

Analytical, Nutritional and Clinical Methods

Volatile aldehydes in smoked fish: Analysis methods, occurrence and mechanisms of formation

Vincent Varlet, Carole Prost, Thierry Serot*

Laboratoire de Biochimie Alimentaire et Industrielle (LBAI ENITIAA), Equipe de recherche Qualité Aromatique des Aliments, ENITIAA, rue de la Géraudière, 44322 Nantes Cédex 3, France

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Abstract

The carbonyl function of volatile aldehydes is discussed from methodological point of view (reactivity and analysis method). From this presentation, an inventory of volatile aldehydes recovered in smoked fishes are carried out. Then, the different pathways possible for the formation of these molecules are explained in order to better understand their occurrence in smoked fish aroma. Maillard reactions for the “smoked” aroma and lipid oxidation for “fishy” aroma are the two main pathways of creation of odorant volatile aldehydes. Each odorant aldehyde recovered in smoked fish is characterized by its descriptors, its odour thresholds and its origins are investigated. Volatile aldehydes in smoked fishes are also studied according to the others organoleptic roles that they play in this kind of food matrices especially about their contribution in organoleptic properties of smoked products. Finally, the toxicity of several aldehydes identified in smoked fishes is discussed in order to assess their roles in smoked fish safety.

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Keywords: Volatile aldehydes; Smoked fish; Maillard reaction; Strecker reaction; Lipid oxidation; Odour thresholds; Organoleptic quality; Aldehyde toxicity

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* Corresponding author. Tel.: +33 2 51 78 55 14; fax: +33 2 51 78 55 20.
E-mail address: serot@enitiaa-nantes.fr (T. Serot).

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1. Introduction

Because of its original flavours and thanks to the technological development in food analysis, the aroma compounds of smoked fishes are very studied, especially salmon. The high value of smoked salmon and the volumes of production – about 88,000 tons produced in Europe in 2003 (Clément, 2004) – can explain the particular attention brought to the smoking process, the storage and the microbiological stability of this product. The world production of farm and fishery salmon has increased from 850,000 tons in 1985 to over 1,800,000 tons in 2001 (Eagle, Naylor, & Smith, 2004). Indeed, salmon seems to be the most investigated smoked fish but herring (Sérot, Baron, Knockaert, & Vallet, 2004; Sérot & Lafficher, 2003), had-dock and a lot of other fishes (Guillén & Errecalde, 2002; Guillén, Errecalde, Salmerón, & Casas, 2006) can be also processed by this technique. Smoking is practiced since old times in order to preserve food from the natural degradations and oxidation. Indeed, it consists in the application of smoke produced by the pyrolysis of the wood on the food. This smoke can be at gaseous state the most often, but the development of liquid and solid smokes offers new possibilities of smoking (Guillén & Ibargoitia, 1999; Guillén & Manzanos, 1996; Guillén & Manzanos, 1999). The preservation of the food is guaranteed by the antioxidant and antimicrobial properties of certain molecules (Cornu et al., 2006). For example, phenolic compounds generated by the combustion combined with the temperature and the conditions of smoking can reduce the microbiological development and the oxidation (Kjällstrand & Petersson, 2001). The smoking process is nowadays very looked after for the flavouring of the food and the typical organoleptic qualities that this process confers to the smoked food.

In all the studies which deal with smoked fishes aroma, carbonyl compounds and especially aldehydes form a group very important among the hundreds of volatile components identified. Aldehydes are molecules very interesting because they can be observed as indicators of the oxidative state and of microbiological contamination of the products. Indeed, they can constitute degradation products of microbiological metabolism reactions (Girard & Nakai, 1994b) and can return account of bacterial activity. On smoked salmon, it has been shown that numerous

microorganisms as *Brochotrix thermosphacta*, *Photobacterium phosphoreum* (Stohr, Joffraud, Cardinal, & Leroi, 2001) and lactic acid bacteria are responsible for the production of typical sour, rancid and sulfurous off odours. These unpleasant odours can be related to the products of the bacterial metabolism which are known to originate from the main catabolic pathways of lipids, carbohydrates and amino acids, then among them, a lot of carbonyls compounds and precursors of aldehydes. They can also constitute degradation products of oxidation reactions from fatty acids and illustrate the level of alteration of a product because they have frequently off-flavour odours (McGill, Hardy, Burt, & Gunstone, 1974). For example, propanal can serve as a reliable indicator of flavour deterioration for fish products and hexanal for meats (Augustin, Sanguansri, & Bode, 2006; Ross & Smith, 2006). These molecules are also very reactive towards oxidation-reduction transformations and represent intermediaries in a lot of biochemical reactions. However, numerous aldehydes coming from the wood smoke or created during lipid peroxidation are carcinogenic and can cause mouth, stomach or oesophageal diseases. The genotoxicity and cytotoxicity is especially due to the nucleophilic attack to amino and sulfhydryl functional groups of biomolecules such as proteins, nucleic acids, glutathione and cysteine (Kataoka, Kondo, & Sumida, 1998). For this reason, it is obvious that the fact to survey these molecules is also necessary. For example, α,β -unsaturated aldehydes like 4-hydroxy-(*E*)-2-hexenal or (*E*)-2-butenal are cytotoxic because (*E*)-2-butenal in drinking water was shown to cause liver tumors in rats suggesting that these aldehydes may be potential carcinogens (Chung, Tanaka, & Hecht, 1986; Munasinghe et al., 2003; Witz, 1989). Aldehydes in smoked fishes have also others organoleptic roles in the colour and the texture of the food matrices even if they mainly contribute to the global aroma of food matrices (Sainclivier, 1985).

The aims of this paper are to summarize the information about aldehydes in smoked fish. The chemical properties of aldehydes are firstly presented in order to better understand the ways of extraction and analysis of these molecules in smoked fishes. Then, the different possible pathways for aldehydes formation in smoked fishes will be presented in relation with their origins and odorant properties. We will conclude with the others organoleptic

roles of aldehydes in smoked fishes and their potential toxicity.

2. Analysis of volatile aldehydes

2.1. Extraction methods

Aldehydes are in the same time oxidant and reductor molecules. They can be formed by oxidation of primary alcohols and they can be further oxidized in the correspondent carboxylic acid, then they have a good reductor character. The chemical properties of the carbonyl function imply the aldehydes in a lot of reactions because even if the C=O bond. Indeed, the oxygen atom is more electronegative than the carbon atom ($\chi_{\text{O}} = 3.5 > \chi_{\text{C}} = 2.5$). The inductive attractive effect polarizes the carbonyl system which leads to an important polarity of the carbonyl group even if the alkyl group has a little inductive giver effect. Thus, as there is very little steric obstacle near the functional carbon, the C=O bond is very reactive (Curioni & Bosset, 2002). However, for the extraction, it is a consequent drawback because the compounds can evolve during the extraction.

Extraction methods developed for volatiles aldehydes are mainly those used for volatile compounds and are very linked to the analysis method chosen after the extraction step. Because of the reactivity of aldehyde function, a derivatization step can occur in order to protect the chemical structure. When a derivatization is planned, it is obvious that an extract at liquid state will be easier to derivatize. Then, in this case, extraction by reduce pressure steam distillation is used (Shibamoto & Horiuchi, 1997). According to the results of certain studies, aldehydes can also be extracted by headspace techniques but the aim of these studies was more an identification of the volatile compounds from a food matrix than identification especially focused on volatile aldehydes. Then, solid-phase micro extraction (SPME) and dynamic headspace/static headspace (DHS/SHS) extractions are used on seafood aroma analysis: SHS on salmon (Girard & Nakai, 1991; Girard & Nakai, 1994a, 1994b), DHS on crayfish waste (Tanchotikul & Hsieh, 1989) or sardine (Prost, Hallier, Cardinal, Serot, & Courcoux, 2004), SPME on smoked swordfish and cod (Guillén et al., 2006) or sea fish and prawns (Mansur, Bhadra, Takamura, & Matoba, 2003).

Liquid–liquid extractions (LLE) are not very suitable to recover the volatile aldehydes. However, LLE recent devices like supercritical fluid extraction (SFE) (Aro, Brede, Manninen, & Kallio, 2002) or microwave assisted extraction (MAE) (Grimm, Lloyd, Batista, & Zimba, 2000) are more and more used.

When specific aldehydes are studied, others extraction methods can be developed. It is the case of formaldehyde. All the previously described methods are possible but absorption or adsorption on solid support with a step of solid-liquid extraction with adequate solvents are also used (INERIS, 2004; INRS, 2004a). It consists in trapping the

aldehyde at gaseous state on absorbants and in eluting this trap by solvents. The same sampling can be used when aldehydes are at gaseous state. In the case of cooking fumes analysis, aldehydes can also be collected in special bags and directly analyzed at gaseous state (Fullana, Carbonell-Barachina, & Sidhu, 2004a).

Concerning the efficiency of the extraction methods, headspace techniques allow to recover very volatile aldehydes with low boiling point but these techniques are based on gaseous equilibrium phenomenon. These methods can be criticized about their efficiency because the content of aroma compounds which is moved in the headspace is not totally known. Reduce pressure steam distillation (RPDE) and simultaneous steam distillation solvent extraction (SDE) allow to obtain compounds of higher boiling point (Varlet, Prost, & Sérot, 2006). With reduce pressure steam distillation, the boiling point is reached with lower temperatures than simultaneous steam distillation solvent extraction. Therefore, the possible artefacts generated by thermal degradation can be reduced but this method implies a long time of extraction and a lot of material. SFE seems to be very efficient but it is limited according to the fat matter rate of the food matrix analyzed. MAE is not enough developed for volatile aldehydes analyses and the recovery yields can be very different according to the molecules searched. Moreover, the conditions of extraction are too strong and lead to generation of aldehydes by lipid oxidation.

2.2. Analytical methods

For the analysis of aldehydes, several methods have been used and all almost based on the reactivity of the carbonyl group through derivatization steps and/or colored products. The analysis method chosen is very linked to the extraction method used. In function of the detector, a derivatization step is applied, especially when the detection occurs optically (spectrophotometry).

