The Flavour of Milk

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Raw milk has a characteristic flavour although it is generally considered to be bland and of low intensity. The sensory perception is mainly determined by its physical nature: the pleasant mouth feel resulting from the emulsion of the fat globules in an aqueous colloidal protein phase and a slightly salty/sweet taste from the milk salts and lactose.[1] However, since virtually all milk receives some degree of heat-treatment to improve its keeping qualities the flavour of raw milk has little relevance; fresh pasteurized milk, free of defects, is normally regarded as good quality milk. Although chemical changes occur in milk as a result of even the mildest heat-treatment, flavour defects are usually considered to be flavour notes not normally found in good quality, pasteurized milk.

A great many volatile compounds have been isolated from milk since dimethyl sulphide was shown to be an important constituent of raw milk.[2] Workers in the Netherlands have recently isolated over 300 volatile compounds from good quality pasteurized milk.[1] The aroma concentrate obtained from the milk by vacuum distillation, freeze concentration, extraction and micro-concentration was analysed by coupled glass-capillary gas chromatography/mass spectrometry and the volatile compounds that were positively identified are listed below.

Hydrocarbons

Toluene
Ethylbenzene
Styrene
Trimethylbenzene
Dimethylethylbenzene
Biphenyl
Indene
Methylindene
Naphthalene
1-Methylnaphthalene
2-Methylnaphthalene
1,2-Dimethylnaphthalene
1,3-Dimethylnaphthalene
α-Terpinolene

Alcohols

2-Methylpropan-1-ol
Butan-1-ol
Butan-2-ol
2-Methylbutan-1-ol
3-Methylbut-2-en-1-ol
Pentan-1-ol
Pentan-3-ol
3-Methylpentan-3-ol
Hexan-1-ol
Hexan-2-ol
2-Ethylhexan-1-ol
Heptan-1-ol
Octan-1-ol
Decan-1-ol

Phenols

Phenol
p-Cresol
Ionol

Aldehydes

Acetaldehyde
But-2-enal
2-Methylbutanal
3-Methylbutanal
2-Methylbut-2-enal
Pentanal
Hexanal
Heptanal
Octanal
Nonanal
Non-2^{t}-enal
Non-2^{t}, 6^{c}-dienal
Decanal
Benzaldehyde

Ketones

Pentan-2-one
Pentan-3-one
4-Methylpentan-2-one
Hexan-2-one
Cyclohexanone
Heptan-2-one
Nonan-2-one
Decan-2-one
Undecan-2-one
Tridecan-2-one
Diacetyl
Acetophenone

Esters

Ethyl Acetate
Methyl Butanoate
Ethyl Butanoate
Methyl Hexanoate
Ethyl Hexanoate
Ethyl Octanoate
Methyl Decanoate
Ethyl Decanoate
Methyl Benzoate
Ethyl Benzoate

Lactones

δ-Hexalactone
δ-Octalactone
γ-Octalactone
δ-Decalactone
γ-Decalactone
δ-Dodecalactone
δ-Tetradecalactone

Sulphur & Nitrogen Compounds

Pyrrole
2-Methylpyrrole
Pyrazine
2-Methylpyrazine
Pyridine
4-Pentenenitrile
Cyanobenzene
Indole
Skatole
Dimethyl Sulphide
Dimethyl Disulphide
2,4-Dithiapentane
Allyl Isothiocyanate
But-3-enyl Isothiocyanate
Benzthiazole

Other Compounds

1,1-Diethoxyethane

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These volatiles belong to many different classes of compounds, but they are present at very low levels, most at sub-threshold concentration. However, although individually these compounds may be below threshold values, synergistic effects may produce some influence on the flavour of the milk.

The volatile compounds present in milk can result from the metabolism of the cow but may also be transferred from the feed. Chemical, microbial and enzymic reactions can also take place within the milk to produce flavour changes, both in the short term and on storage of the milk. There is however a fine balance between these volatile compounds present in the milk. The right blend will produce a desirable milk flavour but once this balance is disturbed then off-flavours may be produced, making the milk unacceptable.

