of these compounds in dairy products are reported.

Methyl ketones are responsible for the stale off-flavors developed during the storage of heat-processed milk. Methyl ketones are not found in raw milk, but are developed during storage of heat-processed milk. The methyl ketones, 2-heptanone, 2-nonanone, and 2-undecanone, are the largest contributors of stale flavor in UHT milk (6). Moio et al. (33) similarly report that 2-heptanone and 2-nonanone are the most powerful odorants in UHT milk. The precursors of methyl ketones, β -keto acids, are biosynthesized in the bovine mammary gland from acetate (34). These β -keto acids are unfinished fatty acids, i.e., they have not undergone the final reduction, dehydration, and reduction steps that occur during fatty acid biosynthesis (35). Methyl ketones are formed by the thermal decarboxylation of β -keto acids (6,36). Figure (1) shows the proposed formation pathways of methyl ketones from β -keto acids (22). Methyl ketones in dairy products usually contain an odd number of carbon atoms because they are products of β -keto acids with an even number of carbon atoms (37).

Lactones

Dimick et al. (38) stated in their review that raw milk contains no free lactones and that they appear only after heating a milk product. When milk fat is heated or stored in the form of dairy products, the following lactones have been identified: δ -decalactone, γ -dodecalactone, 5-methyl-2-(5H)-furanone, 2-butenic acid- γ -lactone, and α -methyl- γ -butyro-lactones (22,38-41). Lactones are generally formed in dairy products from the thermal breakdown of γ - and δ -hydroxyacids, Figure (2).

Lactones contribute milky, buttery, coconut-like flavor notes to milk and are generally favorable. However, Arnold et al. (42) identified δ -decalactone from stale sterile concentrated milk, and

Ferretti and Flanagan (43) found α -methyl- γ -butyrolactones in stale nonfat dry milk. The presence of lactones may contribute to the stale flavor of heated milk, but to a lesser extent than ketones.

Aldehydes

Prolonged storage of casein in dairy products, particularly milk powders, results in an unpleasant stale off-flavor. Researchers have identified that stale flavor caused by stored casein is largely due to the increased quantity of carbonyl compound. Aldehydes seem to be particularly problematic with alkanal compounds and benzaldehyde being the largest contributors to casein derived stale flavors (44-46). The formation of alkanal compounds during storage is believed to occur by the oxidation of lipids bound by casein (46). Elevated levels of benzaldehyde can be produced by reactions occurring between phenylalanine and lactose over an extended period of time (46). Benzaldehyde is also formed during the caramelization of sugars (26).

Furans

Furan derivatives, particularly furfural and hydroxymethylfurfural, are major volatile constituents of heated milk (8). Furans are not found in raw milk, but appear in milk heated above 90°C (22). Furan derivatives are formed in heated milk by the lactose-casein browning system, that occurs by the casein catalyzed degradation of lactose in the presence of elevated temperatures (>80°C) (32)

Alcohols

Acetol and acetoin are the largest contributors of alcohol induced flavor compounds in heated milk. Acetol and acetoin are found in raw milk, but their concentrations increase at temperatures above 90°C (22). The taste of acetol is characterized by many descriptors depending upon the medium. In aqueous solutions, acetol is described as sweet and roasted. In contrast, acetol is described as yogurt-like in emulsions. Acetol is formed as the product of carbohydrate fragmentation or degradation that occurs during nonenzymatic browning reactions (22,26,27,32,47,48). Acetoin is generally formed by the reduction of diacetyl (2,49). The off-flavor of heated milk is partly due to the formation of acetol and acetoin. It should be noted that

sugar alcohol compounds, particularly maltol and iso-maltol, are found in heated milk, but these compounds are usually present at subthreshold concentrations and do not contribute significantly to heated milk flavor (6,22).

Acids

When milk is exposed to temperatures above 100°C the concentrations of acetic, butyric, hexanoic, octanoic, and decanoic acids increase (22). Butyric and hexanoic acids are the major free fatty acids in non-fat milk and whole and non-fat milk powders (22,43). These acids contribute to the chemical and rancid flavor of heated milk.

Sulfur Containing Compounds

A cooked flavor is present in milk products that undergo high-temperature pasteurization and sterilization procedures. This flavor is caused by hydrogen sulfide. Hydrogen sulfide is formed indirectly by the liberation of free sulfhydryl groups arising from the denaturation of β -lactoglobulin. The free sulfhydryl groups are then oxidized forming hydrogen sulfide (50). The concentration of hydrogen sulfide in milk increases linearly with the intensity of heating (6). It should be noted that some researchers believe that sulfhydryl groups that are activated by heating may contribute to the oxidative stability of milk (24).

Dimethyl sulfide is a constituent of raw milk and is also found at lower concentrations in heated milk. However, higher concentrations of dimethylsulfone is found in heated milk. Shibamoto (22) suggests that dimethyl sulfide is oxidized to dimethylsulfone via dimethyl sulfoxide as the intermediate.