Indeed, the carbonyl compounds can be revealed by the action of 2,4-dinitrophenylhydrazine (2,4-DNPH) which leads to an orange precipitate of hydrazones (Kataoka et al., 1998). High performance liquid chromatography with UV detection (HPLC-UV) has been optimized to analyze these aldehydes with a preliminary derivatization step of the aldehydes as their 2,4-dinitrophenylhydrazine derivatives (Wilkes et al., 2000) generally with a wavelength of 360 nm (Jacob, Denis, & Foster, 1998; Pichard et al., 2005). The wavelength can be chosen in a range from 330 to 580 nm in function of the aldehydes (INRS, 2004a). The range from 330 to 390 nm allows generally to obtain the most part of the aldehydes (for example the maximal absorption wavelength of acetaldehyde is 350 nm and 390 nm for furfural). Although HPLC-UV method is very commonly used for the volatile carbonyl compounds, the identification is not easy (formation of both syn and anti forms, difficulties in mixtures analysis). Besides, the preparation of 2,4-DNPH derivatives requires strong acidic

conditions that may cause undesirable reactions, such as decomposition of carbohydrates, which can trouble the analysis. This kind of method has been widely used (Da Cunha Veloso, Da Silva, Vieira Santos, & De Andrade, 2001), even now in qualitative measurements but less and less used for quantifying because of its lack of repeatability.

Others colorimetric methods are individually used for certain aldehydes like formaldehyde which can be analyzed after reaction with chromotropic acid by absorption spectrophotometry because the purple complex formed absorbs at 580 nm (INERIS, 2004). However, these methods can not be apply to all the aldehydes as it is possible with 2,4-DNPH.

Others methods have been developed and also used the derivatization of aldehydes but as their benzyloxime or thiazolidine derivatives. These methods analyze the derivatives with gas chromatography (GC) coupled with specific detector. The benzyloxime or thiazolidine derivatives are very selectively and sensitively detectable by GC-NPD (nitrogen phosphorus detection) (Yasuhara & Shibamoto, 1995). Cysteamine method for aldehyde analysis is simple and specific. Indeed, volatile aldehydes react with cysteamine to form thiazolidines derivatives under mild conditions of neutral pH and room temperature (Fig. 1). The derivatization is nearly complete, fast (15 min) and reaches 95% (Shibamoto & Horiuchi, 1997). There is only one derivative for each aldehyde and an excess of reagent does not interfere with GC analysis. Another detector system can also be coupled after the GC separation. It is the flame photometric detection (FPD) which allows a selective and sensitive determination of saturated and unsaturated aldehydes. The detection limits on a panel of various standard aldehydes at a signal-to-noise ratio of 3 were from 4 to 100 pg injected (Kataoka et al., 1998). GC/MS (mass spectrometry) analysis can also be used, especially to understand the structures of the derivatives. A molecular ion peak $[M]^+$ was observed for each derivative and others decomposition peaks were characteristic for the elucidation like $[M-CH_3]^+$, $[M-SCH_2]^+$, $[M-SCH_2CH_2]^+$, $[M-SCH_2CH_2NH]^+$ and $[M-SCH_2CH_2NHCH]^+$ (Kataoka et al., 1998).

Recently, a new procedure of derivatization was developed for the microscale determination of aldehydes with SPME, especially for aliphatic aldehydes. It consists in a derivatization on-fiber by exposing the fiber to an aqueous solution of (2,3,4,5,6-pentafluorophenyl)hydrazine (PFPH) (Stashenko, Puertas, Salgar, Delgado, & Martinez, 2000). Using GC/MS method after SPME, the mass fragments obtained are very specific according to the aldehydes (Rochat & Chaintreau, 2005). *O*-(2,3,4,5,6-pentafluoroben-

zyl)hydroxylamine oximes can also be used (PFBO) (Hsu et al., 1999) but molecular ions with this type of derivatization are often missing which limits the specificity. PFPH derivatization seems to be very specific thanks to a more abundant molecular ion. These new types of derivatization are very efficient but only carried out at microscale and with SPME headspace technique (Stashenko & Martinez, 2004). These types of derivatization might be developed for a wider use in food analysis in general and for other extraction methods (Stashenko, Ferreira, Sequeda, Martinez, & Wong, 1997).

With food aroma extraction techniques, the derivatization is not obliged when all the aroma compounds and not especially aldehydes are studied. The detectors used can be various and the most frequently used are MS and FID (Fullana, Carbonell-Barrachina, & Sidhu, 2004b). When particular aldehydes are studied, especially in air analysis, others detectors coupled to GC can be used like pulsed Helium Ionization Detector (pHID). This detector overcomes the insensitivity of FID in the case of the study of ambient formaldehyde (Hopkins et al., 2003). Mass spectrometry was (Josephson, Lindsay, & Stuiber, 1987) and is, especially now, used for the quantification of volatiles in fish and among them aldehydes (Milo & Grosch, 1996; Fukami et al., 2002). This analytical method allows to quantify aldehydes in $\mu\text{g kg}^{-1}$ concentrations.

Finally, aldehydes can be analyzed by nuclear magnetic resonance (NMR). (*E*)-2-alkenals, *n*-alkanals, (*E,E*)-2,4-alkadienals can be particularly measured with this method (Guillén & Ruiz, 2005) but the determination is again qualitative.

3. Identification of volatile aldehydes recovered in smoked fish flesh

Table 1 presents a list of aldehydes the most frequently found in smoked fishes. Table 1 was carried out from seven main teams of scientists, then with different objectives in the investigation of aldehydes. Guillén and Errecalde (2002) and Guillén et al. (2006) identified by SPME the different volatiles present in smoked swordfish, cod, trout and bream. Cardinal, Berdagué, Dinel, Knockaert, and Vallet (1997) investigated the volatile components of smoked salmon in order to characterize four processes of smoking. Jørgensen, Huss, and Dalgaard (2001) and Joffraud, Leroi, Roy, and Berdagué (2001) worked on spoiled smoked salmon. Jørgensen et al. (2001) studied volatile components like aldehydes which are responsible of off-flavours in smoked salmon spoiled with bacteria. These two last references attest the presence of volatiles aldehydes in smoked fish but can not surely insure the origin of the aldehydes (lipid oxidation, wood smoke or production of microorganisms, or both). Headspace extractions are used in the whole works. This extraction method is used especially for the extraction of volatile components with a low boiling point. The group of volatile aldehydes identified corresponds to these properties. Indeed, volatile aldehydes with

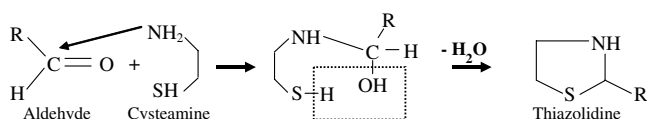


Fig. 1. Reaction mechanism of cysteamine and aldehydes.

Table 1
Volatile aldehydes found in smoked fish

Aldehydes	Smoked fishes				
	Trout	Bream	Salmon	Cod	Swordfish
Ethanal (acetaldehyde)	X ⁽⁶⁾				
butanal			X ⁽³⁾		
3-Methylbutanal			X ^(2,3,4,7)		
2-Methylbutanal			X ⁽⁴⁾		
2-Butenal			X ⁽²⁾		
2-Methyl-2-butenal			X ⁽⁴⁾		
Pentanal			X ⁽²⁾		
(<i>E</i>)-2-Pentenal			X ⁽³⁾		
2-Furancarboxaldehyde (furfural)			X ^(2,3,7)	X ⁽¹⁾	
5-Methyl-2-furancarboxaldehyde (5-methyl-furfural)			X ^(2,3,7)	X ⁽¹⁾	
Benzaldehyde	X ⁽⁶⁾	X ⁽⁶⁾	X ^(3,7)	X ⁽¹⁾	X ⁽¹⁾
4-Methylbenzaldehyde			X ⁽²⁾		
Benzeneacetaldehyde	X ⁽⁶⁾	X ⁽⁶⁾	X ⁽⁷⁾		X ⁽¹⁾
Hexanal	X ⁽⁶⁾	X ⁽⁶⁾	X ^(2,3,4)		
4-Hydroxy-2-(<i>E</i>)-hexenal			X ⁽⁵⁾		
Heptanal	X ⁽⁶⁾		X ^(2,7)		
2-Heptenal		X ⁽⁶⁾			
Octanal			X ⁽²⁾		
Nonanal	X ⁽⁶⁾	X ⁽⁶⁾	X ^(2,7)		
Decanal	X ⁽⁶⁾	X ⁽⁶⁾	X ^(2,4)	X ⁽¹⁾	X ⁽¹⁾
2,4-Hexadienal			X ⁽⁷⁾		
2,4-Heptadienal			X ⁽⁷⁾		
2,4-Hecadienal		X ⁽⁶⁾			
2-Decenal	X ⁽⁶⁾		X ^(2,4,7)	X ⁽¹⁾	X ⁽¹⁾
2-Undecenal	X ⁽⁶⁾				
Dodecanal	X ⁽⁶⁾	X ⁽⁶⁾		X ⁽¹⁾	
Tetradecanal	X ⁽⁶⁾	X ⁽⁶⁾		X ⁽¹⁾	X ⁽¹⁾
Hexadecanal	X ⁽⁶⁾	X ⁽⁶⁾	X ⁽⁷⁾		X ⁽¹⁾
(1 <i>H</i>)-Pyrrole-2-carboxaldehyde			X ⁽⁷⁾	X ⁽¹⁾	X ⁽¹⁾

X = presence, in brackets are reported the numbers corresponding to the scientific teams who have worked on the respective kind of smoked fish (1: Guillén et al. (2006); 2: Cardinal et al. (1997); 3: Jørgensen et al. (2001); 4: Joffraud et al. (2001); 5: Munasinghe et al. (2003); 6: Guillén and Errecalde (2002); 7: Varlet et al., 2006, 2006; Varlet et al. (2006)).

a diversity of the structure of molecules (aliphatic, aromatic, straight chain, branched chain) from C4 to C16 in smoked fishes are studied. Munasinghe et al. (2003) were only focused on 4-hydroxy-(*E*)-2-hexenal and used liquid–liquid extraction with dichloromethane. Finally, Varlet et al. (2006) studied odour-active compounds of smoked salmon with SDE extraction. This method allows to obtain volatile compounds with higher boiling point than headspace extractions, but for the aldehydes the results are similar to headspace methods.