Research into milk flavour has tended to investigate the compounds responsible for the off-flavours, the cause of their production and hence their prevention, rather than those compounds responsible for the true milk flavour. Six sources are recognized as the main causes of off-flavour in milk: feed, heat-treatment, oxidation, microbial action, lipolysis and light induced. A summary of these main off-flavours and their origins is given in Table I. Many of the compounds responsible for these off-flavours are present in good quality milk and it is only when their levels become excessive that taints are produced.

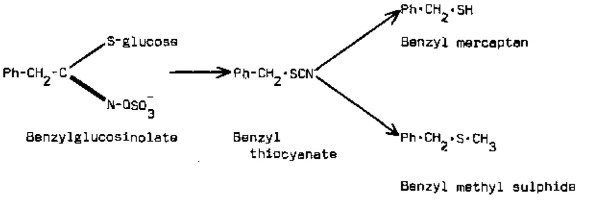
Weed Taints and Off-flavours

Forage may contain labile compounds which can be converted by the cow's metabolism to flavour compounds which in turn may be transmitted to the milk. When a cow consumes or inhales the strong odour of many dairy feeds (silage, green forage) 2-4 hours before milking, the milk may have an aromatic taste and odour characteristic of that feed.[3] Although milk is considered a bland product some flavour enhancement could be an advantage. Forss has suggested that milk might be more appealing if it had an attractive cowy flavour due to the presence of dimethyl sulphide in the milk when cows are fed lucerne.[4-5]

Table I. Off-flavours Found in Milk

Off-flavour	Origin
Weed flavours, cowy, faecal, fishy	Feed
Cooked, caramelized	Heat treatment
Papery, cardboardy, metallic, tallowy	Oxidation
Acid, fruity, malty, putrid, bitter	Microbial
Rancid, butanoic	Lipolysis
Burnt, burnt-feather, oxidized	Light induced

When consumed by the cow, many species of weed found in pasture can cause serious off-flavours in the milk. One of the most important and readily recognized defects is that resulting from the eating of wild garlic.[5] Land cress (*Coronopus didymus*), a cruciferous weed now prevalent in most dairy countries, has been shown to impart a burnt, unclean flavour to milk which is intensified by heat-treatment.[6] Benzyl methyl sulphide and benzyl mercaptan are thought responsible for this burnt flavour, being produced from benzyl thiocyanate, which is liberated enzymatically from benzylglucosinolate when the plant is crushed.



Faecal odours have been traced to the breakdown of tryptophan to indole and skatole resulting from the ingestation of pepper cress (*Lepidium spp*),[7] while it is postulated that the breakdown of lignin can produce milk tainted with vanillin[8] and phenol derivatives.[9] Cows grazed on wheat pasture can produce milk contaminated with trimethylamine which gives it a fishy note.[10]

Recent work has shown that changes in diet can cause subtle changes in milk fat flavour due to modifications to the rumen microflora.[11] Butter from cows fed on a low lipid diet, such as lucerne hay, has a high potential for a coconut flavour due to the formation of δ-octalactone and δ-decalactone. However this potential is greatly reduced when the diet is rich in unsaturated fats, such as sunflower seeds which have been protected against biohydrogenation in the rumen. A diet with a high proportion of concentrates, for example, crushed oats, produces a fall in pH of the rumen, which changes its microflora. Under these conditions oleic and linoleic acids are more readily hydrated to the corresponding 10-hydroxyacids which then undergo β-oxidation to form the γ-lactones. Thus cows fed on a diet of protected sunflower seeds and crushed oats can produce butter having a raspberry-like flavour due to the presence of γ-dodec-cis-enolactone and γ-dodecanolactone.