Flavors Developed From the Autoxidation of Lipids

Introduction

Autoxidation products are formed from unsaturated fatty acids by non-enzymatic autocatalytic oxidation reaction resulting in the formation of hydroperoxides (7). These hydroperoxides often dismutate to secondary oxidation products such as aldehydes and ketones. Flavors and odors developed from the autoxidation of lipids render a food unpalatable and are described as rancid or oxidized. Typically, the term rancid is reserved to describe flavors

developed as a result of milkfat hydrolysis by lipase in dairy products. Oxidized flavors are associated with products of autoxidation.

Formation of Hydroperoxides

The fundamental mechanisms of lipid oxidation involve free-radical chain reactions. The reaction of unsaturated fatty acids with oxygen to form hydroperoxides occurs by a free-radical process involving an initiation, propagation, and termination stage, Figure (3). The formation of free radicals (RO^\bullet , ROO^\bullet) in the initiation stage takes place by thermal or photodecomposition of hydroperoxides, by metal catalysis and/or by ultraviolet irradiation. The initiation process can also start by the loss of hydrogen radicals on a carbon atom in the α -position with respect to the double bond in the presence of trace metals, heat, or light (51).

The fatty acids or alkyl radicals that are formed during the initiation stage react with oxygen to form peroxy radicals in the propagation reaction. The peroxy radical (ROO^\bullet) then abstracts a hydrogen from the α - CH_2 group of another unsaturated lipid molecule to form hydroperoxide. The termination stage involves the formation of non-radical, stable products by the interaction of R^\bullet and ROO^\bullet through three reactions (51).

Decomposition of Hydroperoxides and Types of Off-flavor Compounds

Hydroperoxides are very unstable and break down readily into many volatile and non-volatile products. The decomposition products include: aldehydes, ketones, alcohols, acids, hydrocarbons, lactones, furans, and esters. However, most volatiles that impart undesirable flavors are carbonyl compounds (51).

Hydroperoxide forms an alkoxy radical and a hydroxy radical by the homolytic cleavage of its $-\text{OOH}$ group. The alkoxy radical then undergoes β -scission of C-C bond to form an aldehyde and alkyl or vinyl radical (3). The alkyl or vinyl radical can then react with aldehydes, ketones, or alcohols in a general sense to produce volatile off-flavor compounds. Numerous mechanisms have been proposed to characterize the formation of specific volatile compounds from hydroperoxides, but most of these mechanisms take the general form presented in Figure (4) (3,10,15,16,18,24,52-57).

Aliphatic aldehydes are the most important breakdown products of hydroperoxides

because they are major contributors of unpleasant odors and flavors in food products. The polyunsaturated acids: oleic, linoleic, linolenic, and arachidonic are the most important precursors for the formation of aldehyde compounds due to their prevalence in milk products. (37). Table (2) lists the possible origin to some aldehydes obtained from the oxidation of oleic, linoleic, linolenic, and arachidonic acids (24).

Aldehydes resulting from autoxidation may undergo further reaction and contribute to the flavor of dairy products. For instance, saturated aldehydes such as nonanal oxidize to the acid, but further autoxidation may occur with unsaturated aldehydes. Other aldehydes may arise through a secondary reaction such as isomerization or from other isomeric polyunsaturated fatty acids present in trace amounts. Aldehydes derived from amino acids or lipids may react with themselves or with other carbonyl compounds by aldol condensation to a wide range of compounds, Figure (5) (37).

Flavors Developed From Light Exposure

Introduction

Exposure of milk to radiant energy produces two types of flavors (23). These types of flavors arise from the degradation of proteins or by the oxidation of lipids. Off-flavors developed as a result of protein degradation are often described as resembling burnt hairs or feathers or cooked cabbage. Light-induced flavors that develop in milk products from protein degradation are referred to as the sunlight or activated flavor. Photo-induced lipid oxidation produces metallic and cardboard like off-flavors similar to the autoxidized or metallic induced oxidized flavor.

Promotion of Light-induced Flavors by Riboflavin

Riboflavin acts as a photosensitizer by two limiting mechanisms, (Type I and II) (58-65). Type I reactions occur when triplet riboflavin, as an electronic excited state with two unpaired electrons, is directly deactivated by electron abstraction from a substrate which then is oxidized. Riboflavin can subsequently abstract another electron to form reduced riboflavin or react with ground-state oxygen to form a superoxide radical. Type II reactions occur when triplet riboflavin is deactivated physically by oxygen and singlet oxygen is formed. Singlet oxygen then reacts with methionine to produce a host of volatile compounds. Conditions which affect

the reactive state of riboflavin have dramatic effects on light-induced changes in dairy products. For instance, Korycka-Dahl and Richardson (65) showed that blocking the carboxyl group of methionine derivatives reduced the production of superoxide anion by 50%.

Light-induced flavors by Photo-induced Lipid Oxidation (Type I)

Differences between the volatile carbonyl compounds in milk exposed to light versus autoxidized milk samples demonstrate that the photooxidation of lipids is different from autoxidation or metal-induced oxidation. Milk samples exposed to light show the presence of alkanals and 2-enals. These compounds are not present in autoxidized milk samples. Similarly, 2,4-dienals are present in autoxidized milk samples, but are not present in milk samples exposed to light. Based on the above evidence, several researchers have postulated that photooxidation involves the monoene fatty acids of the triglycerides while autoxidation involved the polyene of the phospholipids (24,59). However, hydroperoxides are formed by both the autoxidation or photo-induced oxidation of fatty acids and are the principle source of off-flavors developed by lipid oxidation. The decomposition of hydroperoxides to form aldehydes, ketones, alcohols, acids, hydrocarbons, lactones, furans, and esters was discussed previously.

