ARTICLES

Flavour Staling : Some Aspects

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Introduction

Staling is one of the more nebulous or indistinct term used in sensory evaluation. It is a rather non-descript term, denoting a lack of fresh character. This lack of freshness may be due to the formation of one or more compounds. It could also be the result of serious disturbances of various compounds constituting the flavour of a food product. This usually results in a poor organoleptic quality thereby reducing its economical value. Stale flavour is described in many terms as sour, mousy, fishy, sulphury, moldy or even fruity as the case may be. Thus, it can be seen that a flavour acceptable in a particular food may be an off flavour in another. For example, a fruity smell in cheese is an off flavour, but it is acceptable in jams and jellies. Also, strawberry flavour is unacceptable in wines but would be preferred in certain fruit preparations. Thus, stale flavour is a flavour which is not natural or up to standards owing to deterioration or contamination.[1]

Compounds causing such off flavours can be formed from fruit constituents or they can migrate into the food by contamination. The term "staleness " is associated with bread which at a typical storage temperature gives a stale, sour, green, sulphury character notes. Stale flavours have also been a problem in the brewing industry which attributes this off flavour to aldehyde formation and its concentration. A stale and musty flavour is also noted in dried dairy products as dried lactic casein and evaporate milk powders.[1]

Causes of off flavour

Lipid Oxidation : Lipid degradation basically can be classified into 2 routes : Auto-oxidation and Enzymatically Induced Degradation.

Lipid oxidation (LO) either due to auto-oxidation or enzymatically induced degradation is a detrimental reaction leading to the off flavour during storage of foods. Most foods especially those having low moisture content are most susceptible to lipid oxidation. Lipid Oxidation involves the reaction of molecular oxygen with unsaturated fatty acids via free radical mechanism.[2-4]

The reactions are self propagating and can produce as many as 100 hydroperoxides before its termination. Off flavour arises from LO via secondary reaction products. Lipid hydroperoxides are very unstable and breakdown to produce short chain volatile flavour compounds as follows :

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1. R – CH – R          ——> R – CH – R + .OH
       |                      |
       C – OH                 O.
2. R – CH – R          ——> R – CH      + R·
       |                      ||
       O.                     O.
3. R – CH – R + R1H    ——> R – CH – R + R1·
       |                      |
       O.                     OH
4. R – CH – R + R1·    ——> R – C – R   + R1H
       |                      ||
       O.                     O.
5. R – CH – R + R1O    ——> R – C – R   + R1OH
       |                      ||
       O.                     O
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Steps 2-5 result in the production of short chain saturated or unsaturated aldehydes, ketones and alcohols. These primary reaction products can undergo further oxidation if unsaturated, or a secondary reaction to yield a host of off flavour volatiles. These final products are generally aldehydes, ketones, acids, alcohols, lactones and esters yielding various off flavours.

This is especially seen with unhardened fish oil which contain varying amounts of long chain polyunsaturated n-3 fatty acids (n-3 PUFA) such as eicosapentanoic acid and docosahexanoic acid. Trace metal particularly Co, Cu and Fe greatly increase the rate of lipid oxidation and influences peroxide decompositon. Water activity also strongly influences LO. Dry products such as dry milk potatoes, potatoes chips and dry cereals are very susceptible to LO. LO is temperature dependent, the rate being faster at higher temperatures. It is also influenced by light. The shorter wavelengths are higher in energy and therefore are more effective in enhancing the rate of LO. Presence of antioxidants such tocopherols in vegetable oils impedes LO. The number and type of the double bonds in a fatty acid have a strong influence on the rate of LO. Hence, very dry products, high in polyunsaturated fatty acids are more prone to LO and develop off flavours.

Lipoxygenases and lipases are also known to participate in lipid oxidation. A relatively high moisture content is needed for enzyme action. Lipoxygenase initiates lipid oxidation by exchanging a hydrogen radical from fatty acid especially cis-cis double bonded methylene interrupted fatty acid . After this initiation step, the process follows auto-oxidation pathway. This type of enzyme is quite common in plant tissues. Legumes, especially soyabeans contain substantial quantities of lipoxygenase. The beany flavour of soyabean is believed to be due to lipoxygenase activity in the bean, once the tissue is damaged. The flavour of soyabean oil is also believed to be due to the same and produces 2-pentyl furan as an oxidation product responsible for this off flavour. Many vegetables must be blanched prior to frozen storage in order to inactivate lipoxygenase which otherwise results in oxidised off flavour.