Among the volatile aldehydes recovered in smoked fish, several approaches can be considered. A first sorting might be carried out on the basis of their natural origin that is to say if they come from wood smoke or fish flesh. Indeed, there are some compounds met in smoked fishes which come firmly from wood smoke because they are not met in the unsmoked fish flesh and others known to make part of volatile aldehydes involved only in fish metabolism. However, this sorting can be difficult because certain alde-

hydes could be created by the extraction method and the smoking method (Maillard compounds) or are present in small quantities in unsmoked fish flesh. There are also sometimes ubiquitous compounds that is to say, present in wood smoke and unsmoked fish flesh as hexanal. Another characteristic can be used to distinguish volatile aldehydes of smoked fish based on the structure of the aldehydes. Indeed, the aromatic or aliphatic forms of the aldehydes are deeply linked to the pathways of creation. Aromatic aldehydes mainly come from the wood smoke through thermal degradation and aliphatic aldehydes mainly come from the fish flesh through lipid oxidation (Cardinal et al., 1997).

4. Volatile aldehydes of smoked fish coming from Maillard and Strecker reactions

4.1. Maillard reaction mechanism

In smoked fish, the origin of aromatic aldehydes could be attributed to enzymatic reactions but especially to thermal degradations as Maillard reactions (Fig. 2). These reactions occur during thermal process (cooking, smoking, roasting, etc.) and are facilitated when temperature raises (Ames, 1998; Fernandez, Kerverdo, Duñach, & Lizzani-Cuvelier, 2002). The process consists in the formation of a non-enzymatic bond between the carbonyl group of an aldose or ketose and the free amino group of an amino

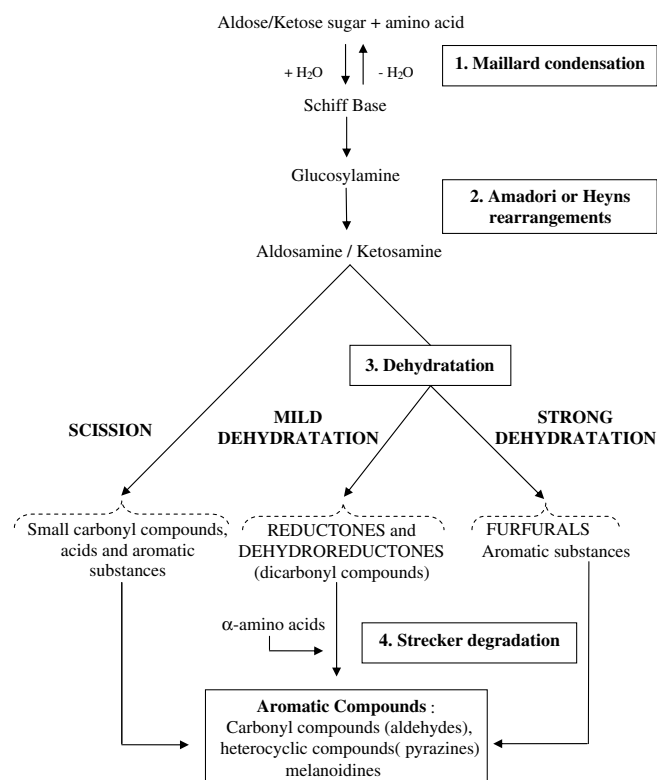


Fig. 2. An example of reaction of Maillard: Principle and different steps for aldehydes formation.

acid. As result, a product very unstable in aqueous solution, by the loss of water molecule can lead to Schiff base. These reactions are reversible. However, a non-reversible isomerisation of Schiff base gives glucosylamines named Amadori products (aldosamines) or Heyns products (ketosamines) (Yaylayan & Huyghues-Despointes, 1994). Thanks to rearrangements, these compounds are more stabilized. The products of these rearrangements can also be transformed. Three cases are possible: a break in the molecule, a soft dehydration or a strong dehydration. The break leads to small carbonylated or acidic molecules (Weenen, 1998). Dehydrations are very important reactions because they produce others intermediaries which are precursors of a lot of aldehydes. Indeed, a sweet dehydration transforms Amadori or Heyns intermediaries in reductones or dehydroreductones which are dicarbonyl compounds. When the dehydration is stronger, reductones and dehydroreductones can form rings and dehydrate to form furfurals and furans very present in liquid smoke used for food flavourings (Guillén & Manzanos, 2005; Simon, De La Calle, Palme, Meier, & Anklam, 2005).

Reductones and dehydroreductones can produce also others aldehydes by retro-aldol reaction reactions which is the reverse of an aldol condensation. Aldol condensation allows the addition of two carbonyl compounds with the fixing of the α -carbon of one on the carbonyl carbon of the other. This product can easily dehydrate in order to form unsaturated carbonyl compounds. In retro-aldol reaction, the unsaturated carbonyl group is hydrated at the double bond to finally form two smaller carbonyl molecules. These reactions are very important and can explain the origin of numerous aldehydes in smoked fish (Josephson & Lindsay, 1987).

4.2. Possibility of aldehydes formation during Maillard reactions

A lot of furannic aldehydes are also found in smoked fishes in important quantities as furfural (2-furancarboxaldehyde) and 5-methyl-2-furancarboxaldehyde (5-methylfurfural) (Guillén et al., 2006; Varlet et al., 2006). These compounds could come only from the wood smoke or could be generated between the wood smoke and the fish flesh through Maillard and Strecker reactions. Indeed, the possibility that furfural and 5-methylfurfural could come from Maillard reactions during smoking process between fish components has not been proven. In wood smoke, these generations are mainly due to the separation of water from pentoses which are degradation products of hemicelluloses (Jira, 2004) whereas Maillard and Strecker reactions have not been undoubtedly proven in wood smoke. However, these pathways could be involved because several products indicators of these reactions are found in liquid smoke and smoked fishes such as pyrazines (Guillén & Ibargoitia, 1996; Guillén, Manzanos, & Ibargoitia, 2001; Varlet et al., 2006). These compounds could be Maillard and Strecker aldehydes created during smoking

and could derive from wood smoke (Cardinal et al., 1997; Maga, 1987). Recently, the analysis of the pyrolysis profile of oak has permitted to detect pyrone and furan structures in the smoke (Nonier et al., 2005). These products have been attributed to Maillard reactions. The *N*-glucoside derivative formed by the reaction of sugars with certain amino compounds leads to an unstable Amadori derivative after several rearrangements which finally generates aromatic compounds with enolone structure when it is heated. The composition in carbohydrates of wood can explain the possibility of the creation of such compounds (Guillén et al., 2001). Indeed, wood is composed of three main polyoses: cellulose (homopolymer of D-glucose with β 1–4 links), hemicellulose (homo or heteropolysaccharides) and lignin. The thermal breakdown of cellulose forms firstly glucose and secondly acetic acid and homologs, water, a few furans and phenolic compounds. The thermal breakdown of hemicellulose produces furans and carboxylic acids. Finally, lignin, whose structure is deeply linked to two main rings (guaiacyl-propan ring and syringyl-propan ring) leads by its combustion to phenolic compounds and phenolic ethers with little amounts of carbonyl, acidic and alcoholic compounds (Sainclivier, 1985; Miler & Sikorski, 1990). Reductor sugars which initiate Maillard reaction are thus very present in wood. The necessary high temperature is also reached by the pyrolysis of the wood. The only disadvantage concerns the essential nitrogen source which is not very clear. Indeed, in the element composition of wood without bark, a ratio of 0.2% of nitrogen by report to the dry matter is observed. This nitrogen is in very weak quantity and depends of the wood type (Alén, Kuoppala, & Oesch, 1996; Alén, Oesch, & Kuoppala, 1995; Maga, 1987). Nitrogen occurrence during wood combustion is obligatory because nitrogen oxides (NO_x) and ammonia emissions are found in wood combustion (Welfring & Weidenhaupt, 2000). NO_x are known to be produced during wood combustion from three pathways. Firstly, NO_x can be created from ambient nitrogen (N_2) and oxygen at very high temperatures (>1300 °C) obtained very close to the flames (Welfring, Weidenhaupt, Offermann, & Gouy, 2000). The second pathway involves a spontaneous formation in the flames thanks to hydrocarbure radicals. However, these conditions are never reached in smoking process because flames production must be avoided in order to have an adequate wood smoke. The third pathway is the most important and involves the nitrogen of the wood even if atmospheric nitrogen seems also to contribute to Maillard reactions in wood smoke. Nitrogen in wood is present under amine and proteins forms and with oxygen, can form NO_x at temperatures two times lower than the two first pathways (Welfring & Weidenhaupt, 2000; Welfring et al., 2000). Thus, all the conditions are met to allow the aldehydes formation through Maillard and Strecker reaction.