Light-induced Flavors by Protein Oxidation (Type II)

Light-induced flavors formed by the Type II reaction of riboflavin are attributed to the degradation products of the amino acid methionine. Methionine undergoes Strecker degradation in the presence of singlet-oxygen to form methional, dimethyl disulfide, and many other aldehyde and sulfur compounds, Figure (6) (10,66,67). Strecker degradation occurs when an amino acid is deaminated and decarboxylated by α -dicarbonyl compounds to an aldehyde (37).

The primary source of photosensitive amino acids are high molecular weight immunoglobulins (68,69). Gilmore and Dimick (70) demonstrated that purified α lactalbumin, β lactoglobulin, and acid whey proteins underwent photodegradation in a model system.

The burnt feather or cooked cabbage flavor produced when milk is exposed to sunlight is largely attributed to the concentration of methional present (2,63,71,72). Other sulfur compounds, including dimethyl disulfide, contribute to this flavor, but not to the extent that methional does.

Conclusions

Obviously, photooxidation can be prevented by avoiding exposure of milk to light. However, complete protection from light is not possible. In addition, recent packaging trends for milk products contribute to flavor problems. Consumers prefer transparent and translucent containers offering little light protection. Efforts have been made to lower the length of exposure and the amount of light of shorter wavelengths (73,74). Exposure of milk to light in the 400-460 nm range seems to produce the most rapid photodegradation (24).

Flavors Developed From Package Migration

Introduction

The term migration is used to describe the transfer of substances from a package into a food system. Substances that are transferred to the food from the packaging material are called migrants. Migrants are often monomers (or residual reactants) and processing additives (75). Migration is typically divided into two areas, global migration and specific migration. Global migration is the sum of all mobile packaging components transferred into the food. Specific migration refers to one or two individual and identifiable compounds.

Acetaldehyde Migration

Acetaldehyde is generated during the polymerization melt phase and subsequent processing of PET and other polyesters (76). The formation of acetaldehyde specifically occurs by thermal decomposition of the hydroxy terminal group and main chain of the polymer. This decomposition is not specific to PET, but to all polyesters comprising ethylene glycol as the diol component (77).

Residual acetaldehyde is often present in finished articles. The presence of acetaldehyde in food packaging material is problematic because of the ease at which this compound can migrate in foodstuffs. Small amounts of acetaldehyde adversely affect the flavor and aroma retaining property of foods and beverages (78). The amount of residual acetaldehyde present in finished polyester products depends on the conditions used to process these items. Rigid containers formed from PET resin prepared using dimethyl terephthalate (DMT) shows a residual acetaldehyde concentration of 9-10 ppm. However, rigid containers formed from

terephthalic acid (TPA) based PET resins leads to lower residual acetaldehyde concentrations, 5-6 ppm (76).

PET is becoming an increasingly popular packaging choice for water, beer, and milk products (79). These products are especially susceptible to acetaldehyde off-flavors because they do not contain any flavor notes that mask or compliment the pungent flavor of acetaldehyde. For instance, van Aardt et al. (79) reports the flavor threshold for acetaldehyde in spring water and milk as 167 ppb and 4 ppm, respectively.

Packaging trends for water, beer, and milk show that consumers are demanding single serving size units for convenience. Smaller size bottles have a higher ratio of PET surface area in contact with the beverage than do larger bottles. The increased contact area ultimately increases the amount of acetaldehyde that can migrate into a beverage. The development of low acetaldehyde grades of PET is being explored by many companies, which manufacture these products. A review of acetaldehyde scalping agents and low acetaldehyde PET packaging materials is provided in chapter 5.

References

- (1) Walstra, P.; Jenness, R. *Dairy Chemistry and Physics*; John Wiley & Sons: New York, 1984.
- (2) Adda, J. Flavour of dairy products. In *Developments in Food Flavours*; G. G. Birch and M. G. Lindley, Eds.; Elsevier Applied Science Publishers: New York, 1986; pp 151-172.
- (3) Azzara, C. D.; Campbell, L. B. Off-flavors of dairy products. In *Developments in Food Science. Off-Flavors in Foods and Beverages*; G. Charalambous, Ed.; Elsevier Science Publishers: New York, 1992; pp 329-374.
- (4) Badings, H. T. Reduction of cooked flavour in heated milk and milk products. In *Progress in Flavour Research*; D. G. Land and H. E. Nursten, Eds.; Applied Science Publishers Ltd.: London, England, 1978; pp 263-265.
- (5) Badings, H. T.; Neeter, R. Recent advances in the study of aroma compounds of milk and dairy products. *Neth. Milk Dairy J.* **1980**, *34*, 9-30.
- (6) Badings, H. T.; van der Pol, J. J. G.; Neeter, R. Aroma compounds which contribute to the difference in flavour between pasteurized milk and UHT milk. In *Flavour '81*; P. Schreier, Ed.; Walter de Gruyter: New York, 1981; pp 683-692.
- (7) Badings, H. T. Milk. In *Volatile Compounds in Foods and Beverages*; H. Maarse, Ed.; Marcel Dekker: New York, 1991; pp 91-106.
- (8) Burton, H. *Ultra-High Temperature Processing of Milk and Milk Products*; Elsevier Applied Science Publishers: New York, 1988.
- (9) Dumont, J. P.; Adda, J. Flavour formation in dairy products. In *Progress in Flavour Research*; D. G. Land and H. E. Nursten, Eds.; Applied Science Publishers: London, England, 1978; pp 245-262.
- (10) Forss, D. A. Review of the progress of Dairy Science: mechanisms of formation of aroma compounds in milk and milk products. *J. Dairy Research* **1979**, *46*, 691-706.
- (11) Hashim, L.; Chaveron, H. Comparison study of UHT milk aroma. In *Developments in Food Science. Food Flavors: Formation, Analysis and Packaging Influences*; E. T. Contis; C. T. Ho; C. J. Mussinan; T. H. Parliment; F. Shahidi and A. M. Spanier, Eds.; Elsevier Science Publishers: New York, 1998; pp 393-400.

