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Comparison of Odor-Active Volatile Compounds of Fresh and Smoked Salmon

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The odorant volatile compounds of raw salmon and smoked salmon have been investigated by two gas chromatography−olfactometry methods (frequency detection and odorant intensity) and gas chromatography−mass spectrometry. After simultaneous steam distillation−solvent extraction with diethyl ether and the recovery of the aromatic extract in ethanol, qualitative olfactometric characterization and identification followed by a quantitative assessment of the odorant volatile compounds were carried out. The origin of many odorant compounds of smoked salmon can be attributed to wood smoke. Another part of smoked salmon aroma is due either to the odorant compounds of the raw fish flesh or to an evolution of fish flesh aroma thanks to the smoking process conditions. Forty-nine odorant compounds have been identified in fresh salmon and 74 in smoked salmon. Carbonyl compounds, such as heptanal or (*E*,*Z*)-2,6-nonadienal, show a high detection frequency and odorant intensity in unsmoked fish, giving the flesh its typical fishy odor. For smoked salmon, phenolic compounds, such as cresol or guaiacol, and furanic compounds seem to be responsible for the smoked odor.

KEYWORDS: Smoked salmon; olfactometry; odorant volatile compounds; mass spectrometry; SDE extraction; phenolic compounds; wood smoke

INTRODUCTION

The origins of smoked food are lost in antiquity. Initially, the smoking process served primarily to preserve food by hanging it over a fire. Nowadays, this process is widely investigated and controlled. Moreover, much equipment has been developed. The smoking process is preceded by a salting and drying steps, which decrease the water activity and the microbial development in more of the antioxidant, antimicrobial, and flavor characteristics supplied by the wood smoke. With the growth of the smoked salmon industry, several new smoking processes have been developed from the traditional cold-smoking process. Liquid smoking, friction smoking, and hot-smoking have allowed a significant quantity of various products to be targeted. Since then, through these smoking processes, the whole of the salmon industry, from harvest to frozen storage of fish, has been studied and improved to better understand the relationship between the industrial processing of smoked salmon and its sensory characteristics, such as odor and quality (*1*−*5*). The investigation of smoked salmon aroma, to our knowledge, has never been addressed. Many studies are available on the volatile compounds in processed salmon (*6*−*10*) or in raw salmon (*11*, *12*), but very few studies have assessed odorants, and then only in boiled salmon (*13*). Indeed, concerning smoked fish aroma, some studies have characterized volatile compounds (*14*, *15*) or overall odor thanks to sensorial analysis and aromatic profiles (*16*), but very few studies are available concerning the odorant volatile compounds in smoked salmon (*17*). Similarly, although knowledge about wood smoke used in the smoking of salmon is considerable, only volatile compounds have been investigated (*18*−*21*). Nevertheless, more research has been done on the role that several volatiles of wood smoke play in smoke flavor. It is known that in wood smoke, phenolic compounds are antioxidant and antimicrobial agents and carry a "smoky" flavor. These phenolic compounds are also found in smoked fish (*22*). Carbonyl compounds play a role in the color and texture of the final product (*23*) and are more responsible for the "fishy" odor. Thus, the volatile odor-active compounds in smoked salmon are unknown, even though some information is available about the volatile odorant compounds of wood smoke, because no study has yet related the volatile compounds with their odor in smoked salmon. Until now, the olfactive studies have focused on the observation or reduction of off-flavors, and then only on very few compounds and especially on fresh fish. Indeed, they have been investigated

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because they constitute good indicators of the deterioration and spoilage of food because some volatile compounds are produced by microbiological organisms (*17*, *24*, *25*). They have also been studied because certain volatiles, such as phenols, are good indicators of the intensity of the smoking process (*16*), or certain compounds have been investigated to improve smoking techniques by comparing processes or by evaluating food contaminants such as polycyclic aromatic hydrocarbons (*26*, *27*). This knowledge about the volatile odorants of smoked salmon is therefore incomplete. Olfactometry with the frequency detection method and mass spectrometry coupled to gas chromatography will allow their characterization in order to elucidate individually all of the odor-active compounds of smoked salmon.

This study has identified and evaluated the odorant compounds of smoked and fresh salmon and points out the odorant evolution between raw and smoked material. First, the different odorant notes are quantified in smoked salmon, and the origin of the odor-active compounds is discussed according to their presence in wood smoke. Second, odor-active compounds of fresh salmon are studied to explain the origin of odorants in smoked salmon that have not been reported in wood smoke. Finally, a comparison between unsmoked and smoked aroma profiles is carried out and the evolution of odors related to the evolution of the concentrations of odor-active compounds is proposed.