Lipase is responsible for lipolysed flavour through hydrolysis of fatty acid from triglycerides. Higher fatty acids have a higher flavour threshold value. Hence off flavour due to lipolysis will be most abundant in products containing short fatty acids such as dairy products and coconut oil. Flavour description is goaty/bitter in nature. In coconut oil, lauric acid is the major fatty acid and tastes soapy when hydrolysed from the triglyceride. Lipases are relatively heat stable enzymes.

Microbial off flavour

Products not sterile or preserved via antimicrobial agents are susceptible to microbial off flavour growth and hence produce a disagreeable odour. Off flavours may arise mainly due to following causes :

a) Planned fermentation going wrong, for instance starter culture failure in a cheese vat resulting in poor acid production giving bitter and unclean odour.

b) Enzymes from lysed micro-organisms can catalyse reactions in foods leading to off flavour. Microbial enzymes are frequently quite stable to heat denaturation, therefore heat may kill the cells but leave the enzymes active. e.g. lipase and proteases producing off flavours.

c) Microbial growth in foods and the

resulting contamination with primary or secondary metabolites. e.g. fresh fish and dairy products.

Fresh fish has a mild odour which when stored above freezing temperatures develops putrid and foul fishy odour. Fish is susceptible to microbial growth since the fish muscles have substantial soluble material. Cells tend to lyse after the fish has been killed. The fish muscle provides a rather ideal growth medium for microbial off-flavour. Fishy off-flavour is due to generation of trimethylamine in bacterial action. Trimethylamine (TMA) is formed from trimethyloxide which is a natural constituent of fish muscle. This reduction is accomplished through bacterial enzymes and involves the coupled oxidation of lactic acid and CO_2. The latter stages of fish spoilage involves the production of various nitrogen and sulphur compounds which gives putrid sulfury notes. In fish, the bacteria responsible for off-flavour are Pseudomonas, *Acetobacter* and *Vibrio.*[1]

In milk, the spoilage is due to *Streptococcus lactis* growth which results in acid, sour off-flavour, however pasteurisation can effectively kill *S. lactis.* The off-flavour is generally unclear, foreign, fermented or bitter. Characteristic off-flavour in milk are fruity and malty. Fruity flavour is due to *Pseudomonas* attributed to initial hydrolysis of short chain fatty acid from the milk lipids and subsequent esterification of these acids to the corresponding ethyl ester. Ethyl butyrate and ethyl caproate have been found to be the off flavour responsible for this defect. Malty off flavour occurs at storage temperature 10°C and above caused by *S.lactis, Lactic maltygenes* or *Lactobacillus maltrominus,* primarily due to 3-methyl butanal production.[5]

Non Enzymatic Browning (NEB)

Flavour changes occur during heat treatment, the reason being NEB and as a result, food especially the canned food does not taste as their fresh counterparts. The browning reaction produced during storage is undesirable. The pathways of NEB depends on water activity, reactant present, temperature and pH, but the primary reason for off flavour is temperature during which toasted, roasted nutty and meaty flavours are not produced and NEB pathway then leads to stale green, sulphury notes and do progress at typical storage temperature.

Like LO, nearly all foods have sufficient reactants (including sugar and amino acids) for NEB to occur. Thus, NEB will result in an off flavour unless some other mode of deterioration occur before NEB become significant. Benzothiazole and O-amino acetophenone are 2 compounds believed to be formed via NEB and which contributes to stale flavour. O-amino acetophenone is responsible for the gluey flavour of the old casein.

Food-Packaging Interactions

Improper packing and packaging material can lead to flavour loss. Packing should protect food from hostile environment of unfavourable temperature, humidity, light, nutrients, atmospheric composition etc. These factors help to deteriorate the food by catalysing enzymatic reaction or increasing microbial growth or bringing about biochemical reactions.[6]

Off flavour may also result from direct contamination of packaging materials such as printing inks, lacquers, glues etc. present at high concentration or at high odour threshold values. Contamination can occur from packaging material itself such as plastic and polyethylene from which off flavour such as musty, soapy or rancid are reported, formed by oxidation products of alkanes and alkenes being present at low concentration. Thermooxidative degradation of PE or PVC leads to fatty acid and aldehyde inducing off flavour.[7]

Off flavours in some typical examples of food products are as follows:

Bread : Stale flavours occur in bread during storage yeilding characterstic notes of volatile compounds from crust and crumb. GC analysis gives a data on the level of compounds which strongly depends on both the fermentation of the dough and the baking process.