- (12) Jeon, I. J. Undesirable flavors in dairy products. In *Food Taints and Off-Flavours*; Blackie Academic & Professional: New York, 1996; pp 139-167.
- (13) Marsili, R. T.; Miller, N. Determination of the cause of off-flavors in milk by dynamic headspace GC/MS and multivariate data analysis. In *Developments in Food Science. Food Flavors: Formation, Analysis and Packaging Influences*; E. T. Contis; C. T. Ho; C. J. Mussinan; T. H. Parliment; F. Shahidi and A. M. Spanier, Eds.; Elsevier Science Publishers: New York, 1998; pp 159-171.
- (14) Mottram, D. S. Changes in thiol and disulfide flavour compounds resulting from the interaction with proteins. In *Flavour Science. Recent Developments*; A. J. Taylor and D. S. Mottram, Eds.; Thomas Graham House: Cambridge, England, 1996; pp 413-418.
- (15) Heath, H. B.; Reineccius, G. *Flavor Chemistry and Technology*; AVI Publishing Company: Westport, CN, 1986.
- (16) Grosch, W. Reactions of hydroperoxides - products of low molecular weight. In *Autoxidation of Unsaturated Lipids*; H. W.-S. Chan, Ed.; Academic Press: New York, 1987; pp 95-139.
- (17) Newberne, P.; Smith, R. L.; Doull, J.; Feron, V. J.; Goodman, J. I.; Munro, I. C.; Portoghese, P. S.; Waddell, W. J.; Wagner, B. M.; Weil, C. S.; Adams, T. B.; Hallagan, J. B. GRAS Flavoring Substances 19. *Food Technol.* **2000**, *54*, 66-84.
- (18) Nijssen, B. Off-flavors. In *Volatile Compounds in Foods and Beverages*; H. Maarse, Ed.; Marcel Dekker: New York, 1991; pp 689-735.
- (19) Reineccius, G. *Source Book of Flavors*, 2nd ed.; Chapman and Hall: New York, 1994.
- (20) Schmidt, R. H. Bitter components in dairy products. In *Developments in Food Science. Bitterness in Foods and Beverages*; R. L. Rouseff, Ed.; Elsevier Science Publishing: New York, 1990; pp 183-204.
- (21) Shankaranarayana, M. L.; Raghavan, B.; Abraham, K. O.; Natarajan, C. P. Sulfur compounds in flavours. In *Food Flavours. Part A. Introduction*; I. D. Morton and A. J. Macleod, Eds.; Elsevier Scientific Publishing: New York, 1982; pp 169-281.
- (22) Shibamoto, T. Flavor volatiles formed by heated milk. In *The Analysis and Control of Less Desirable Flavors in Foods and Beverages*; G. Charalambous, Ed.; Academic Press: New York, 1980; pp 241-265.