Nevertheless, Strecker degradation and Maillard reactions can also occur during the smoking process between

the components of the fish flesh or between sugars of the wood smoke and amino acids of the fish flesh. Indeed, the quantity of carbohydrates in fish flesh is very low. Therefore, Maillard and Strecker reactions could occur more easily between very abundant sugars of wood smoke and the most important nitrogen source during smoking process that is to say amino acids of the fish flesh. Then, it is difficult to distinguish volatile aldehydes coming from the wood smoke and those coming from the fish flesh. Nevertheless, they can be assessed in function of their origin by comparing individually the quantities of aldehydes present in wood smoke to those present in smoked fish flesh. Besides, the possibility of Maillard and Strecker aldehydes formation during smoking process without involving wood smoke is strengthened by the study of methional case. Methional (3-methylthiopropional) generally comes from methionine via Strecker degradation and is not present in wood smoke (Maga, 1987) but can be identified in unsmoked seafood flesh like lobster tail (Lee, Suriyaphan, & Cadwallader, 2001), crab (Chung & Cadwallader, 1994; Chung, 1999), shells (Pennarun, Prost, & Demaimay, 2002; Chung, Yung, Ma, & Kim, 2002), turbot (Sérot, Regost, Prost, Robin, & Arzel, 2001) or anchovy (Triqui & Reineccius, 1995). It is important to notice that sometimes the matrix is cooked-processed but sometimes, the product is raw and Maillard and Strecker compounds are also present in both cases. This illustrates the fact that

Maillard and Strecker reactions are possible without taking into account wood smoke effects. These compounds could be formed from the amino groups of amino acids and carbonyl groups of reductor sugars presents in small quantities in fish flesh under temperatures of smoking or during the extraction step if the temperature is too important. However, even if sometimes Maillard and Strecker products have been recovered in fish flesh, several studies have permitted to conclude that in general, cyclic compounds such as furfural, 1H-pyrrole-carboxaldehyde, benzaldehyde, 5-methylfurfural (reported in Table 1) and all the derived molecules come from the wood smoke (Cardinal et al., 1997; Guillén et al., 2006; Varlet et al., 2006). Moreover, it is also commonly admitted that Maillard reactions lead to products having caramellic, baked, cooked even roasted odorant descriptors. These descriptors are very often in adequation with those found for wood smoke odorants.

4.3. Volatile Maillard aldehydes in smoked fishes

Maillard compounds such as benzaldehyde and derived compounds are present in smoked fish. However, it is difficult to say if these molecules come from the wood smoke or fish flesh because the two pathways are possible. Indeed, as it is reported in Tables 2 and 3, benzaldehyde and derived compounds have been found in unsmoked fish flesh

Table 2
Occurrence of benzaldehyde and methylated derivatives in seafood products

Compound	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
Benzaldehyde	Fruity, almond, nutty, creamy	SDE	Mussel juices	1524 (Stabilwax)	Cros et al. (2004)
		RPDE	Cooked mussels	1539 (DB-Wax)	Le Guen et al. (2000b)
		SDE	Crab	1530 (Supelcowax 10)	Chung (1999)
		SDE	Scallops	1530 (Supelcowax 10)	Chung et al. (2001, 2002)
		Headspace	Oysters	1525 (DB-Wax)	Piveteau et al. (2000)
		Headspace	Canned salmon	1538 (Supelcowax 10)	Girard and Durance (2000)
		SDE	Anchovy, herring, shrimp	1522 (Supelcowax 10)	Cha and Cadwallader (1995)
		RPDE	Anchovy	960 (DB5-MS)	Triqui and Reineccius (1995)
4-Methylbenzaldehyde	Almond	Headspace	Smoked salmon	1080 (DB5-MS)	Cardinal et al. (1997)
		SDE	Scallops	1654 (Supelcowax 10)	Chung et al. (2001)
4-Ethylbenzaldehyde	Fruity, anised	RPDE	Turbot	1728 (DB-Wax)	Sérot et al. (2001)
			Cooked mussels	1752 (DB-Wax)	Le Guen et al. (2000b)
		SDE	Scallops	1714 (Supelcowax 10)	Chung et al. (2001, 2002)
3,4-Dimethyl benzaldehyde	Not described	SDE	Crab	1790 (Supelcowax 10)	Chung (1999)
3-Methylbenzaldehyde	Not described	SDE	Scallops	1624 (Supelcowax 10)	Chung et al. (2001, 2002)

LRI: linear retention indices, SDE: simultaneous steam distillation – solvent extraction, RPDE: reduce pressure distillation extraction.

Table 3
Occurrence of benzaldehyde and methylated derivatives in wood smoke

Compound	Extraction – analysis method	Wood matrix used	References
Benzaldehyde	2,4-DNPH, HPLC/UV	Oak, pine, eucalyptus	Hedberg et al. (2002)
	LLE, GC/MS	Thyme	Guillén and Manzanos (1999)
	Not described	Wood	Maga (1987)
<i>o</i> -Tolualdehyde	2,4-DNPH, HPLC	Oak, pine, eucalyptus	Hedberg et al. (2002)
<i>p</i> -Tolualdehyde	2,4-DNPH, HPLC	Oak, pine, eucalyptus	Hedberg et al. (2002)
2,5-Dimethylbenzaldehyde	2,4-DNPH, HPLC	Oak, pine, eucalyptus	Hedberg et al. (2002)

2,4-DNPH: 2,4-dinitrophenylhydrazine, HPLC/UV: high performance liquid chromatography coupled to ultraviolet detector, LLE: liquid–liquid extraction, GC/MS: gas chromatography coupled to mass spectrometric detector.

and also in wood smoke (Hedberg et al., 2002). Quantities recovered, possibilities of Maillard reactions and cyclic structures can make us to say that these molecules recovered in smoked fishes come from wood smoke (Guillén & Errecalde, 2002; Guillén & Ibargoitia, 1999; Maga, 1987). In fact, it is mainly produced by combustion process (Kataoka et al., 1998) like wood combustion (Maga, 1987). Benzaldehyde and derivatives could also be produced, in a weak part, by oxidation or by photochemical degradation of toluene or others hydrocarbons like styrene or methylstyrene. These aromatic hydrocarbons can derive from wood smoke and carotenoids (Josephson, Lindsay, & Stuber, 1991a). Finally, benzaldehyde and derivatives could also be adsorbed in the flesh fish through its environment because these molecules are lipophilic and can easily cross the biological membranes.

The cyclic aldehydes from wood smoke can be easily absorbed by the fish flesh which is rich in lipids. Indeed, the aromatic structure of the most part of Maillard aldehydes gives to themselves lipophilic properties. Thus, furfurals and aldehyde phenolic compounds (Lustre & Issenberg, 1969) present in important quantities in wood smoke (Guillén & Ibargoitia, 1999; Guillén & Manzanos, 1997; Guillén & Manzanos, 1999; Hedberg et al., 2002) are recovered in smoked fish flesh. Furfurals are known to derive from the strong dehydration of glucosylamines (aldosamine/ketosamine) in Maillard reaction (Fig. 2).

4.4. Strecker degradation mechanism

Reductones and dehydroreductones from Maillard reaction have also another interest due to their dicarbonylated structure. Combined with α -amino acids, dicarbonylated compounds are the seat of Strecker degradation (Rizzi, 1999). This degradation leads to an aldehyde that has one less carbon than the original amino acid and α -amino carbonyl. This reaction consists in a decarboxylation of the Schiff base formed after dehydration, followed by the rehydration of the molecule. Thus, it has been established for example that 2-methylpropanal (isobutyraldehyde) comes from valine (Scarpellino & Soukup, 1993). Strecker aldehydes are very present in wood smoke (Maga, 1987) even if Strecker degradation is not the only mechanism of generation for these compounds.

4.5. Volatile Strecker aldehydes in smoked fishes

The origin of several aldehydes reported in Table 4 are well known. Ethanal (acetaldehyde) from alanine, 2-methyl-2-butenal from isoleucine, 3-methylbutanal (isovaleraldehyde) from leucine, phenylacetaldehyde (benzeneacetaldehyde) from phenylalanine are volatile aldehydes coming from Strecker degradation (Lee et al., 2001) through Maillard reactions. Formed by the action between α -dicarbonyl compound and an amino acid, all these Strecker aldehydes are very present in many seafood products (Table 4). The attribution of a single origin to these compounds is difficult because even if a lot of Strecker aldehydes are present in wood smoke, another part seems to be linked to the smoking process or to be accumulated by the fish from its environment.

5. Volatile aldehydes of smoked fish coming from lipid oxidation

5.1. Lipid oxidation: aliphatic aldehydes formation

Aliphatic aldehydes are commonly known to derive from lipid oxidation which occurs in fish flesh (Sérot, Regost, & Arzel, 2002). Even if small quantities of aliphatic aldehydes like butanal, pentanal, hexanal have been recovered in wood smoke in weak quantities (Maga, 1987; Guillén & Ibargoitia, 1999; Guillén & Errecalde, 2002; Hedberg et al., 2002), the most part of aliphatic volatile aldehydes in smoked fish comes from the fish flesh lipid oxidation under smoking process conditions. The important quantities of *n*-alkanals found in smoked fish flesh (from 1.32 equiv of dodecane for heptanal to 34.82 μ g equivalents of dodecane for hexadecanal per 100 g in smoked salmon) could be related to the important amount of their lipidic precursors found in unsmoked fish flesh (Varlet et al., 2006). Indeed, it is commonly admitted that saturated or unsaturated aldehydes in fish flesh come from the degradation of the fatty acids and triglycerides by autoxidation (Lindsay, 1994; Farmer, McConnell, & Graham, 1997; Min & Lee, 1999). It is important to notice that autoxidation is a non-enzymatic autocatalytic oxidation reaction resulting in the formation of hydroperoxides. Nevertheless, autoxidation of