The compounds, 2-acetyl tetrahydro pyridine, 2-acetyl-1-pyrroline and E-2-nonenal are important odourant of bread giving a cracker like odour of fresh bread. Generally, off flavour due to NEB is labelled stale and the major compounds believed to be formed are benzothiazole and O-amino acetophenone.

The increase in the volatile fatty acid in the crumb leads to stale flavour. Acetic acid concentration is found to increase by 20% in 10 days, also pentanoic acid and hexanoic acid formation takes place which leads to sweaty flavour.[8]

Meat: A major factor influencing the quality of foods and especially meat products is lipid oxidation which results in rancid odours in the raw and warmed over flavour (WOF) in the cooked state of the products. The off flavours and odours generated by oxidation of lipids shorten the shelf life of the raw as well as precooked, uncured meat items such as restructured meat products. A key product of lipid oxidation is malonaldehyde which has been found to be toxic, mutagenic and potentially carcinogenic. Also, contamination of cholesterol with its auto-oxidation products may be the reason for its undesirable effects on human health.[9] The oxidative changes in meat products occur through autocatalytic type reactions which produce several byproducts that contribute to the rancid odours and flavours.[3]

Initial reaction resulting in the free production is thermodynamically diffficult and must be catalysed by direct thermal dissociation, metal catalysts or by light with or without the presence of photosensitisers such as chlorophyll, riboflavin and hemoprotiens.[3, 10] In meat, hemoprotiens may either catalyse lipid oxidation or be the source of nonheme iron that causes the rapid oxidation of cooked meats.[11]

The hydroperoxides produced by lipid oxidation are unstable and degrade by a free radical mechanism to produce several secondary contributors to the oxidised flavours in foods since hydroperoxides has very little or no flavour in foods.[4, 12]

Wine: Classification of undesirable flavours in wine can be based on the source thereof [13-16]:

Cultivar : Certain foreign flavours in wine are caused by compounds that are typically present in the grapes of that cultivar.

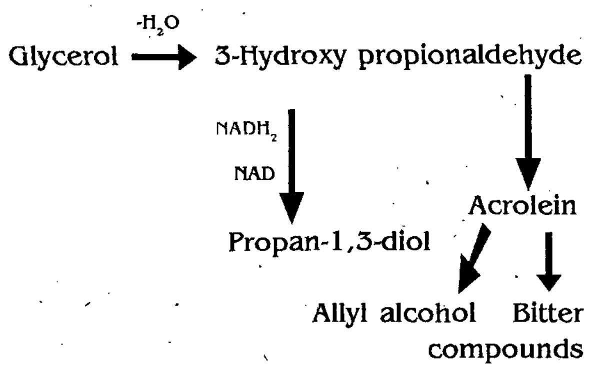
Fermentation : Off flavours are caused by compounds formed during alcoholic fermentation.

Maturation : Undesirable compounds are formed in the wine by oxidative conditions and microbial spoilage during maturation in wooden barrels or bottles.

A vinegary off flavour in wine is the most common and the best known fault encountered.[17] It is often the cause of a decrease in the quality of wine resulting in significant financial losses. The off flavour is mostly caused by acetic acid, wine spoiled to this extent cannot be salvaged. Ethyl acetate which has a pleasant flavour in concentrations below 50 mg/l contribute to the off flavour at conc.above 150 mg/l. When the odour thereof turns vinegary.

Mousiness describes a rather unpleasant aroma character in wine caused by oxidative microbial spoilage during the wine making process. Microorganisms found to be responsible for the odour include yeast of the genus *Bretanomyces* and certain *Lactobacillus* bacteria.[18,19]

Bitterness, one of the three basic important tastes, important in wines is still not completely understood.[20,21] In most cases, where bitterness has been established in wine, it appears to be primarily produced by phenolic substance. The bitterness of some bacteria spoiled wines is explained by formation of acrolein (CH_2=CH-CHO) by enzymatic reaction from glycerol. Bitter wines usually contain small amount of acrolein. The unsaturated aldehyde react nonenzymically with polyphenols in wine to form compounds with a bitter taste.