- (23) Shipe, W. F.; Bassette, R.; Deane, D. D.; Dunkley, W. L.; Hammond, E. G.; Harper, W. J.; Kley, D. H.; Morgan, M. E.; Nelson, J. H.; Scanlan, R. A. Off-flavors of milk: Nomenclature, standards, and bibliography. *J. Dairy Sci.* **1978**, *61*, 855-869.
- (24) Shipe, W. F. Analysis and control of milk flavor. In *The Analysis and Control of Less Desirable Flavors in Foods and Beverages*; G. Charalambous, Ed.; Academic Press: New York, 1980; pp 201-239.
- (25) Van Straten, S.; Maarse, H. *Volatile Compounds in Food. Qualitative Data*, 5th ed.; Krips Repro Meppel: The Netherlands, 1983.
- (26) Hodge, J. E. Origin of flavor in foods. Nonenzymatic browning reactions. In *Symposium on Foods: The Chemistry and Physiology of Flavors*; H. W. Schultz; E. A. Day and L. M. Libbey, Eds.; AVI Publishing Co.: Westport, CN, 1967; pp 465-491.
- (27) Heyns, K.; Stute, R.; Paulsen, H. Browning reaction and fragmentation of carbohydrates. I. Volatile products from the thermal degradation of D-glucose. *Carbohydr. Res.* **1966**, *2*, 132-149.
- (28) Jenness, R.; Patton, S. *Principles of Dairy Chemistry*; New York: Wiley, 1959.
- (29) Bennett, G.; Liska, B. J.; Hempenius, W. L. Effect of other flavor components on the perception of diacetyl in fermented dairy products. *J. Food Sci.* **1965**, *30*, 35-37.
- (30) Hempenius, W. L.; Liska, B. J.; Bennett, G.; Moore, H. L. Analytical taste-panel studies on diacetyl flavor levels in creamed cottage cheese. *Food Technol.* **1966**, *20*, 334-337.
- (31) Scanlan, R. A.; Lindsay, R. C.; Libbey, L. M.; Day, E. A. Heat-induced volatile compounds in milk. *J. Dairy Sci.* **1968**, *51*, 1001-1007.
- (32) Ferretti, A.; Flanagan, V. P. The lactose-casein (Maillard) browning system: volatile components. *J. Agric. Food Chem.* **1971**, *19*, 245-249.
- (33) Moio, L.; Etievant, P.; Langlois, D.; Dekimpe, J.; Addeo, F. Detection of powerful odorants in heated milk by use of extract dilution sniffing analysis. *J. Dairy Res.* **1994**, *61*, 385-394.
- (34) Lawrence, R. C.; Hawke, J. C. The incorporation of acetate-1-14C into the methyl ketones that occur in steam distillates of bovine milk fat. *Biochem. J.* **1966**, *98*, 25-29.
- (35) Kinsella, J. E.; Patton, S.; Dimick, P. S. Chromatographic separation of lactone precursors and tentative identification of the gamma lactones of 4-hydroxy octanoic and 4-hydroxy nonanoic acids in butterfat. *J. Am. Oil Chem. Soc.* **1967**, *44*, 202-205.

- (36) Schwartz, D. P.; Parks, O. W.; Yoncoskie, R. A. Quantitative studies on methyl ketone formatin in butteroil. *J. Am. Oil Chem. Soc.* **1966**, *43*, 128-129.
- (37) Forss, D. A. Brief reviews of dairy and soy products. In *Flavor Research. Recent Advances*; R. Teranishi and R. A. Flath, Eds.; Marcel Dekker, Inc.: New York, 1981; pp 335-372.
- (38) Dimick, P. S.; Walker, N. J.; Patton, S. Occurrence and biochemical origin of aliphatic lactones in milk fat - a review. *J. Agric. Food Chem.* **1969**, *17*, 649-655.
- (39) Keeney, P. G.; Patton, S. The coconut-flavor defect of milk fat. I. Isolation of the flavor compound from butter oil and its identification as delta-decalactone. *J. Dairy Sci.* **1956**, *39*, 1104-1113.
- (40) Keeney, P. G.; Patton, S. The coconut-flavor defect of milk fat. II. Demonstration of delta-decalactone in dried cream, dry whole milk, and evaporated milk. *J. Dairy Sci.* **1956**, *39*, 1114-1119.
- (41) Maga, J. A. Lactones in foods. In *Critical Reviews in Food Science and Nutrition*; CRC Press: Boca Raton, FL, 1976; pp 1-56.
- (42) Arnold, R. G.; Libbey, L. M.; Day, E. A. Identification of components in the stale flavor fraction of sterilized concentrated milk. *J. Food Sci.* **1966**, *31*, 566-573.
- (43) Ferretti, A.; Flanagan, V. P. Steam volatile constituents of stale nonfat dry milk. Role of the Maillard reaction in staling. *J. Agric. Food Chem.* **1972**, *20*, 695-698.
- (44) Bassette, R.; Keeney, M. Identification of some complex carbonyl compounds from nonfat dry milk solids. *J. Dairy Sci.* **1960**, *43*, 1744-1750.
- (45) Parks, O. W.; Patton, S. Volatile carbonyl compounds in stored dry whole milk. *J. Dairy Sci.* **1961**, *44*, 1-9.
- (46) Ramshaw, E. H.; Dunstone, E. A. Volatile compounds associated with the off-flavour in stored casein. *J. Dairy Res.* **1969**, *36*, 215-223.
- (47) Heyns, K.; Klier, M. Browning reactions and fragmentation of carbohydrates. IV. Comparison o-o-cladinosyl-5-o-desoaminyl-6,11,12-trihydroxy-2,4,6,8,10,12-trihydroxy-2,4,6,8,10,12-hexamethylpentadecane-13-o. *Carbohydr. Res.* **1968**, *6*, 436-448.
- (48) Shaw, P. E.; Tatum, J. H.; Berry, R. E. Base-catalyzed fructose degradation and its relation to nonenzymatic browning. *J. Agric. Food Chem.* **1968**, *16*, 979-982.