Table 4
Occurrence of several Strecker aldehydes in seafood products

Compound	Precursors	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
Phenylacetaldehyde	Phenylalanine	Floral	SDE	Anchovy	1634 (Supelcowax 10)	Cha and Cadwallader (1995) Chung (1999)
			SDE	Crab	1652 (Supelcowax 10)	
			SDE	Scallops	1651 (Supelcowax 10)	Chung et al. (2002)
			RPDE	Anchovy	1046 (DB5-MS)	Triqui and Zouine (1999)
3-Methylbutanal	Leucine	Herbaceous, pungent, cereal, chocolate	Headspace	Smoked salmon	652 (DB5-MS)	Cardinal et al. (1997)
			Headspace	Canned salmon	917 (Supelcowax 10)	Girard and Durance (2000)
			Headspace RPDE	Dried squids Anchovy	622 (DB1) 652 (DB5-MS)	Kawai et al. (1991) Triqui and Zouine (1999)
			Headspace	Crab meat	911 (supelcowax 10)	Matiella and Hsieh (1990)
			Headspace	Canned salmon	2453 min (Ultra 2)	Girard and Nakai (1991)
			SDE, RPDE, Headspace SDE	Lobster tail Anchovy, herring, shrimps	932 (DB-Wax), 651 (DB5-MS) 922 (Supelcowax 10)	Lee et al. (2001) Cha and Cadwallader (1995)
			SDE	Mussel juices	1082 (Stabilwax)	Cros et al. (2004)
2-Methyl-2-butenal	Isoleucine	Green, fruity	SDE	Crab	1097 (Supelcowax 10)	Chung (1999)
			SDE	Scallops	1096 (Supelcowax 10)	Chung et al. (2002)
			SDE	Scallops	1096 (Supelcowax 10)	Chung et al. (2001)
			RPDE	Cooked mussels	1101 (DB-Wax)	Le Guen et al. (2000b)
			SDE	Anchovy	1094 (Supelcowax 10)	Cha and Cadwallader (1995)
			3-(Methylthio)propanal	Methionine	Cooked potatoe, boiled potatoe	Headspace, SDE, RPDE SDE
SDE	Scallops	1461 (Supelcowax 10)				Chung et al. (2002)
SDE RPDE	Mussel juices Oysters	1482 (StabilWax) 1451 (DB-Wax)				Cros et al. (2004) Pennarun et al. (2002)
SDE	Crab	1463 (Supelcowax 10)				Chung (1999)
RPDE RPDE	Turbot Anchovy	1460 (DB-Wax) 911 (DB5-MS)				Sérot et al. (2001) Triqui and Reineccius (1995)
SDE	Cooked mussels	1473 (DB-Wax), 1477 (DB-Wax)				Le Guen et al. (2000a, 2000b)

LRI: linear retention indices, SDE: simultaneous steam distillation – solvent extraction, RPDE: reduce pressure distillation extraction.

unsaturated fatty acids can be initiated by a physical catalyst such as light, or by enzymes coming from the fish flesh or microorganisms presents in fish flesh. These hydroperoxides are often transformed in secondary oxidation products as carbonyl compounds. Then, autoxidation of polyunsaturated fatty acids and triglycerides in fish

leads to aldehydes which can produce off-flavours according to their concentration but also limit the self-life of the fish. Flavour and odours developed from the autoxidation of lipids give to food globally rancid or oxidized descriptors, depending on the oxidation level reached by the food. One of the aims of smoking process is to prevent

the lipid oxidation by adding to the food some antioxidants compounds presents in wood smoke as phenolic compounds.

Lipid autoxidation is based on fundamental mechanisms involving free-radical chain reactions. Hydroperoxides are formed thanks to the reaction of unsaturated fatty acids and triglycerides with oxygen by a free-radical process involving an initiation, propagation and termination stage (Frankel, 1983; Grosch, 1987). They can also be formed from saturated and monounsaturated fatty acids or esters.

The lipid oxidation begins with an attack of molecular oxygen on the double bonds of polyunsaturated fatty acids (PUFA) and triglycerides which generates free-radicals of PUFA. The PUFA are very sensitive towards molecular oxygen which can be produced thanks to transition metals such as iron (the most present in seafoods) especially haem iron. It can interact with dioxygen to lead to molecular oxygen or hydroxyl radical. The initiation of lipid oxidation with molecular oxygen is autoxidation. Another possible initiator of lipid oxidation is singlet oxygen. Some molecules (sensitizers) are able to absorb light and be converted to a high excited state. These sensitizers can react with molecular oxygen in order to form singlet oxygen (an excited high energy state of molecular oxygen). Singlet oxygen interacts directly on the double bond of PUFA and causes the creation of others degradation products. The oxidation caused by singlet oxygen is photooxidation. Finally, enzymes can incorporate one molecule of oxygen at a position of unsaturated fatty acids. In this case, the oxidation is qualified by enzymatic oxidation. Indeed, enzymes such as lipoxygenase, cyclooxygenase, peroxidase and microsomal enzymes can act as initiators of lipid oxidation in fish tissues. Under all these possible catalysts, free radicals can be produced from unsaturated fatty acids and triglycerides (Hultin, 1994). Differences of volatile carbonyl compounds produced between photooxidized fish and autoxidized or metal-induced oxidized fish have been established. In photooxidized fish, alkanals and 2-alkenals are more present whereas 2,4-alkadienals are more present in autoxidized fish. Nevertheless, hydroperoxides are formed oxidation induced by enzymes, by temperature, by metal or photo-induced oxidation of PUFA and are the main source of off-flavours developed by lipid oxidation.

Hydroperoxides are very unstable and break down readily into many volatile and non-volatile products (Pokorný, 1987). The decomposition products includes: aldehydes, ketones, alcohols, acids, hydrocarbons, lactones, furans and esters. Alkyl hydroperoxides, allyl hydroperoxides and fatty ester hydroperoxides decomposition are accompanied by the formation of a lot of products such as carbonyls compounds, alcohols and acids, esters (Frankel, 1983). Indeed, during hydroperoxide decomposition, secondary alkoxy radicals may cleave to form aldehydes. This reaction is also known as β -scission or elimination (Fig. 3). From the aldehyde, a polymerization can occur or, with dioxygen, it can give alkanes, aldehydes with short chain,

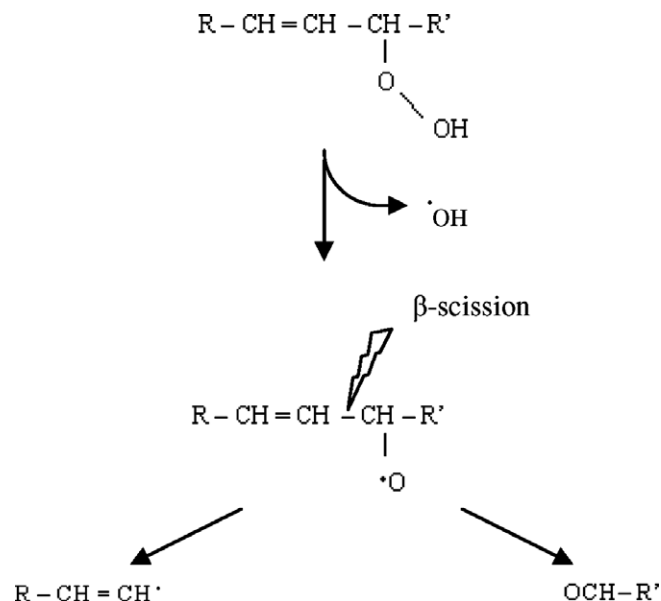


Fig. 3. β -scission of hydroperoxides.

acids and epoxides. From the free radical, several routes are possible: firstly, to keep up the autoxidation, secondly, transformation in hydrocarbons and thirdly, with dioxygen, it can give alkanes, alcohols and aldehydes. A lot of studies have been investigated about the decomposition and the role of hydroperoxides in order to better understand the creation of odours in food (Grosch, 1987; Lindsay, 1994). Indeed, aliphatic aldehydes are the most important breakdown products of hydroperoxides. Table 5 shows the possible origin to some aldehydes obtained from the oxidation of oleic, linoleic, linolenic and arachidonic

Table 5
Possible origin to several aldehydes deriving from PUFA

Fatty acid	Hydroxide position and on hydroperoxides	Aldehyde
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

Table 6
Occurrence of several *n*-alkanals in seafood products

Compound	Main precursors	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
Butanal	Oleic, linoleic acids	Pungent, green	SDE	Anchovy, herring	874 (Supelcowax 10)	Cha and Cadwallader (1995) Girard and Durance (2000)
			Headspace	Canned salmon	877 (Supelcowax 10)	
Pentanal	<i>n</i> – 6 PUFA	Chemical, wine, sweet, fruity	RPDE	Cooked mussels	980 (DB-Wax)	Le Guen et al. (2000a, 2000b) Chung et al. (2001, 2002) Girard and Durance (2000) Chung (1999) Matiella and Hsieh (1990) Cardinal et al. (1997)
			SDE	Scallops	>1000 (Supelcowax 10)	
			Headspace	Canned salmon	981 (Supelcowax 10)	
			SDE	Crab	1000 (Supelcowax 10)	
			Headspace	Crab meat	982 (Supelcowax 10)	
			Headspace	Smoked salmon	697 (DB5-MS)	
Hexanal	<i>n</i> – 3, <i>n</i> – 6 and <i>n</i> – 9 PUFA	Grass cut, green, pungent	SDE	Mussel juices	1073 (Stabilwax)	Cros et al. (2004) Sérot et al. (2001) Le Guen et al. (2000a, 2000b) Chung et al. (2001, 2002) Prost et al. (1998) Cardinal et al. (1997) Lee et al. (2001) Chung (1999) Piveteau et al. (2000) Girard and Durance (2000) Triqui and Reineccius (1995) Matiella and Hsieh (1990) Triqui and Zouine (1999) Cha and Cadwallader (1995)
			RPDE	Turbot	1080 (DB-Wax)	
			SDE, RPDE	Cooked mussels	1088 (DB-Wax), 1089 (DB-Wax)	
			SDE	Scallops	1086 (Supelcowax 10)	
			SDE	Turbot	1090 (DB-Wax)	
			Headspace	Smoked salmon	800 (DB5-MS)	
			Headspace, SDE, RPDE	Lobster tail	1083 (DB-Wax), 808 (DB5-MS)	
			SDE	Crab	1086 (Supelcowax 10)	
			Headspace	Oysters	1091 (DB-Wax)	
			Headspace	Canned salmon	1092 (Supelcowax 10)	
			RPDE	Anchovy	798 (DB5-MS)	
			Headspace	Crab meat	1086 (Supelcowax 10)	
			RPDE	Anchovy	803 (DB5-MS)	
			SDE	Anchovy, herring	1081 (Supelcowax 10)	
Heptanal	Oleic, linoleic acid	Herbaceous, fishy, fatty, pungent	SDE	Mussel juices	1180 (Stabilwax)	Cros et al. (2004) Sérot et al. (2001) Le Guen et al. (2000b) Chung et al. (2001, 2002) Cardinal et al. (1997) Girard and Durance (2000) Matiella and Hsieh (1990) Cha and Cadwallader (1995)
			RPDE	Turbot	1198 (DB-Wax)	
				Cooked mussels	1195 (DB-Wax)	
			SDE	Scallops	1189 (Supelcowax 10)	
			Headspace	Smoked salmon	900 (DB5-MS)	
			Headspace	Canned salmon	1195 (Supelcowax 10)	
			Headspace	Crab meat	1194 (Supelcowax 10)	
			SDE	Herring	1184 (Supelcowax 10)	
Octanal	Oleic, linoleic acid	Grass, vert, fruité, citron	SDE	Mussel juices	1277 (Stabilwax)	Cros et al. (2004) Sérot et al. (2001) Le Guen et al. (2000a, 2000b)
			RPDE	Turbot	1296 (DB-Wax)	
			SDE, RPDE	Cooked mussels	1301 (DB-Wax), 1303 (DB-Wax)	