MATERIALS AND METHODS

Reagents. Dodecane came from Aldrich (Steinheim, Germany), diethyl ether from Fluka (Buchs, Switzerland), and ethanol from VWR (Fontenay-sous-bois, France). All water was purified by a Milli-Q system. All standards used for identification were from Aldrich except acetic acid, which was from Panreac (Barcelona, Spain), and phenol, which was from Merck (Darmstadt, Germany).

Fish Processing. Salmon (*Salmo salar*) reared in Norway were purchased from a seafood wholesaler (Nantes, France). The time between their capture and their filleting was not more than 5 days. The beech smoke was obtained by smoldering. Four gutted fishes of 3−4 kg of the same batch were received in a box in ice. They were directly filleted and put in a cold chamber at 3 °C for 2 h. Each of the eight fillets weighed ∼1 kg. Four fillets were used for aroma analysis on unsmoked salmon, and four fillets were smoked in order to study smoked salmon aroma.

Next, the fillets were hand-salted with refined salt (Salins du Midi, France) for 3 h at 12 °C before being rinsed on grids with water (15 °C) and stored in a cold room at 3 °C for 18 h until smoking (*16*). Smoke was produced by pyrolysis of beech wood sawdust at 400 °C (Thirode, France). The sawdust was wet with water to reach 20% moisture.

The smokehouse was an HMI Thirode (PC90 model) device (Thirode, France), 1500 × 1300 ×2250 mm, with a capacity of 380 kg, mounted on a trolley with 28 grids on which the fillets were deposited. The fillets were placed at the same level (grid 14) at 20 cm of the opening of the door of the smokehouse. The air/smoke circulation was horizontal. The salmon fillets were swept by the smoke for 3 h at a temperature of 32 °C. This temperature was chosen to enrich the odor-active compounds that we could quantify at trace level with cold-smoking at 22 °C. The exhaust valve opening was one-third, and the relative hygrometry was set at 60%. After smoking, the fillets were placed in a cold chamber at 3 °C during one night. The fillets were chopped, and a piece of 100 g taken from the middle of the fillet was put in a polyethylene bag and frozen at −20 °C during one week before extraction. Preliminary biochemical analysis on water and NaCl content was carried out before smoking. The rate of water was 64.57 g/100 g, and the rate of NaCl was 0.23 g/100 g.

Isolation of the Volatiles. A Likens−Nickerson apparatus was used for the preparation of the simultaneous distillation−extraction (SDE) extracts (*28*). A 500 mL round-bottom flask was used as the sample flask to contain 150 mL of purified water and 50 g of salmon or smoked salmon. A 30 mL round-bottom flask containing 30 mL of diethyl ether was linked to the upper arm of the SDE apparatus because the density of diethyl ether is lower than the density of water. The steam was cooled by the circulation of poly(ethylene glycol) at −5 °C. The contents in the sample and solvent flasks were heated to boiling. The temperature of the diethyl ether flask was maintained at 50 °C by a water bath. The distillation−extraction was continued for 3 h. The volume of the extract was reduced to 5 mL by evaporating the solvent using a Kuderna Danish apparatus and to 0.4 mL under a gentle cold stream of nitrogen. The aromatic extract in diethyl ether was introduced into 0.3 mL of ethanol, and diethyl ether was removed by evaporation under a gentle cold stream of nitrogen.

Representativeness of the Extract. SDE with diethyl ether, followed by a step of solvent change to obtain the extract in ethanol by the evaporation of diethyl ether, was carried out. Diethyl ether was used because it is less toxic than dichloromethane and leads to similar recovery yields concerning the smoked salmon matrix. The solvent change step is necessary to remove diethyl ether and obtain the extract in a neutral solvent such as ethanol. Thus, the olfactometric sessions are totally safe. A previous study assessed the representativeness of an aromatic extract of smoked salmon obtained by this method, and it led to a similarity mark of ∼72% (*28*), that is to say, quite satisfactory.