- (49) Collins, E. B. Biosynthesis of flavor compounds by microorganisms. *J. Dairy Sci.* **1972**, *55*, 1022-1028.
- (50) Hutton, J. T.; Patton, S. The origin of sulfhydryl groups in milk proteins and their contribution to "cooked" flavor. *J. Dairy Sci.* **1952**, *35*, 699-705.
- (51) Kochhar, S. P. Oxidative pathways to the formation of off-flavours. In *Food Taints and Off-Flavours*; M. J. Saxby, Ed.; Blackie Academic & Professional: New York, 1996; pp 168-225.
- (52) Badings, H. T. Flavors and off-flavors. In *Dairy Chemistry and Physics*; P. Walstra and R. Jenness, Eds.; John Wiley & Sons: New York, 1984; pp 336-357.
- (53) Pokorný, J. Major factors affecting the autoxidation of lipids. In *Autoxidation of Unsaturated Lipids*; H. W.-S. Chan, Ed.; Academic Press: New York, 1987; pp 141-206.
- (54) Lillard, D. A. Chemical changes involved in the oxidation of lipids in foods. In *Lipids as a Source of Flavor*; M. K. Supran, Ed.; American Chemical Society: Washington, DC, 1978; pp 68-80.
- (55) Litman, I.; Numrych, S. The role lipids play in the positive and negative flavors of foods. In *Lipids as a Source of Flavor*; M. K. Supran, Ed.; American Chemical Society: Washington, DC, 1978; pp 1-17.
- (56) Forss, D. A. Origin of flavors in lipids. In *Symposium of Foods: The Chemistry and Physiology of Flavors*; H. W. Schultz; E. A. Day and L. M. Libbey, Eds.; AVI Publishing Co., Inc.: Westport, CN, 1967; pp 492514.
- (57) O'Brien, P. J. Oxidation of lipids in biological membranes and intracellular consequences. In *Autoxidation of Unsaturated Lipids*; H. W.-S. Chan, Ed.; Academic Press: New York, 1987; pp 233-280.
- (58) Skibsted, L. H. Light-induced changes in dairy products. *Bull. Int. Dairy Fed.* **2000**, *346*, 4-9.
- (59) Wishner, L. A. Dynamic state of milk. Light induced oxidations in milk. *J. Dairy Sci.* **1964**, *47*, 216-221.
- (60) Aurand, L. W.; Singh, A.; Noble, B. W. Photooxidation reactions in milk. *J. Dairy Sci.* **1966**, *49*, 138-143.
- (61) Aurand, L. W.; Singleton, J. A.; Matrone, G. Sunlight flavor in milk. II. Complex formation between milk proteins and riboflavin. *J. Dairy Sci.* **1964**, *47*, 827-830.

- (62) Singleton, J. A.; Aurand, L. W.; Lancaster, L. W. Sunlight flavor in milk. I. Components involved in the flavor development. *J. Dairy Sci.* **1963**, *46*, 1050-1053.
- (63) Patton, S. The mechanism of sunlight flavor formation in milk with special reference to methionine and riboflavin. *J. Dairy Sci.* **1954**, *37*, 446-452.
- (64) Dimick, P. S. Photochemical effects of flavor and nutrients of fluid milk. *Can. Inst. Food Sci. Technol. J.* **1982**, *15*, 247-256.
- (65) Korycka-Dahl, M.; Richardson, T. Photogeneration of superoxide anion in serum of bovine milk and in model systems containing riboflavin and amino acids. *J. Dairy Sci.* **1978**, *61*, 400-407.
- (66) White, S.; White, G. Dairy flavourings. In *Food Flavorings*; P. R. Ashurst, Ed.; Blackie Academic & Professional: New York, 1995; pp 240-275.
- (67) Parks, O. W. Milk flavor. In *Symposium on Foods: The Chemistry and Physiology of Flavors*; H. W. Schultz; E. A. Day and L. M. Libbey, Eds.; AVI Publishing Co., Inc.: Westport, CN, 1965; pp 296-314.
- (68) Finley, J. W.; Shipe, W. F. Isolation of a flavor producing fraction from light exposed milk. *J. Dairy Sci.* **1971**, *54*, 15-20.
- (69) Dimick, P. S. Effect of fluorescent light on amino acid composition of serum proteins from homogenized milk. *J. Dairy Sci.* **1976**, *59*, 305-308.
- (70) Gilmore, T. M.; Dimick, P. S. Photochemical changes in major whey proteins of cow's milk. *J. Dairy Sci.* **1979**, *62*, 189-194.
- (71) Allen, C.; Parks, O. W. Evidence for methional in skim milk exposed to sunlight. *J. Dairy Sci.* **1975**, *58*, 1609-1611.
- (72) Samuelsson, E. G. Experiments on sunlight flavour in milk - S³⁵-labelled milk. *Milchwissenschaft* **1962**, *17*, 401-405.
- (73) Bradley, R. L. Effect of light on alteration of nutritional value and flavor of milk: a review. *J. Food Prot.* **1980**, *43*, 314-320.
- (74) Sattar, A.; DeMan, J. M. Photooxidation of milk and milk products. review. *CRC Critical Reviews in Food Science and Nutrition* **1975**, *7*, 13-37.
- (75) Crosby, N. T. *Food Packaging Materials. Aspects of Analysis and Migration of Contaminants*; Applied Science Publishers: London, 1978.