(continued on next page)

Table 6 (continued)

Compound	Main precursors	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
Nonanal	Oleic, linoleic acid	Green, tallow, citrus, fatty, soapy	SDE	Scallops	1293 (Supelcowax 10)	Chung et al. (2001, 2002)
			Headspace	Canned salmon	1323 (Supelcowax 10)	Girard and Durance (2000)
			RPDE	Oysters	1289 (DB-Wax)	Pennarun et al. (2002)
			Headspace	Oysters	1298 (DB-Wax)	Piveteau et al. (2000)
			Headspace	Lobster tail	1263 (DB-Wax), 1005 (DB5-MS)	Lee et al. (2001)
			Headspace, SDE, RPDE	Smoked salmon	1004 (DB5-MS)	Cardinal et al. (1997)
			SDE	herring	1289 (Supelcowax 10)	Cha and Cadwallader (1995)
			SDE	Mussel juices	1387 (Stabilwax)	Cros et al. (2004)
			RPDE	Cooked mussels	1407 (DB-Wax)	Le Guen et al. (2000b)
			Headspace	Smoked salmon	1106 (DB5-MS)	Cardinal et al. (1997)
Decanal	<i>n</i> – 9 PUFA	Green, marine, cucumber, floral	Headspace	Canned salmon	1409 (Supelcowax 10)	Girard and Durance (2000)
			SDE	Scallops	1398 (Supelcowax 10)	Chung et al. (2001, 2002)
			SDE	Crab	1399 (Supelcowax 10)	Chung (1999)
			RPDE	Oysters	1392 (DB-Wax)	Pennarun et al. (2002)
			RPDE	Anchovy	1109 (DB5-MS)	Triqui and Reineccius (1995)
			SDE	Herring	1393 (Supelcowax 10)	Cha and Cadwallader (1995)
			SDE	Mussel juices	1497 (Stabilwax)	Cros et al. (2004)
			RPDE	Turbot	1510 (DB-Wax)	Sérot et al. (2001)
Decanal	<i>n</i> – 9 PUFA	Green, marine, cucumber, floral	Headspace	Canned salmon	1505 (Supelcowax 10)	Girard and Durance (2000)
			RPDE	Oysters	1497 (DB-Wax)	Pennarun et al. (2002)
			SDE	Scallops	1503 (Supelcowax 10)	Chung et al. (2001, 2002)
			Headspace	Oysters	1510 (DB-Wax)	Piveteau et al. (2000)
			RPDE	Anchovy	1208 (DB5-MS)	Triqui and Reineccius (1995)
			Headspace	Smoked salmon	1204 (DB5-MS)	Cardinal et al. (1997)

LRI: linear retention indices, SDE: simultaneous steam distillation – solvent extraction, RPDE: reduce pressure distillation extraction.

acids and the respective hydroperoxides formed as intermediaries. Thus, the interpretation of aliphatic aldehydes in smoked fish can be explained by the lipid composition of the fish flesh.

5.2. *n*-Alkanals

All the alkanals present in smoked fish and also present in seafood products are reported in Table 6. All *n*-Alkanals are generally produced from PUFA present in fish flesh (Josephson, Lindsay, & Stuibler, 1984; Josephson et al., 1991a, Josephson, Lindsay, & Stuibler, 1991b; Pan, Ushio, & Ohshima, 2005; Stołyhwo, Kołodziejska, & Sikorski, 2006) by oxidation of their double bound carbon–carbon. Alkanals are more produced from *n* – 6 or *n* – 9 PUFA

or MUFA. The precursors of butanal in fish flesh are mainly oleic (MUFA *n* – 9) and linoleic acid (PUFA *n* – 6) or its methyl esters (Grosch, 1987). Aldehydes whose number of carbon is comprised between 4 and 11 can be derived from oleic acid with an intermediary 11-hydroperoxide for octanal, 9 or 10-hydroperoxide for nonanal, 8-hydroperoxide for undecanal (all the hydroperoxides coming from oleic acid). They can also be produced from linoleic acid (*n* – 6 PUFA), especially from propanal to octanal with an intermediary 13-hydroperoxide (coming from linoleic acid) for hexanal. Arachidonic acid is also involved in creation of pentanal and hexanal. The presence of dodecanoic acid, tetradecanoic acid and hexadecanoic acid could be related to dodecanal, tetradecanal, and hexadecanal very present in fish flesh (Varlet et al., 2006).

Docosahexaenoic and eicosapentaenoic acid ($n - 3$ PUFA) are important fish components compared to linoleic and linolenic acid. Nevertheless, the same kind of hydroperoxides are obtained by oxidation and can lead to the same volatiles aldehydes (Hsieh & Kinsella, 1989).

N-alkanals are generally characterized by fat and green descriptors. The odour threshold of butanal is between 9 and 37 ppb in water (Buttery, Teranishi, Ling, & Turnbaugh, 1990) with a pungent and green odour. Except pentanal (odour threshold between 12 and 42 ppb in water (Buttery et al., 1990)) which has an almond, malt and pungent flavour, *n*-alkanals from hexanal to hexadecanal are qualified with aromatic notes like grass, tallow, green and fat for hexanal (odour threshold at 4.5 ppb in water (Buttery et al., 1990)), with aromatic notes like fat, citrus and rancid for heptanal (odour threshold at 3 ppb in water (Buttery et al., 1990)), with odours like fat, soap, lemon and green for octanal (odour threshold at 0.7 ppb in water (Buttery et al., 1990)) and fat, citrus and green for nonanal (odour threshold at 1 ppb in water (Buttery et al., 1990)). Due to their low odour thresholds, the aliphatic aldehydes play a predominant role in food aromas. For example, decanal, with fat, orange peel and tallow flavour, has an odour threshold from 0.1 to 2 ppb in water, dodecanal (Rychlik, Schieberle, & Grosch, 1998) with lily, fat and citrus flavour has an odour threshold about 2 ppb in water. Even tetradecanal with floral and waxy flavour (Chisholm, Wilson, & Gaskey, 2003) presents a low odour threshold (about 60 ppb in water).

5.3. 2-Alkenals

2-Alkenals are found in a lot of seafood products as presented in Table 7. They are known to be produced from PUFA like $n - 3$ PUFA linolenic acid (Ullrich & Grosch, 1988) especially for aldehydes with short chain (from 2-butenal to 2-heptenal), 2-pentenal deriving from 14-hydroperoxide of linolenic acid. 2-Alkenals from 2-hexenal to 2-undecenal are products of oxidation of oleic acid, by the intermediary of 9-hydroperoxide for 2-decenal and of 8-hydroperoxide for 2-undecenal. They also derive from $n - 6$ PUFA. Aldehydes as 2-heptenal or 2-octenal are produced from arachidonic acid. (*E*)-2-alkenals from 2-heptenal to 2-nonenal, 2-nonenal deriving from 9-hydroperoxide-, are generated from linoleic acid. (*Z*)-2-alkenals as 2-octenal and 2-decenal are also known to derive from linoleic acid (Grosch, 1987; Hsieh & Kinsella, 1989).

Long-chain unsaturated aldehydes have very low odour threshold that is the reason why they are prevalent in seafood products just with small quantities. From 2-pentenal to 2-dodecenal, the odour becomes less citrus and fruity and more fat-like, and the odour threshold falls (Rowe, 1998). For example, (*E*)-2-pentenal characterized by strawberry, fruity flavour (Rychlik et al., 1998) has an odour threshold at 1500 ppb in water, (*E*)-2-heptenal characterized by soap, almond flavour (Rychlik et al., 1998) has an odour threshold at 13 ppb in water. The odour thresh-

old is reduced by a factor 100. Similarly, 2-decenal with a tallow flavour (Valim, Rouseff, & Lim, 2003), has an odour threshold close to 0.3 ppb and 2-undecenal with a sweet, fat flavour, has an odour threshold at 5 ppb.

5.4. 2,4-Alkadienals

2,4-Alkadienals are also present in a lot of seafood products (Table 8). 2,4-decadienal has been found in smoked bream and trout (Guillén & Errecalde, 2002) but the configuration is not elucidated. Generally, decadienal and isomers come from $n - 6$ PUFA like linoleic or arachidonic acid (Piveteau et al., 2000; Lee et al., 2001) and by the intermediary of 9-hydroperoxide deriving from linoleic acid, or 11-hydroperoxide deriving from arachidonic acid.

As long-chain unsaturated aldehydes, decadienal and isomers have very low odour thresholds. They are characterized by fat-like odours. Indeed, (*E,E*)-2,4-decadienal for example has a fried, fatty and waxy flavour with an odour threshold at 0.07 ppb in water (Buttery et al., 1990; Potter, 1996; Rowe, 1998), (*E,Z*)-2,4-decadienal is characterized by a fried and fat flavour (Valim et al., 2003).