Gas Chromatography−Olfactometry (GC-O) Analysis. The GC-O system consisted of a 6890N GC (Agilent Technologies, Wilmington, DE) equipped with a FID, a mass detector (5973-Network), and a sniffing port ODP2 (Gerstel, Baltimore, MD) supplied with humidified air at 40 °C. The GC effluent was split 1:1:1 between the FID, the mass detector, and the sniffing port. Each extract (3 μL) was injected in splitless mode into a capillary column (DB-5MS, 30 m length × 0.32 mm id, 0.5 μm thickness) (J&W Scientific, Folsom, CA). The system provides simultaneously a MS signal for the identification and the quantification of the odor-active compounds. The injector and FID detector were set at, respectively, 270 and 280 °C. The flow rate of the carrier gas (helium) was 1.5 mL min^{-1}. The temperature of the oven was programmed according to the following steps: from 70 °C (1 min) to 80 °C (1 min) at 3 °C min^{-1}, then to 150 °C at 5 °C min^{-1}, and, finally, to 280 °C (4 min) at 10 °C min^{-1}.

Frequency-of-Detection (FDT) and Time−Intensity Methods. The panel was composed of eight judges (five females and three males between 24 and 49 years old) from our department]LBAI-ENITIAA (Laboratoire de Biochimie Industrielle et Alimentaire-Ecole Nationale d'Ingénieurs des Techniques pour les Industries Agricoles et Alimentaires]. They were all previously trained in odor recognition and sensory evaluation techniques and had experience in GC-O. Sniffing of the chromatogram was divided into two sessions of 19 min. Each judge participated in the sniffing of both parts, but during two separate sessions to remain alert. The panelists were asked to describe the odor and to give a mark of intensity to each detected odorant on a scale of 1−9 (1 = very weak odor intensity, 9 = very strong odor intensity). Detection of an odor at the sniffing port by fewer than three of the eight assessors was considered to be noise. Thus, two responses were followed with two olfactometric methods: first, the FDT method, given by the number of judges who perceived the odor (*29*), allows the selection of the significant odors and, second, the time−intensity (*30*) method, given by the average of the intensity marks attributed in the time by each judge who has smelled the odor.

Gas Chromatography−Mass Spectromety (GC-MS) Analysis. The GC-MS quantification of the compounds was carried out with the same device as described in the GC-O procedure. The injector and detector were set at, respectively, 270 and 280 °C. Helium was used as carrier gas with a flow rate of 0.5 mL min^{-1}. A quadrupole mass selective detector, with electronic impact ionization (ionization energy = 70 eV) operated in scan mode, with a mass range of 30−300 amu, at 2.0 scans/s, was used to detect the ions formed.

Compound identification was based on a comparison of retention indices (RI) (*31*), mass spectra (comparison with standard MS spectra databases: Wiley 6), injection of standards, and odor properties. When possible, the identification was confirmed by detection of the compounds in single ion monitoring (SIM) mode following, for each noticeable odorant, five of the most predominant ions present in their mass spectra. A confirmation of the presence of the compounds

identified was carried out using other GC-MS results obtained with a polar DB-Wax column (30 m length × 0.25 mm i.d., 0.5 μm thickness) and also with a less polar DB1 column (60 m length × 0.32 mm i.d., 0.5 μm thickness) (J&W Scientific, Folsom, CA).

The quantification was performed using dodecane as standard added just before the concentration step. The concentrations of volatile compounds are expressed in microgram equivalents of dodecane for 100 g of salmon.

RESULTS AND DISCUSSION

Odorant Compounds of Smoked Salmon. Eighty-eight odorant areas were detected in smoked fish extract by GC-O, and 74 were identified by GC-MS. Odor descriptions for compounds detected by GC-O in the aromatic extract of fresh salmon and the quantitative results are given in **Table 1**. Among them, 35 were perceived by at least seven of the eight assessors. As has already been reported with an apolar capillary column (*17*), the chromatogram of smoked salmon aromatic extract can be divided in two parts. The first is more characterized by cooked, fishy, and green odorant descriptors, and the second part is more smoked and burnt with the presence of many phenolic compounds.