- (76) Long, T. E.; Bagrodia, S.; Moreau, A.; Duccase, V. Process for improving the flavor retaining property of polyester/polyamide blend containers for ozonated water. U.S. Patent 6,042,908, March 28, 2000.
- (77) Ikgarashi, R.; Watanabe, Y.; Hirata, S. Thermoplastic polyester composition having improved flavor-retaining property and vessel formed therefrom. U.S. Patent 4,837,115, June 6, 1989.
- (78) Mills, D. E.; Stafford, S. L. Polyester/polyamide blend having improved flavor retaining property and clarity. U.S. Patent 5,258,233, November 2, 1993.
- (79) van Aardt, M.; Duncan, S. E.; Bourne, D.; Marcy, J. E.; Long, T. E.; Hackney, C. R.; Heisey, C. Flavor threshold for acetaldehyde in milk, chocolate milk, and spring water using solid phase microextraction gas chromatography for quantification. *J. Agric. Food Chem.* **2001**, *49*, 1377-1381.
- (80) McMurry, J. M. *Fundamentals of Organic Chemistry*, 3rd ed.; Brooks/Cole Publishing Co.: Pacific Grove, CA, 1994.

Chapter 3 Appendix

Table 1. Amounts of different volatile compounds extracted from heat-treated milk (2).

Volatile Compound	Pasteurized Milk ¹ ($\mu\text{g}/\text{kg}$)	UHT- <i>i</i> Milk ² ($\mu\text{g}/\text{kg}$)
2-Pentanone	0.9	30
Pentanal	3	3
3-Hydroxy-2-butanone	3.1	5
1,1-Diethoxyethane	2	3
Pyridine	2.5	3.3
Ethyl isobutyrate	0.8	1.4
Hexanal	2.3	4
Furfural	0.2	2
Hexanol	3	4
2-Heptanone	0.9	83
Heptanal	0.7	2.1
Benzaldehyde	1.2	5
Octanal	0.7	2
Acetophenone	2	2.6
2-Nonanone	0.9	45
Nonanal	2.5	5
Decanal	0.8	1.6
Benzothiazole	4.5	6
2-Undecanone	8	30
2-Tridecanone	4	8.5
δ -Decalactone	-	25
2-Pentadecanone	0.6	2.3
δ -Dodecalactone	0.9	7

¹ Pasteurized milk heat treatment = 13 sec at 75°C in a plate heat exchanger

² UHT-*i* milk heat treatment = 4.6 sec at 142°C in a plate heat exchanger

Figure 1. Proposed formation pathway of methyl ketones from β -keto acids (22).

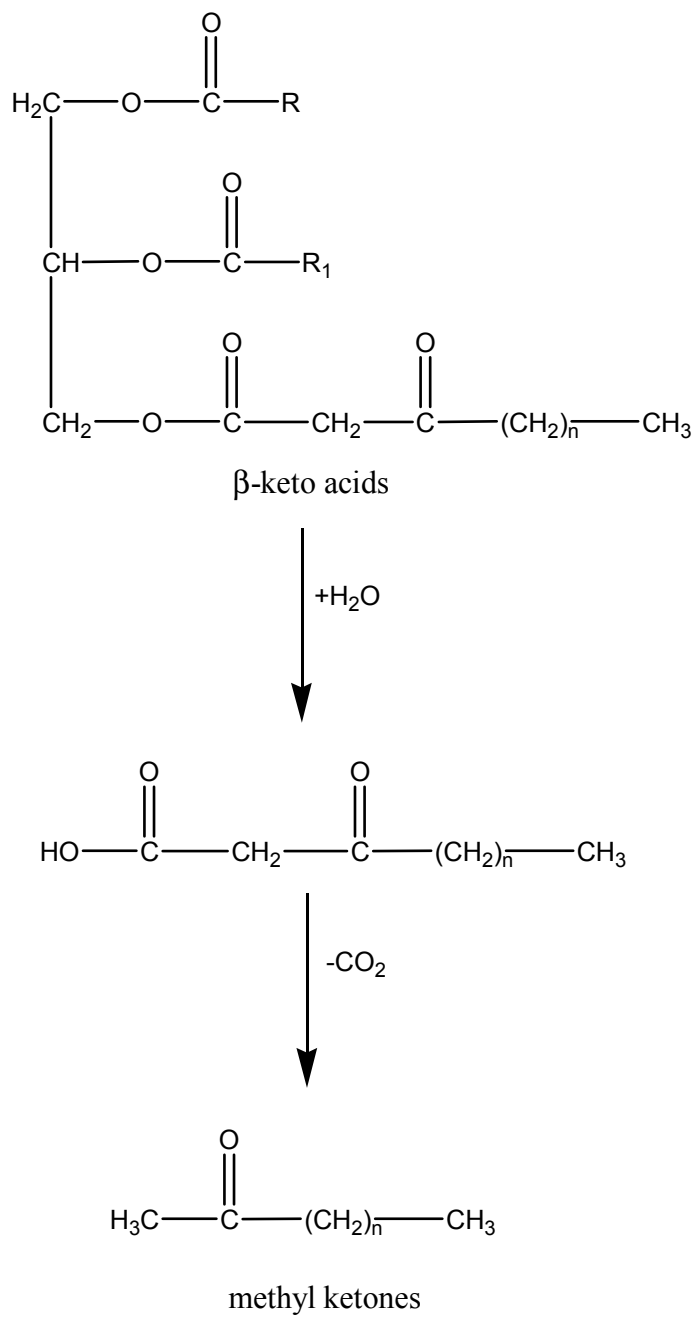


Figure 2. Formation of δ -lactone from the breakdown of a δ -hydroxyacid (37).