2,4-Alkadienals may be nonenzymatically derived products of lipid oxidation (Swoboda & Peers, 1977). 2,4-Heptadienal is produced from $n - 3$ PUFA as linolenic acid through 12-hydroperoxide intermediary (Hsieh & Kinsella, 1989). Its odorant threshold is assessed at 10 ppb with fried odour for (*E,Z*) structure and fatty, nutty odour for (*E,E*) structure (Ullrich & Grosch, 1988; Triqui & Reineccius, 1995).

2,4-Hexadienal is found in smoked salmon and known as lipid peroxidation product (Claxson et al., 1994). It is characterized by a low odour threshold from 10 to 60 ppb in water (Boehlens & Van Gemert, 1987) and aromatic notes like green and rancid (Qian & Reineccius, 2002).

6. Organoleptic roles of aldehydes in smoked fishes

6.1. Aldehyde participation in flavour of smoked fishes

One of the main organoleptic role of aldehydes is the contribution to the global aroma.

Benzaldehyde and derived compounds are known to have an almond, bitter almond (Triqui & Reineccius, 1995) and nutty odour. Its odorant detection threshold is about from 100 ppb to 4.6 ppm and recognition threshold from about 330 ppb to 4.1 ppm (Burdock, 2002). The great differences of odorant perception are mainly due to the different matrices (water, oil, food, etc.) used to carry out the assessment of the odorant perception.

Furfurals and aldehyde phenolic compounds have characteristic odorant descriptors. For example, furfural is stamped by bread, almond and sweet characteristics (Rychlik et al., 1998). Its odorant threshold is between 280 ppb and 8 ppm in water. Its taste characteristics at 30 ppm are brown, sweet, woody, bread-like, nutty caramellic with

Table 7
Occurrence of several 2-Alkenals in seafood products

Compound	Main precursors	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
2-Butenal		Woody, sulphury	Headspace	Smoked salmon	647 (DB5-MS)	Cardinal et al. (1997)
			SDE	Mussel juices	1002 (Stabilwax)	Cros et al. (2004)
			SDE	Scallops	1042 (Supelcowax 10)	Chung et al. (2001, 2002)
			SDE	Shrimp	1042 (Supelcowax 10)	Cha and Cadwallader (1995)
			Headspace	Canned salmon	1047 (Supelcowax 10)	Girard and Durance (2000)
<i>(E)</i> -2-Pentenal	PUFA $n - 3$	Herbaceous, green	SDE	Anchovy	1130 (Supelcowax 10)	Cha and Cadwallader (1995)
			SDE	Crab	1132 (Supelcowax 10)	Chung (1999)
			RPDE	Oysters	1124 (DB-Wax)	Pennarun et al. (2002)
			SDE	Scallops	1132 (Supelcowax 10)	Chung et al. (2001, 2002)
			Headspace Headspace	Oysters Canned salmon	1138 (DB-Wax) 1144 (Supelcowax 10)	Piveteau et al. (2000) Girard and Durance (2000)
<i>(E)</i> -2-Heptenal	PUFA $n - 3$, $n - 6$	Mossy, sulphury, cooked fish, roasted	SDE	Mussel juices	1309 (Stabilwax)	Cros et al. (2004)
			RPDE	Turbot	1339 (DB-Wax)	Sérot et al. (2001)
			SDE, RPDE	Cooked mussels	1338 (DB-Wax), 1342 (DB-Wax)	Le Guen et al. (2000a, 2000b)
			SDE	Anchovy	1328 (Supelcowax 10)	Cha and Cadwallader (1995)
			SDE	Mussel juices	1425 (Stabilwax)	Cros et al. (2004)
<i>(E)</i> -2-Octenal	PUFA $n - 6$	Roasted, almond, cucumber, nutty, fatty	Headspace, SDE, RPDE	Lobster tail	1430 (DB-Wax), 1045 (DB5-MS)	Cha and Cadwallader (1995)
			SDE	Turbot	1447 (DB-Wax)	Le Guen et al. (2000a)
			RPDE	Anchovy	1066 (DB5-MS)	Lee et al. (2001)
			Headspace	Oysters	1434 (DB-Wax)	Prost et al. (1998)
			Headspace	Canned salmon	1443 (Supelcowax 10)	Triqui and Zouine (1999)
<i>(E)</i> -2-Nonenal	PUFA $n - 6$	Earthy, fishy, cucumber, green	SDE	Mussel juices	1534 (Stabilwax)	Piveteau et al. (2000)
			RPDE	Turbot	1549 (DB-Wax)	Girard and Durance (2000)
			SDE	Cooked mussels	1563 (DB-Wax)	Chung (1999)
			Headspace	Canned salmon	1541 (Supelcowax 10)	Piveteau et al. (2000)
			SDE	Crab	1542 (Supelcowax 10)	Prost et al. (1998)
2-Decenal	PUFA $n - 6$	Tallow, orange	Headspace	Oysters	1541 (DB-Wax)	Piveteau et al. (2000)
			SDE	Turbot	1555 (DB-Wax)	Prost et al. (1998)
			SDE, RPDE	Lobster tail	1528 (DB-Wax), 1163 (DB5-MS)	Lee et al. (2001)
			RPDE	Anchovy	1166 (DB5-MS)	Triqui and Zouine (1999)
			Headspace	Canned salmon	1655 (Supelcowax 10)	Girard and Durance (2000)

LRI: linear retention indices, SDE: simultaneous steam distillation – solvent extraction, RPDE: reduce pressure distillation extraction, PUFA: polyunsaturated fatty acid.

Table 8
Occurrence of 2,4-alkadienal isomers in seafood products

Compound	Main precursors	Odorant descriptor	Extraction method	Matrices	LRI (and column)	References
(<i>E</i>)-(<i>Z</i>)-2,4-Decadienal	Arachidonic acid	Green, fatty	RPDE	Anchovy	1302 (DB5-MS)	Triqui and Zouine (1999)
(E,E)-2,4-Decadienal	Linoleic acid	Buttery, green, cut grass, deep fried, cucumber	SDE	Mussel juices	1827 (Stabilwax)	Cros et al. (2004)
			SDE, RPDE	Lobster tail	1883 (DB-Wax), 1275 (DB5-MS)	Lee et al. (2001)
			SDE	Turbot	1828 (DB-Wax)	Prost et al. (1998)
			RPDE	Anchovy	1315 (DB5-MS)	Triqui and Zouine (1999)
			SDE	Herring	1807 (Supelcowax 10)	Cha and Cadwallader (1995)
(E,E)-2,4-Heptadienal	Linolenic acid	Green, marine, fatty, nutty	SDE	Mussel juices	8.20 (Carbowax 20 M)	Cros et al. (2004)
			RPDE	trout	1498 (Supelcowax 10)	Sérot et al. (2002)
			SDE	Cooked mussels	1479 (Supelcowax 10)	Le Guen et al. (2000a)
(E,Z)-2,4-Heptadienal		Not described	EDT	Cooked red salmon	1508 (DB-Wax)	Josephson et al. (1991a)

LRI: linear retention indices, SDE: simultaneous steam distillation – solvent extraction, RPDE: reduce pressure distillation extraction.

a burnt astringent nuance notes (Burdock, 2002). 5-Methylfurfural is characterized by similar descriptors. Its odorant detection is possible at 6 ppm in water with odours of almond, caramel and burnt sugar (Valim et al., 2003) and its taste characteristics at 50 ppm are sweet, brown, caramellic, grain and maple-like.

Volatiles Strecker aldehydes are also known to be potent odorants in foods. For example, acetaldehyde has a pungent flavour but with fruity and green nuance (Scarpellino & Soukup, 1993). Its odorant threshold is comprised between 15 and 120 ppb in water (Buttery, Turnbaugh, & Ling, 1988). 2-Methyl-2-butenal is characterized by a green and fruity flavour (Berger, Drawert, & Kollmannsberger, 1989) and 3-methylbutanal by an almond, chocolate and malt flavour (Beal & Mottram, 1994) with an odorant threshold between 0.2 and 2 ppb in water (Buttery et al., 1990). As the others aldehydes from Strecker reaction, phenylacetaldehyde has also a low odour threshold about 4 ppb in water (Buttery et al., 1988). Phenylacetaldehyde odour is floral-roselike, fruity and green. Its taste characteristics are floral and honey-like with a sweet waxy nuance at 5 ppm (Scarpellino & Soukup, 1993).

Volatile aliphatic aldehydes odours decline important and various aromatic notes which are sometimes wanted and sometimes avoided. Indeed, thanks to their low threshold value, aldehydes produced by lipid oxidation seem to have a wide odour evolution according to their concentration. They can bring sweet, fatty and green aromatic notes but if the lipid oxidation becomes more important, the aromatic notes become stronger, unpleasant and cause undesirable flavours. This is the reason why the aldehydes odour is often smelt with several descriptors combining fatty odours (wax, tallow, butter, etc.) and green odours (floral, fruity, citrus, orange, etc.). Maillard and Strecker aldehydes show also these evolutions of odours because the aromatic notes can evolve from cooked vegetable to burnt sugar, roasty, car-

amellic in function of their concentrations, food matrix and intensity of process.

It is also very important to note that some phenolic compounds frequently contain aldehyde function which can confers nuanced odours: syringaldehyde, coniferaldehyde, etc. (Clifford, Tang, & Eyo, 1980). These functional groups might strengthen the predominance of the phenolic compounds in smoked fishes flavour. Odour and taste are deeply linked together and gathered under the flavour term. Flavour and odour of smoked fishes have been extensively investigated but to our knowledge, no study has been carried out on the role of aldehydes compounds on smoked fishes taste.

6.2. Others organoleptic roles of aldehydes

Maillard and Strecker aldehydes in a large part are responsible for the colour of the smoked flesh (Sainclivier, 1985). The colour varies from golden yellow to dark brown according to the nature of the wood and the intensity of smoking process. In liquid smoking process, the product must also be placed in a dry and hot ambience during few times in order to favorize colour formation. Thus, an important deposition of Maillard aldehydes leads to a darker colour of fish flesh (Tilgner, 1977). A brown colour can also be caused by an increase of the dehydration step in Maillard reaction drying briefly the fillet after smoke absorption. After scission and dehydration, melanoidines could be created by polymerisation through aldolic condensations. These compounds give to the final product a brown colour (beer, bread, coffee, etc.) (Borrelli et al., 2003). For our knowledge, no study has again dealt with the creation of melanoidines as colour component in smoked fish flesh.