Odorant Compounds of Smoked Salmon: Phenolic Odorant Compounds in Smoked Salmon. These compounds constitute the main odorant compounds, and they were all detected with an intensity of >5 and perceived by more than five judges with little burnt/roasted and spicy differences. Twelve compounds in particular seem to contribute to the overall odor of smoked salmon: *o*-cresol, *m*-cresol, guaiacol, 4-methylguaiacol, thymol, 4-ethylguaiacol, 4-vinylguaiacol, syringol, eugenol, 4-propylguaiacol, (*Z*)-isoeugenol, and (*E*)-isoeugenol. All of the phenolic compounds found in smoked salmon come from the thermal degradation of wood through the pyrolysis of lignin (*14*). Many studies have indicated that phenolic compounds present in the vapor phase of smoke may contribute to imparting a smoky flavor to foods. Some 85 different phenolic compounds have been characterized in smoke condensate but only 20 phenols in smoked product (*32*). It has been reported that only phenolics with a boiling point of 76−89 °C at 5.33 hPa carry a smoke-like flavor (*33*). Among them, syringol, guaiacol, 4-methylguaiacol, and eugenol may be the dominant contributors to the pleasant smoke-like aroma (*33*). By comparison with these results, we have found that guaiacol, 4-methylguaiacol, syringol, and cresol compounds are especially responsible for the smoke and burnt odor, whereas the other guaiacol derivatives, thymol, eugenol, and isoeugenol compounds, contribute more to spicy notes such as clove, vanilla or curry, licorice, and cinnamon. Guaiacol is the major compound in smoked salmon with a concentration of 345 μg of IS/100 g. It is important to note that odor thresholds of phenolic compounds are very different because thymol and guaiacol were detected by the same number of judges and with the same intensity mark of 5; however, thymol is 70 times less concentrated (4.84 μg of IS/100 g). Other phenolic compounds are also present at a concentration between 20 and 100 μg of IS/100 g: dimethylphenols (such as 3,4-dimethylphenol) or trimethylphenols (such as 2,4,6-trimethylphenol) are also found in smoked salmon and supply phenolic odors such as roasted, smoked, earthy, or burnt. Their odorant role is less obvious because they are perceived with a weaker intensity (from 4 to 6), by a lower number of judges (six or seven), but especially at a lower concentration (under 15 μg of IS/100 g). The exception is 2,5-dimethylphenol, found by seven assessors with an intensity of 7, probably due to its higher concentration of 28.60 μg of IS/100 g. The quantification of phenolic compounds seems to be satisfactory because the coefficients of variation calculated with each mean and standard deviation (SD) value were not often >10%. Nevertheless, for phenolic compounds with weak chromatographic signals such as 2,3-dimethylphenol and thymol, which leads to weak quantities, the SD values are more important because of the difficulty of quantification.

Odorant Compounds of Smoked Salmon: Furanic, Maillard, and Strecker Odorants Compounds in Smoked Salmon. Other compounds of smoked salmon with pleasant roasted notes were detected by the judges. They are furanic compounds created during the smoking process by thermal degradation. In wood smoke (*18*−*20*), furanic compounds such as furfuryl alcohol and furfural are mainly generated by separation of water from pentoses, which are decomposition products of hemicelluloses (*34*). Maillard reactions (and Strecker degradation) could also be proposed as pathways of creation for these compounds because Maillard reactions occur during smoking process and are responsible for the color of many smoked products (*35*). The fact that furanic compounds are not found in unsmoked salmon shows that it is not the extraction method used here but the smoking process that is responsible for the formation of these compounds. They are also present in processed seafood (ripening, curing, roasting) at a lower concentration than in wood smoke (*36*−*38*). The smoking process favors the generation of furanic compounds, which are deposited (if they come from the wood) or eventually generated in the fish flesh. They are all known to give burnt/cooked and roasted aromas to the food. Furanic compounds do not have strong odorant intensity (from 4 to 6) but were perceived by a large number of judges (never fewer than five). Their concentrations are lower than those of phenolic compounds, except for furfural, which is the second most common odorant in smoked salmon (299 μg of IS/100 g), and furfuryl alcohol (143.50 μg of IS/100 g). Nevertheless, the quantifications of furanic compounds in smoked salmon are less precise because of high SD values. As their chromatographic peaks are sufficiently significant, problems of quantification cannot be involved. As the furanic compounds such as furfural seem to derive from wood smoke because they are not found in fresh fish (*17*), heterogeneities of the wood smoke in the smokehouse or differences in the deposition of wood smoke odorants on fish flesh could better explain these variations. Two other furanic compounds are detected in smoked salmon, acetylfuran and 5-methylfurfural, which are often found in wood smoke. Acetylfuran has a strong impact on the smoked salmon aroma because it was found by seven judges with an intensity of 7. The contribution of 5-methylfurfural is lower. 2-Acetyl-5-methylfuran and benzofuran derivatives carry more green/chemical odors, which are sometimes unpleasant like rotten/moss for benzofuran. As for phenolic compounds, the weaker the signal is, the more difficult the quantification is and the higher the variation can be.