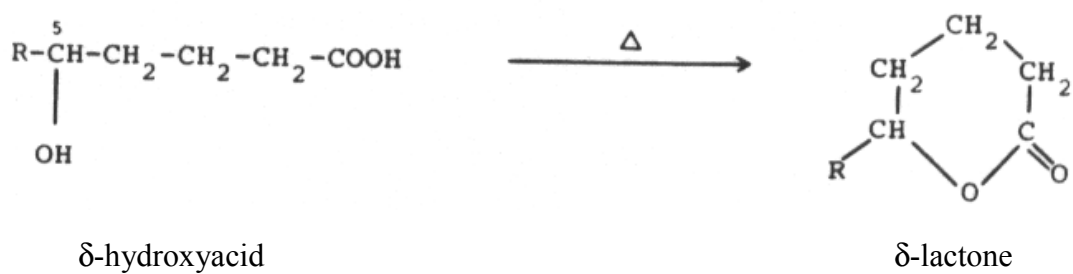
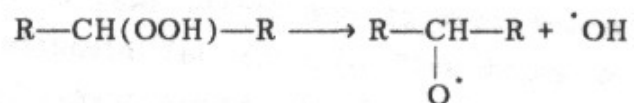
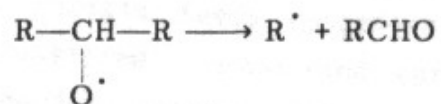


Figure 4. Formation of aldehydes, alcohols, and ketones from the decomposition of hydroperoxides (3).

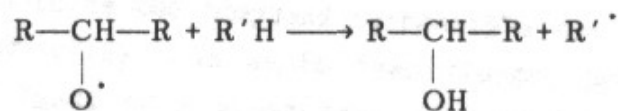
(i) Decomposition of hydroperoxide



(ii) Aldehyde formation



(iii) Alcohol formation



(iv) Ketone formation



Table 2. Possible origin to some aldehydes obtained from the oxidation of oleic, linoleic, linolenic, and arachidonic acids (24).

Fatty Acid	Hydroxide Position	Aldehyde Obtained
Oleic	C11	Octanal
	C8	2-undecenal
	C9	2-decenal
	C10	Nonanal
Linoleic	C13	Hexanal
	C9	2,4-decadienal
	C11	2-octenal
Linolenic	C16	Propanal
	C14	2-pentenal
	C12	2,4-heptadienal
	C13	3-hexenal
	C11	2,5-octadienal
	C9	2,4,7-decatrienal
Arachidonic	C15	Hexanal
	C13	2-octenal
	C12	3-nonenal
	C11	2,4-decadienal
	C10	2,5-undecadienal
	C7	2,5,8-tridecatrienal

Figure 5. Aldol condensation reaction between two aldehydes or ketones, leading to a β -hydroxy aldehyde or ketone product (80).

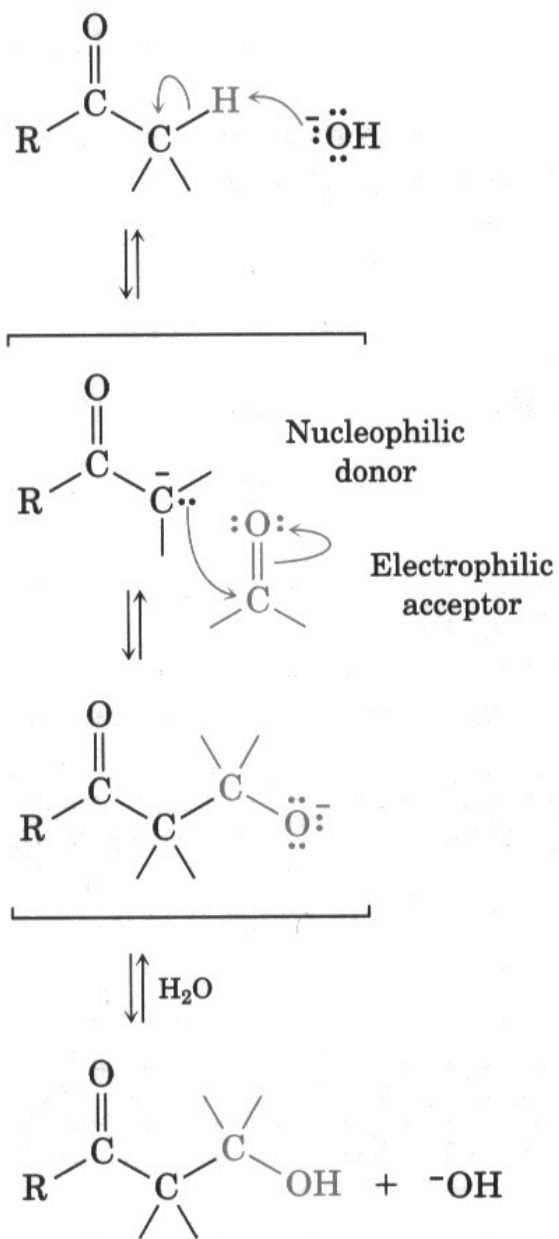


Figure 6. Formation of methional and dimethyl disulfide from the Strecker degradation of methionine (37).