Certain native American grapes have a disagreeable flavour described as " foxy ." Methyl anthranilate has been suggested as an important component of the characterestic concord aroma and has subsequently been implicated as a major contributor to foxiness in American wines.

Beer : In beer, the nature and concentration of the volatiles is dictated primarily by raw materials i.e barley malt, hops, brewing process conditions, e.g. during mashing, wort boiling and hopping, yeast strain and fermentation and maturation conditions. The interactions between these principle variables determines the presence of volatiles in the final beer.

The occurance of contaminations like microbial and packing material at any time in the process as a variable capable of forming volatile compounds in beer. A stale flavour in beer is caused by oxidation reaction resulting in formation of carbonyls such as E-2-nonenal and E,E-2,4-nonadienal.

The various routes which have been proposed are Strecter degradation of amino acids, Oxidation of alcohols to aldehydes, Alcohol condensation of aldehydes, Oxidative degradation of isohumulones, Enzymatic degradation of lipids, Autoxidation of lipids, Secondary autoxidation of long chain polyunsaturated aldehydes. Since these processes occurs simultaneously, they will promote or inhibit one another, for example, an increase in melanoidins stimulates the reaction of amino acid but inhibits the photodegradation of alcohols. A high isohumulone content promotes the former reaction at the expense of the other reaction. The formation of polyunsaturated aldehydes is counteracted by degradation reaction. Among compounds causing off flavour are 2 - (4 - hydroxyphenyl) ethanol or tyrosol which gives undesirable yeasty flavour, ethyl nicotinates which gives papery off flavour, dimethyl sulphide giving sulphury notes, butanoic acid and 3-methyl butanoic acid casuing cheesy sticky odour. Compounds like H_2S and SO_2 have rather low threshold values and while acceptable in trace amounts can cause unpleasant odour at elevated concentrations.

Table 1 summarises the off flavours associated with various foods, the chemical constituents responsible and the mechanism of its formation.

Table 1 : Off flavours of different food products[1, 30]

Product Description	Off flavour off flavour	Components causing off flavour	Causes /pathway for
Bread[8]	Stale, green sulphury,sour	Benzothiazole, O-aminoacetophenone, volatile acids	Non-enzymatic browning
Barley	Musty	3-methylbutanol, 3-octanone, octanol	Microbial contamination (Fungi)
Rice	Pungent	Dimethyl sulphide	Fumigant
Rice vinegar	Peroxidised flavour	Propanoic acid, 2-methyl propanoic acid	Bacterial (Aceto-bacter)

Dried casein	Stale/musty	o-amino acetophenone, P-cresol,2-phenyl ethanol, indole, benzaldehyde	Lipid oxidation or NEB
Spray dried milk	Gluey, stale	(E) - 6-Nonenal	Ozonolysis of lipid component.
Cheddar cheese	Fruity	Ethyl butanoate & ethyl hexanoate	Bacteria
Yoghurt	Metallic lead like	1,3-pentadiene	Preservative (Sorbic acid)
Frozen meat	Warm of flavour, rancid	Pentanal, hexanal,heptanal	Lipid oxidation [2,3]
Irradiated meat	Wet dog	Dimethional	Irradiation
Water	Earthy, musty, stale	(E)-1,10-dimethyl -9-decanolol, 2-methyl isoborneol	Bacteria
Fish (Canned)	Oily	Dimethyl sulphide	Chemical decomposition of dimethyl-β- propioacetic (90-100°C)
Shrimp	Stale	Trimethyl amine	Chemical decomposition or reduction of trimethyl oxide
Potatoes	Bitter off flavour	Glycoalkaloids	High concentration of glycoalkaloids in soanum genes
Potato chips	Rancid, cheese like	Pentanol, hexanol	Oxidation (light induced)
French fries	Feacal like, nauseous,Cheese like	Methional, skatol geosim combination	Air borned (from potato process waste)
Canned mushroom	musty, earthy stale	2-methyl isoborneol	water borned bacterias.
Green peas	Hay like	3-alkyl-2-methoxy pyrazine	LO and enzymatic
Orange juice	Stale, musty	α-terpineol etc. decrease in geranial & neral	Thermal degradation
Lemon juice	Stale	p-cymene, 4-isopropenyl-1-methyl benzene	Thermal degradation of neral and geranial
Papaya	Sulphury, sour,	Phenyl	Microbial and enzymic

