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Flavour Compounds in Fish and Shellfish

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Abstract

Seafood flavour is a complex phenomenon obtained from the interaction of compounds present in fish and shellfish. The prominent flavour bearing compounds in seafood are mainly nitrogenous and non-nitrogenous substances and it varies based on their species, age, sex, diet, season, environment and post-mortem handling. Several processing and storage conditions, like cooking, freezing, smoking, drying and canning, result in the production of desirable and undesirable flavours. The most important flavour substances in shrimp and lobster are bromophenols and geosmin. In order to control the undesirable flavours, the quality of desirable flavours in seafood can be improved by understanding flavour compounds and their interactions, short processing conditions and coating of flavour compounds with encapsulants.

Keywords: Desirable flavours, Encapsulants, Processing conditions, Seafood

Introduction

The flavour is the sum of sensations induced by chemical compounds present in foods and beverages and is in equilibrium at the time of consumption (Hall and Merwin, 1981). Some of these flavour components arise from the normal biosynthetic processes of animal and plant metabolism and hence are present in the raw meats, fish, fruits and vegetables, which constitute the basic components of our normal diet. Other components exist only as precursors and develop characteristic flavouring effects during subsequent cooking or processing due to chemical reactions induced by the effects of heat or fermentation. Some may be intentionally incorporated as flavourings at any stage of the product preparation or used as condiments when the product is served. Whatever the source, the observed odour, flavour impact and quality of the end product are the total effects of the individual flavouring components which in turn are determined by their relative proportion and their flavour rating.

Classification of Flavour in Foods

The flavour in foods may be classified as:

a) Natural Flavor: Pre-existing in the diet, particularly in fruits, vegetables, herbs and spices.

b) Process Flavor: Arising in end-products as a result of conventional processes involving heat or fermentation.

c) Compounded Flavor: Intentionally added flavourings formulated to produce a desired sensory effect using selected flavourants of natural and/or synthetic origin.

d) Taste Modifiers: Additives which affect the basic taste sensations (*e.g.*, salt, sugar, food acids and bittering agents).

e) Abnormal flavours and taints-off-odours and off-flavours arising in products as a result of degradation, adventitious contamination or package/product interaction.

The flavour of what we eat and drink is not a static attribute but one that is in dynamic equilibrium, capable of change depending on many factors. In raw materials of both animal and plant origin, it changes during growth and maturation and further during post-mortem or post-harvest handling and preparation for market. Flavours arising from cooking depend on the time/temperature ratio employed in the preparation of the food; the flavour of the freshly prepared product may undergo further modification during subsequent storage. Microbiological growth in products may produce significant flavour changes, some of which are desirable, others detrimental to product acceptability.

Flavour changes within the end-product may be due to:

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• Chemical transformation induced by pH, Maillard reaction, hydrolysis, oxidative rancidity, *etc.*

• Volatile losses which upset the relative concentration of aromatic components.

• The removal of flavour components by adsorption onto solid surfaces within the product.

• Differential partition between aqueous and lipid phases which significantly affects flavour perception.

Because there are so many variables, the formulation and production of foods and other consumable products are far from a precise science and depend to a large extent on subjective trial and error to achieve a product profile having maximum consumer acceptance. It is well recognized that flavour plays a significant part in product acceptance by inducing hedonic responses and hence consumer satisfaction or dissatisfaction. Poor flavour is a major cause of product rejection (Moskowitz and Chandler, 1978).

Seafood Flavour

Fresh fish is a rich source of flavour bearing compounds like proteins, amino acids, lipids, lipid derived compounds, carbohydrates, nucleotides and other minor compounds and Shellfish flavour is made up of a matrix of complex compounds such as free amino acids, nucleotides, organic acids, sulphur-containing compounds and unsaturated aldehydes and alcohols. These compounds are responsible for the distinct flavour of seafood. The flavour bearing compounds are affected by several interactions such as protein and lipid degradation, Maillard reaction, enzymatic reaction and lipid oxidation (Lindsay, 1994). Natural extracts are complex, diverse products obtained from animal, plant or microbial origin, or by physical processes such as distillation, extraction and concentration. They retain the full complexity of the original biological matrix and are highly valued in premium seafood flavour formulations. Synthetic components are developed by industries. They synthesize chemicals that are available in nature with a more stable and stronger unique flavour profile. Currently, there are about 1000 available synthetic flavour compounds developed by the industry.

Flavour Substances in Seafood

The flavour compound in the seafood is categorised into two broad categories such as nitrogenous and non-nitrogenous constituents and their concentration varies based on the type of species, stage of maturity, freshness and type of processing.