A high grain diet promotes the formation in the milk of methyl-branched fatty acids, such as 4-methyloctanonic acid, which is important in the flavour of mutton.[12]

Heat-treatment Induced Flavours

To enable milk to have a sufficiently good keeping quality it must be subjected to a heat-treatment to delay microbial, chemical and enzymic deterioration. Two types of treatment are normally employed: pasteurization in which the milk is heated for 15 sec at 72°C and ultra-high-temperature treatment (UHT) where it is heated at between 135° and 150°C for a few seconds.

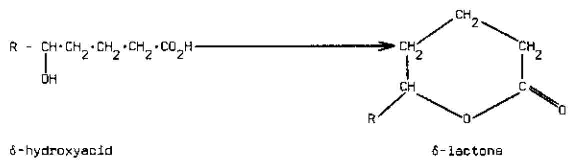
Flavour changes occur as a consequence of the severity of the thermal treatment the milk has been subjected to. There are three major routes for the formation of these flavour volatiles:[13]

- cyclization or degradation of labile precursors found naturally in the milk
- the lactose-casein reaction and secondary reactions of its reaction products
- the release of sulphur containing compounds

Both pasteurized and UHT milk have a cooked flavour, mainly due to hydrogen sulphide which is released from the activated sulphydryl groups of the β-lactoglobulin present.[14] In pasteurized milk only a slight cooked or sulphurous flavour is detected but it is more pronounced with an increase in the severity of the heat-treatment. However, on storage, the level of hydrogen sulphide decreases with a corresponding dissipation of the cooked flavour which may not be noticeable after two or three days.[15] Many attempts have been made to reduce this cooked flavour, one of the more recent being the addition of L-cystine to the milk, preferably before heat-treatment. This effectively removes the hydrogen sulphide.[16]

The triglycerides in milk fat are not formed from just simple fatty acids but also from substituted acids such as β-ketoacids and hydroxyacids. These acids can originate in the diet of the cow but may also result from the normal metabolism of the cow. β-ketoacids on heating decarboxylate to form methyl ketones while δ- and γ-hydroxyacids ring close to produce the corresponding lactone. Both methyl ketones and lactones can impart flavour to the milk.[17]

$$\underset{\beta\text{-ketoacid}}{R - CO\cdot CH_2\cdot CO_2H} \xrightarrow{\text{heat}} \underset{\text{methyl ketone}}{R\cdot CO\cdot CH_3} + CO_2$$



Dimethyl sulphide although at low concentration imparts a desirable flavour to milk; at high concentration it produces a malty or cowy defect.[2] S-methyl-methionine sulphonium salt, which is present in plant material, has been isolated from milk and on heating decomposes with the production of dimethyl sulphide.[18]

The Maillard type reaction of lactose with casein can lead to a wide variety of products, many of which are aroma compounds. The initial reaction products can degrade into α-diketones, aldehydes and acids or dehydrate and cyclize to form furan derivatives. The newly formed α-diketones can undergo a Strecker degradation reaction with any amino acid present to form aldehydes. Severe heat-treatment of milk results in caramelization.

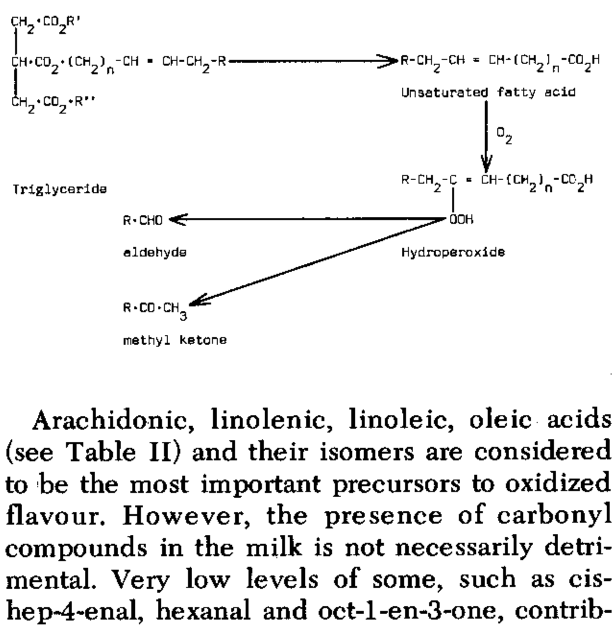
In UHT milk the initial cooked flavour goes after the first few days of storage but prolonged aseptic storage results in increasingly unacceptable stale flavours. These flavours often appear within a month of the storage at room temperature, and are due to increasing concentrations of carbonyl compounds.[19] Although methyl ketones, such as pentan-2-one, heptan-2-one and nonan-2-one, are the most abundant carbonyl compounds present, the aldehydes n-hexanal, propanal, n-pentanal and n-heptanal appear to contribute most to the off-flavours in stored UHT milk.[19,20]