Carbonyl-amino reactions could play a main role in smoked food products. Protein-bound lysine, the most present essential amino acid in fish (Huss, 1999), thanks

to its terminal amino group, is considered as major source of the amino components in such reactions, but a loss in arginine and histidine is also observed. Methanal is known to be very reactive towards amino groups but the adduct does not seem to be involved in the smoked fishes colour. However, glycolic aldehyde, methylglyoxal and 2-oxopropional are considered to be important colour precursors (Clifford et al., 1980; Miler & Sikorski, 1990). Then, aldehydes contribute to the colour of smoked fishes but are also responsible of a certain loss about nutritional value by the degradation of amino acids. However, all the aldehydes involved in the smoked fish colour have not all been reported as volatiles aldehydes.

A part of the final colour could derive from phenolic compounds with aldehyde function. Coniferaldehyde and syringaldehyde are considered to be irreversibly bound to proteins and to contribute orange tints to the products (Clifford et al., 1980).

Finally, the glossy aspect noticeable on certain smoked products is the result of reactions between phenolic com-

pounds and aldehydes (Girard, 1988). They lead to resinous substances (phenoplasts). The polymerization is favored by the heat and the degrees of reticulation of the molecule vary in function of the time (Fig. 4).

Aldehydes intervention in texture of smoked fishes is unknown. Texture of smoked fishes is due to coagulation of proteins. Formaldehyde which has been reported in wood smoke and smoked meat (Toth & Potthast, 1984) but not in smoked fishes (probably due to the extraction method) can react with proteins. Formaldehyde was shown to react with the amino group of the N-terminal amino acid residue and the side-chains of arginine, cysteine, histidine, and lysine residues (Metz et al., 2004). Formaldehyde seems to be involved in texture of smoked fishes and to be responsible of the dark layer at the dried surface of fishes (Sainclivier, 1985).

7. Toxicity of volatile aldehydes in smoked fishes

Among the aldehydes found in smoked fishes, several can be considered as potentially toxic. Aldehydes effects on human health are not very investigated. Aldehydes could have narcotic properties but at concentrations very higher than those found in smoked fishes.

4-Hydroxy-2-(*E*)-hexenal has been found in smoked salmon (Munasinghe et al., 2003). It has been reported that its formation occurs during lipid peroxidation of *n*-3 polyunsaturated fatty acids. It is a α,β -unsaturated aldehyde and therefore suspected to be carcinogen (Chung et al., 1986; Witz, 1989) like 4-hydroxy-2-nonenal found in others smoked products (Munasinghe, Ichimaru, Matsui, Sugamoto, & Sakai, 2003). 4-Hydroxy-2-nonenal has even been reported with the same toxicity as others alkenals such as (*E*)-heptenal (Nishikawa, Sodum, & Chung, 1992) in rats. The kidney and the liver are known to be the main organs affected by the cytotoxicity of such aldehydes. It is also known that 4-hydroxy-(*E*)-2-hexenal can react readily with the sulphhydryl groups of proteins (cysteine) and with amino groups of lysine but the toxicity mechanism and aldehyde catabolism decomposition are not still very well investigated. As smoking process implies wood pyrolysis and thus combustion of organic material, α,β -unsaturated aldehydes can be found in smoked fishes. These aldehydes are also considered as endogenously formed substances in animals and humans during lipid peroxidation or arachidonic acid oxidation. They form a group of mutagenic compounds inside which some were shown as carcinogens like 2,4-hexadienal (Picchiottino & Lee, 2002). Their toxic activities are considered as a result of their ability to create exocyclic DNA-adducts, in particular 1,*N*²-propanodeoxyguanosine adducts (Eder & Deininger, 2002). This type of adducts is considered as promutagenic DNA-lesion. 2-Butenal, which was identified in smoked fishes, given in drinking water was shown to cause liver tumors in rats (Munasinghe et al., 2003) and 2-heptenal, also found in smoked fishes, have been reported to contribute to a general cancer risk (Eder & Deininger, 2002). Individually, these aldehydes are not

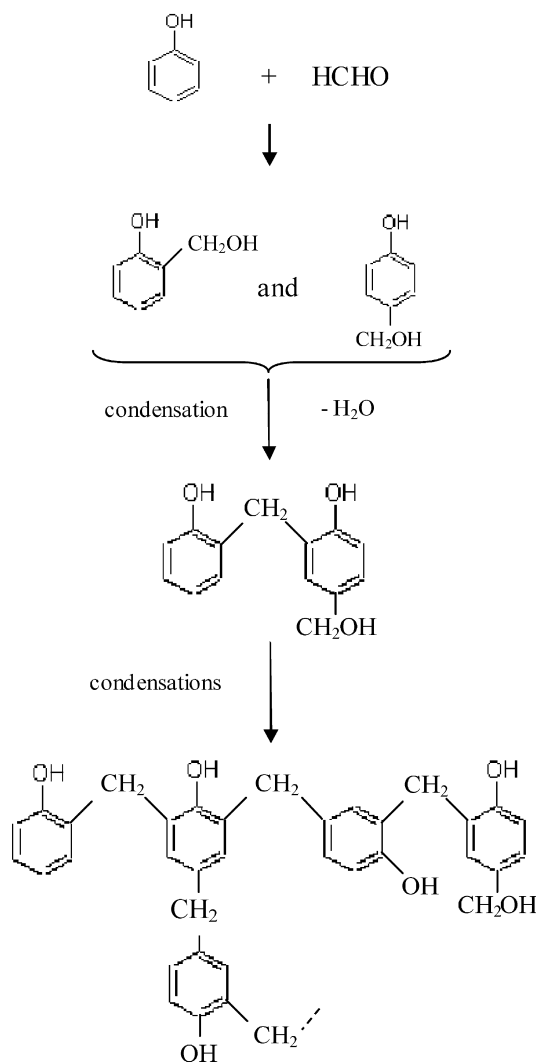


Fig. 4. Reaction between a phenolic compound and an aldehyde (Girard, 1988).

in adequate quantities in smoked fishes to be responsible of toxic activity. However, the effect of mixes of several α,β -unsaturated aldehydes have not been studied and synergic effects could occur between these aldehydes.

Formaldehyde is not found in smoked fishes but is present in wood smoke at levels higher than 200 mg/100 g and in smoked meat products at levels higher than 50 mg/kg (Toth & Potthast, 1984; Maga, 1987). It might be more investigated in smoked fishes because its toxicity was well investigated and assessed (Vargova et al., 1993; Nilsson et al., 1998). Like formaldehyde, acetaldehyde detected in smoked fishes was also shown as toxic aldehyde (Til et al., 1989). On humans, the action of acetaldehyde is nearly unknown on account of the lack of studies. It has only been reported as respiratory and eye irritant (INRS, 2004b). Studies on animals have assessed acetaldehyde toxicity but at high concentrations. A no-observed-adverse-effect level of acetaldehyde is 125 mg/kg body weight/day for rats (Til, Woutersen, & Feron, 1988). Its genotoxicity is assessed on bacteria through DNA alterations and mutagenic action. On rats, carcinogenesis is evaluated from 750 ppm (6 h/j, 5 j/week, during 28 weeks) and reproduction alterations were illustrated by teratogenic effects and hormonal modifications on mice (INRS, 2004b).

Aromatic aldehydes can also be toxic. Benzaldehyde toxicity studies have established its irritant action at the level of the skin and mucous membranes (Pichard et al., 2005). No study about the genotoxicity and effect on reproduction of benzaldehyde on humans is available. However, on mice, the carcinogen activity of benzaldehyde was shown (NCI/NTP, 1990). The main targeted organs of benzaldehyde are brain, kidneys, liver and stomach. Benzaldehyde has been shown as able to specifically inhibit in vitro the glutathione peroxidase. This enzyme plays an important role in the brain protection against antioxidants (Tabatabaie & Floyd, 1996). This reaction illustrates the indirect toxicity that benzaldehyde could have as enzymatic inhibitor. These results can explain the indirect neurotoxicity of benzaldehyde. However, benzaldehyde is found in smoked fishes in quantities very lower than the toxic concentrations.

Furfural is not a carcinogenic compound but it increases carcinogenesis due to polycyclic aromatic hydrocarbons (PAH) as benzo(a)pyrene, known to be carcinogens present in smoked food. It has been reported as respiratory and eyes irritant (INRS, 1999). In France, a threshold value of exposition has been assessed at 2 ppm for workers. This concentration is 1000 times more important than the concentration of furfural found in smoked fishes (Varlet et al., 2006). However, important quantities of furfural have been measured in wood smoke. Toxicity of furfural in wood smoke has not been studied but its concentration makes us to think that it has a potential role in wood smoke toxicity.

Even if some aldehydes found in smoked fishes can be carcinogens, their concentrations are very lower than those necessary to induce toxic effects. The toxicity of smoked fishes is more attributed to PAH content. Never-

theless, even if aldehydes in smoked fishes are found under the individual toxic concentrations, cumulative and synergic effects could be possible and should be better investigated.

8. Conclusion

Volatile aldehydes constitute key molecules for a better comprehension in quality of food products, especially smoked fish. Indeed, volatile aldehydes can be used as indicators of parameters such as intensity of smoking process by the detection of Maillard and Strecker products. Volatile aldehydes can also illustrate the level of oxidation and/or toxicity in smoked fishes. More investigations must be carried out in order to improve the odorant quality of smoked fish because volatile aldehydes will be good organoleptic indicators to optimize a process, to produce food with required odours or to reduce off-odours when once identified, the mechanisms of creation are known. This kind of study might be extended to others food matrices because lipid oxidation and Maillard reaction are very frequent in all industrial food processes. Finally, due to their reactivity and sometimes toxicity, the study of aldehydes in food brings knowledge in health research in order to understand some unexpected phenomena.

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