Nitrogenous Constituents:

• Trimethylamine (TMA) and nitrogenous bases.

• Free Amino acids and peptides.

• Nucleotides and their derivatives.

Non Nitrogenous Constituents:

• Sugars and sugar phosphates.

• Volatile Sulphur compounds.

• Carbonyls and alcohols derived from lipid oxidation.

• Organic and inorganic constituents.

TMAO and Their Derivatives

Trimethyl amine oxide is a compound naturally present in fish particularly in elasmobranchs, rather than in teleost fish and it helps in osmoregulation in high saline conditions. TMAO gets degraded in two different pathways after death such as enzymatic and microbial pathway. In enzymatic degradation, it gets converted into formaldehyde and dimethylamine responsible for protein denaturation and textural damage, whereas in the microbial pathway it is degraded into trimethylamine. The compound TMA is responsible for fishy odour and flavour. It acts as an indicator of freshness and levels above 5 mg per 100 g are considered an indicator of spoilage.

Free Amino Acids and Their Peptides

Fish and shellfish contain a rich source of free amino acids which contribute to their characteristic sweet flavour. The most prominent free amino acids present in fish are glycine, glutamic acid, alanine, aspartic acid, histidine, taurine, lysine, *etc.*, which contribute to flavour development and in enhancing the nutrition. Bioactive peptides are low-molecular-weight compounds containing 2-20 amino acid residues extracted from protein either by fermentation or by enzymatic hydrolysis that exhibit several properties like antioxidant, antihypertensive, antimicrobial properties. Carnosine, anserine and histidine dipeptides are some of the examples of bioactive peptides.

Nucleotides and Their Derivatives

Nucleotides are compounds that act as coenzymes and cofactors and possess several physiological and biochemical functions. The nucleotides are made up of nitrogenous base, ribose/ deoxyribose sugar and one or more phosphate groups. As a result of post-mortem changes the nucleotides are decomposed subsequently into compounds such as Adenosine triphosphate (ATP), Adenosine diphosphate (ADP), Adenosine monophosphate (AMP), Inosine monophosphate (IMP), Inosine and Hypoxanthine (Hx). The Inosine monophosphate is an indicator of fresh fish smell and hypoxanthine is responsible for spoiled, bitter flavour. A method used for identifying fish freshness is called the K value and it is defined as the ratio of hypoxanthine and inosine to the total ATP related compounds. K Value will be very low for fresh fish and it gets increased during spoilage and values above 50-60% are considered spoiled (Olafsdottir *et al.*, 1997).

Non-Nitrogenous Constituents

Non-nitrogenous compounds include sugar and sugar phosphates, sulfur containing compounds, carbonyls and alcohols, organic acids and inorganic constituents that contribute to overall flavour and taste.

Sugars and Sugar Phosphates

Glucose, ribose and traces of maltose in free-state occur in the extractive fraction of both fish and shellfish**.** Shellfish such as shrimp and crab contain a larger concentration of glucose than that which occurs in finfish. The most available sugar phosphates in fish muscle are glucose1-phosphate, glucose6-phosphate, fructose1-phosphate, fructose1,6-diphosphate.

Sulphur-Containing Compounds

The most common sulphur containing compound of seafood is hydrogen sulphide and dimethyl sulfide, resulting from the degradation of sulfur amino acids by endogenous enzymes and they contribute to volatile sulphur compounds responsible for the nauseating foul smell. The sulphur bearing compounds in shellfish are listed in table 1.

Table 1: Sulphur bearing compounds in shellfish

Compound	Source
Dimethyl sulfide	Shrimp
Dimethyl trisulfide	Cooked crayfish, oyster
Methanethiol	Cooked shrimp
Methional	Raw, fermented, cooked shrimp
Dimethyl sulfoxide	Oyster, roasted shrimp
Methyl trithiomethane	Roasted clam

Carbonyls and Alcohols

The carbonyl and alcohols are a group of compounds that result in the odour and flavour profile of a fish and shellfish at different stages of freshness, during storage conditions and in fish products. These components are obtained mainly due to the oxidative degradation of Polyunsaturated fatty acids or by the enzymatic degradation of PUFA catalyzed by lipoxygenase producing rancid odour and flavour.

Organic Acids and Inorganic Constituents

Lower fatty acids namely, formic acid, acetic acid, propionic acid, n-butyric acid and valeric acid have been identified in many fishes. The two persistent acids related to seafood are lactic acid which occurs in high concentrations (0.005 to 0.5%) in the muscle of the fish and succinic acid which mostly occurs in mollusks and gives a meaty flavour. It is noted that succinic acid content becomes abundant in fish after death, particularly in shellfish, reaching a level of 150-650 mg per 100 g. The major cations and anions of fish muscle are sodium, potassium, calcium, magnesium and chlorine, phosphorus and phosphate respectively and the ions contribute mainly to the salty flavour of cooked fish.