In stored UHT milk the rate of increase of odd carbon-number methyl ketones (C_{3-13}) is dependent upon storage temperature, whereas aldehyde production is dependent upon storage temperature and oxygen content of the milk.[19] The type of carton the milk is stored in also effects the formation of stale off-flavours; milk stored in aluminum foil lined cartons retains its desirable flavour for a longer period than milk stored in polyethylene lined cartons.[20,21]

Sometimes a bitter flavour develops in UHT milk due to the breakdown of protein by proteinases. Milk proteinases will be deactivated by normal heat-treatment but some bacterial proteinases will resist very severe heat treatment such as 6 minutes at 142°C.[22,23]

Oxidized Flavour

Oxidized flavours in milk are most commonly described as "cardboardy or cappy," although the terms metallic, tallowy, oily and fishy are also used. These very undesirable flavours result from the oxidation of the milk lipids with the formation of carbonyl compounds.[24] Autooxidation proceeds via a chain reaction with the addition of oxygen to the methylene group adjacent to the double bond in an unsaturated fatty acid derived from the milk triglyceride. The allylic hydroperoxides which are formed then decompose into straight chain aldehydes and methyl ketones.[25]



Arachidonic, linolenic, linoleic, oleic acids (see Table II) and their isomers are considered to be the most important precursors to oxidized flavour. However, the presence of carbonyl compounds in the milk is not necessarily detrimental. Very low levels of some, such as cis-hep-4-enal, hexanal and oct-1-en-3-one, contribute to the flavour of milk but an excess causes the oxidized off-flavour.[1] Indeed oct-1-en-3-one has been shown to give a metallic flavour to milk products,[26,27] whereas with the association of an aldehyde a cardboard flavour is produced.[27]

Table II

C20:4	Arachidonic acid	$CH_3(CH_2)_3(CH_2CH{:}CH)_4(CH_2)_3CO_2H$
C18:3	Linolenic acid	$CH_3(CH_2CH{:}CH)_3(CH_2)_7CO_2H$
C18:2	Linoleic acid	$CH_3(CH_2)_4CH{:}CHCH_2CH{:}CH(CH_2)_7CO_2H$
C18:1	Oleic acid	$CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$

Off-flavour from Bacterial Activity

The growth of bacteria in both raw and pasteurized milk can result in the formation of serious flavour defects. These are produced by the contaminating organisms complex enzyme system reacting on the constituents of the milk. To prevent the flavour quality of milk being impared, good hygiene and rapid cooling of the raw milk to and holding at 4°C must be observed. Proper pasteurization will destroy all pathogenic and a very high proportion of non-pathogenic bacteria in milk but will not greatly affect any off-flavours from bacterial origin which have developed prior to pasteurization.[3]

The growth of gram-negative psychrotrophic bacteria which may develop at ⩾4°C can produce an unclean flavour due to the production of dimethyl sulphide.[1] Fruity flavours, which may develop in pasteurized milk, result from the growth of *Pseudomonas fragii*.[28,29] This organism produces a lipase which liberates butanoic and hexanoic acid from the milk and an esterase which then esterifies them with ethanol to produce the fruity flavour.