Pepper	Earthy, musty	1-terpinene-4-ol	From E & Z- sabinene (Hydrate. heat at 120°C)
Black currant	Sickly, burnt, smoky	Acetaldehyde, dimethyl sulphide furan, furfural, prapanol	Thermal degradation at 70°C
Wine[13, 14]	Geranium odour	2-ethoxy-3,5-hexadiene	Lactic acid bacteria causing reduction of sorbic acid
	Mousy	2-ethyl-3,4,5,6-tetrahydropyridine	*Lactobacillus bretanomyces* yeast infection
	Oxidised flavour	Unsaturated fatty acid	Autoxidation
	Strawberry	2,5-dimethyl-4-hydroxy-3(2H)-furanone and 2,5-dimethyl-4-methoxy-3(2H)-furanone	Improper breeding
Beer[10, 11]	Stale	Aldehyde conc.	Oxidation and autoxidation
	Cabbage like	High concentration of dimethyl sulphide	Thermal degradation
	Cheesy-sickly flavour	Excess quantitiy of butanoic acid and 3-methyl butanoic acid	Anaerobic bacteria *(Clostridium butyricum)*
	Sun struck	3-methyl-2-butene-1-thiol	Degradation by light of isohumolones
Coconut	Rancid	Free fatty acid	Fungal growth

Remedies to Reduce Off Flavour

Packaging should be appropriate in order to prevent food contamination from light, oxygen, microbial off flavour. It is also important to have a good hygeine and proper environment during processing and packing to prevent contaminants from air to spoil the food. Deterpenation is used to prevent off flavours as woody, piney, soapy in citrus fruits.[6, 22]

Nisin is a highly effective inhibitor of *Streptococci, Lactobacilli,* Gram positive spore forming *Clostridium* species as well as other bacteria associated with spoilage of canned foods such as processed cheese, evaporated and sterilised milk, canned soups and vegetables.[23, 24] Nisin is regarded as a safe preservative for use in foods since no harmful effects have been reported.[25]

A common procedure inhibiting or delaying lipid oxidation is through the use of antioxidants in the formulation of products like butylated hydrotoluene(BHT), butylated hydroxyanisole(BHA), Tertiary butyl hydroquinone (TBHQ) and propyl gallate(PG).[2] Smoking of meat products is believed to inhibit rancidity due to phenolic compounds present in the smoke.[26] Antioxidants like polyphosphates increase the water holding capacity of meat and delay or prevent lipid oxidation in cooked products.[11,27] Incorporation of antioxidants such as oxygen scavengers on the packaging material also inhibits LO.[28] Elimination of oxygen by vacuum packaging, gas flashing or shrink and skin packaging used in combination with oxygen carrier films retards LO, if the oxygen level is less than 2%.[2,11,29]

In spray dried milk powder, off flavour such as fishy, fatty, green can be prevented by using antioxidants such as lecithin, ascorbic acid and tocopherol. Good quality yeast should be used during manufacture of beer since yeast autolysis gives undesirable sulphury note due to increase content of H_2S. Masking of aldehydes producing stale flavour can be done by addition of H_2S in beer. Encapsulation techniques are used to prevent loss of flavour e.g. in dry soup mixes, instant beverages etc.

Continuous High Temperature Short Time (HTST) sterilisation of liquid foods and food materials is applied industrially to an increasing extent. The very short period of severe heat treatment compared with bath sterilisation processes minimises the adverse effects of the high temperatures on the organoleptic and nutritional quality of the product.[30] Lower temperature is maintained during grinding operation to prevent certain loss of flavour as well as hydrolysis during manufacture of oleoresins.

Over the years, a number of antistaling agents have been developed for use in bread making out of which, the surfactants make a very important class of additives. The surfactants especially those containing long carbon chain fatty acids are found to inhibit the gel formation of the starch by associating with the helical structure and preventing the swelling of starch granules to counteract staling. The commonly used surfactants to counteract staling in bread are Sodium steroyl-2-lactylate (SSL), Mono- and Diglycerides, Diacetyl tartaric acid (DATA), Polysorbate 60 and Calcium steroyl-2-lactylate.[8]

Thus, a knowledge of the cause of off flavour would enable preventing or at least minimises this undesirable effect. However, each food has a unique profile off flavour with respect to mechanism and compounds responsible and should therefore be treated as an individual case. This is an interesting area of investigation and is being tackled globally.

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