Flavour Compounds in Shrimp and Lobster

Iodoform-like Flavour of Prawn

The most consistently novel flavour in prawn is an iodine or iodoform-like note. Iodine/iodoform-like and phenolic-like flavours have been linked to 2,6-dibromophenol and 2-bromophenol respectively, both of which have been identified in extracts of the prawn. These bromophenols are believed to originate from the bromination of phenols by marine organisms in the prawn's diet, particularly marine algae and polychaete worms.

Garlic-like Flavour

This flavour is associated with deep-water prawns and certain species of lobster. The compounds responsible have been identified as bis(methylthio)-methane and trimethylarsine. The organoarsenic compound trimethylarsine is formed from arsenobetaine present in the marine diet of these crustaceans and contributes an unusual garlic or metallic note to the cooked product.

Muddy Flavour in Cultured Prawns

Muddy or earthy flavour in pond-fattened prawns has been widely reported as a significant quality problem in aquaculture. It has been speculated that geosmin and/or 2-methylisoborneol compound are responsible for such flavour. These compounds are highly lipophilic and accumulate readily in the fatty tissue of prawns, making them difficult to eliminate through processing.

Off-Flavours

Some material develops many strong "off flavours" that distract from the value of the food. The typical aroma of seafood that has not been stored properly is attributed to TMA and other amines. Dimethyl amine is also found in marine fish and this compound is also attributed to the fishy aroma of seafood products that have not been properly stored. Dimethyl sulfide (sulfur containing compound) of cooked clams and oysters and bis-(methylthio)-methane as reported from several species of prawn and lobsters are associated with seafood off aroma and flavour. The most common flavour enhancers in food are explained in table 2.

Table 2: Common flavour enhancers used in food

Salts	Description
Glutamic acid salts	Monosodium glutamate (MSG) is one of the most commonly used flavour enhancers in food processing.
Glycine salts	Simple amino acid salts typically combined with glutamic acid as flavour enhancers.
Guanylic acid salts	Nucleotide salts typically combined with glutamic acid as flavour enhancers.
Inosinic acid salts	Nucleotide salts created from the breakdown of AMP, due to high costs of production, typically combined with glutamic acid as flavour enhancers.
5'-ribonucleotide salts	Nucleotide salts typically combined with other amino acids and nucleotide salts as flavour enhancers.
Methyl trithiomethane	Roasted clam

Effect of Processing on Seafood Flavour

Processing conditions result in the development of both desirable and undesirable flavours. The outcome depends on the nature of the process, its intensity, duration and the composition of the raw material.

Desirable Flavour Changes

The desirable flavours involve some browning flavours obtained from Maillard (a non-enzymatic reaction) and caramelization which are developed during baking, roasting, grilling and boiling. Maillard reaction is a reaction that takes place between reducing sugars and amino acids accelerated by heat and produces aromatic compounds such as pyrazines, furans, thiazoles, pyrroles. Caramelization at high temperature gives a coffee-like flavour in shrimp and scallop with high sugar content.

Undesirable Flavour Changes

The prominent undesirable flavours occur primarily due to lipid oxidation and protein degradation. The lipid oxidation produces aldehydes and ketones that create off odour and an offensive smell. The protein degradation either occurs by enzymes or by microbes which produce amines and sulphur compounds that contribute to putrid and faecal aromas. In order to protect flavour integrity, the compounds will be protected with flavour encapsulants made of modified starch, maltodextrin, cyclodextrin *etc.,* which help in preventing degradation that occurs during heat and lipid oxidation.

Conclusion

Seafood flavour is a result of complex chemical compounds, including nitrogenous elements like TMA, free amino acids and nucleotides and non-nitrogenous substances such as sugars, sulfur compounds and organic acids. The compounds and the flavour profile of seafood vary based on the species, diet, environment, post-mortem treatment, storage conditions and are collectively influenced by the processing techniques such as the Maillard reaction, caramelization and lipid oxidation. A few illustrations of flavour-bearing compounds based on species are bromophenols in prawns, geosmin in farmed crustaceans and lipoxygenase-derived aldehydes in salmonids. The preservation of compounds and their interactions is crucial for seafood quality, managing off-flavours, optimizing processing conditions and creating efficient flavour enhancers and natural flavour systems which meet consumer demands in fresh and processed seafood items.

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