Malty flavours in milk are mainly caused by the presence of 3-methylbutanal and 2-methylpropanal. These aldehydes result from the metabolism of *Streptococcus lactis var. maltigenes*.[30] Acid off-flavours are associated with the growth of *Streptococcus lactis*, and the conversion of lactose to lactic acid. Although lactic acid is odourless and has a clean acid taste, its development in milk is accompanied by the production of very small amounts of acetic and propanoic acid, which gives a sour note.[3]

In-bottle sterilized milk occasionally develops a phenolic flavour due to contamination from spores of certain types of *Bacillus circulans*[1,3] Cresol formation is probably responsible for this defect.

Lipolyzed Flavours

Lipases from both milk and bacterial origin catalyse the hydrolysis of the milk fat triglycerides with the production of free short-chain fatty acids which impart a rancid flavour to the milk. Microbial lipases can also produce bitterness in the milk, resulting from concurrent protein breakdown.[3]

There is a relationship between milk fat acidity, short-chain fatty acid concentration and rancid flavours in the milk;[31] an increase in both the free short-chain fatty acids and the milk fat acidity causes an increase in the rancidity of the milk. In normal milk the total free acid concentration is about 360 mg/kg but in rancid milk this rises to 500-1500 mg/kg,[32] whereas if milk fat acidity rises above 1.5 meq alkali/100g fat from its normal value of 0.7, then rancidity can be detected.[33]

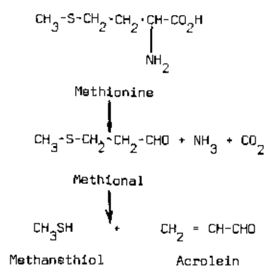
Not all fatty acids contribute to the rancid flavour. The even carbon-number fatty acids: butanoic, hexanoic, octanoic, decanoic and dodecanoic acids, are the major flavour contributors but the higher acids have little effect.[34] However, no single acid predominates in its effect, the acids combining to produce the rancidity.

Radiation Induced Off-flavours

When milk is exposed to direct sunlight, fluorescent light or even diffused sunlight, off-flavours develop. An exposure as short as ten minutes to direct sunlight will produce a noticeable off-flavour but the intensity of it does diminish with prolonged exposure.[35] Raw milk is more likely to develop this defect than heat-treated milk.[36] Homogenization of the milk also increases its susceptibility.[37,38]

Light induced flavour is made up of two distinct components: "Light-activated" flavour, a burnt or burnt-leather note which develops rapidly, and an "oxidized" flavour which develops more slowly. The latter is very similar to oxidized off-flavour and is due to the presence of volatile carbonyl compounds formed by the light induced break-down of the milk triglycerides.

"Light-activated" flavour results from the degradation of the serum protein. The amino acid, methionine, in the presence of riboflavin and oxygen undergoes a Strecker degradation with the formation of methional, ammonia and carbon dioxide.[38,40] Methional has a potato odour but undergoes a further breakdown to give the very odorous sulphur compounds methanethiol, dimethyl sulphide and dimethyl disulphide, which gives the milk a cabbagey, burnt-feather taint.[41]



Milk can be affected by light when it is contained in glass, polycarbonate, polyethylene or paperboard.[42] The traditional clear glass bottle offers little protection, 95% of the energy in the critical region 380 to 480 nm being transmitted,[43] and although ruby glass would give good protection,[44] it is not used due to cost and consumer acceptance. Paperboard containers with a large print area of dark ink or made from an aluminum foil laminate provide the best protection by minimizing the amount of light transmitted.[42]

The extent of the flavour development is related to the length of exposure, the strength of the light and the size of the milk surface exposed.[42] Higher milk temperatures increase the reaction rate and so increase the degree of off-flavour production.[45] The wider use of homogenized milk has resulted in a greater problem and the recent trend away from doorstep delivery to supermarket shelves has changed the source of light induction from sunlight to fluorescent light. There can be positions in illuminated retail cabinets where stock tends to remain unsold for a longer time.[46] Some cartons can therefore be exposed to fluorescent light for an extended time, which can result in cartons of unacceptable milk being present in a batch of that which is acceptable.

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