Pyrazines and heterocyclic nitrogen compounds could also be generated from Maillard reaction products with roasted, cooked, and smoked odors. Thus, 2-methylpyrazine, 2-acetyl-1-pyrroline, tetrahydropyran-2-one, and 1(*H*)-pyrrole carboxaldehyde with more chemical and resinous notes were identified in smoked salmon. 2-Methylpyrazine and 1(*H*)-pyrrole carboxaldehyde have already been reported as components of smoked fish (*10*, *14*), and 2-acetyl-1-pyrroline has been reported as a component of processed seafood (*39*, *40*). In smoked salmon, these two compounds are almost at trace level, especially 2-acetyl-1-pyrroline, but they have a strong odorant impact because they were perceived by eight judges for 2-acetyl-1-pyrroline and by six judges for (1*H*)-pyrrole carboxaldehyde.

Table 1. Identification and Odorant Charcteristics of Volatile Odor-Active Compounds of Smoked Salmon

compound	LRI (DB5)	means of identification or mass fragments of its mass spectrum[a]	odorant descriptors given by judges	intensity[b]	no. of judges[c]	concentration[d] (mean ± SD)
diacetyl	600	LRI	butter	4	6	Tr
3-methylbutanal	645	LRI, STD	green, coffee	4	4	Tr
acetic acid	680	MS, LRI, STD	sour, garlic, NC[e]	3	4	2.05 ± 1.78
1-penten-3-ol	688	MS, LRI, STD	fat, chemical	2	4	Tr
furfural or isomer	840	MS, LRI, STD	roasted, nutty	3	6	7.83 ± 1.68
furfural	859	MS, LRI, STD	roasted, nutty	4	6	299.02 ± 135.58
2-methylpyrazine	845	MS, LRI, STD	roasted nuts	3	5	5.99 ± 4.14
furfuryl alcohol	875	MS, LRI, STD	cooked	5	8	143.49 ± 57.98
2,4-hexadienal	904	MS, LRI	cooked vegetable, fishy, earthy	7	6	3.24 ± 1.86
tetrahydropyran-2-one	908	MS	cooked, smoked	6	7	0.14 ± 0.16
heptanal	914	MS, LRI, STD	cooked, leather, plastic	6	8	1.32 ± 0.50
2-methyl-2-cyclopentenone	920	MS, LRI, STD	soup, cooked food	7	7	21.72 ± 6.48
acetylfuran	925	MS, LRI, STD	cooked, sweet	7	7	33.68 ± 8.82
2-acetyl-1-pyrroline	935	LRI	oily, roasted, nuts, bread	7	8	Tr
5-methylfurfural	970	MS, LRI, STD	cooked, earthy, coffee	3	5	58.08 ± 14.02
benzaldehyde	980	MS, LRI, STD	floral, fresh, green	5	5	29.49 ± 7.70
phenol	992	MS, LRI, STD	marine, vinegar, metallic, sulfury	5	5	78.28 ± 24.18
benzonitrile	1003	MS, LRI	cooked potato, mushroom, fishy	5	6	0.64 ± 1.12
unknown	1012	39 (47), 41 (85), 67 (50), 69 (100), 112 (80)	NC	4	5	NQ
benzofuran	1015	MS, LRI	rotten	5	6	1.34 ± 2.60
(*E*,*E*)-2,4-heptadienal	1019	MS, LRI, STD	plastic, fat	5	5	Tr
1(*H*)-pyrrole carboxaldehyde	1030	MS	leather, resinous, chemical	5	6	1.78 ± 1.34
2-ethyl-1-hexanol/2-hydroxy-3-methyl-2-cyclopentenone	1038	MS, LRI, STD MS, LRI	spicy, green	5 6	6 6	4.34 ± 4.36 11.39 ± 8.32
2-acetyl-5-methylfuran	1048	MS, LRI	vegetal, solvent	6	7	2.33 ± 2.10
2,3-dimethyl-2-cyclopentenone	1052	MS	moss, woody, burnt rubber	5	8	19.10 ± 4.32
benzyl alcohol	1057	MS, LRI, STD	moss, solvent, chemical	5	6	Tr
benzeneacetaldehyde	1062	MS, LRI, STD	moss, solvent	5	7	2.90 ± 0.52
o-cresol	1068	MS, LRI, STD	smoke, burnt rubber	6	8	50.82 ± 5.50
unknown	1077	39 (18), 43 (25), 95 (100), 108 (15), 138 (25)	woody	5	6	NQ
unknown	1083	55 (95), 77 (90), 95 (75), 105 (100), 109 (85)	woody	4	4	NQ
acetophenone	1086	MS, LRI	vegetal, plastic	5	7	5.43 ± 1.88
p-cresol	1093	MS, LRI, STD	burnt, licorice, medicinal	7	8	67.92 ± 13.54
guaiacol/nonanal[f]	1110	MS, LRI, STD	smoke, vanilla, medicinal	7	8	344.98 ± 40.92
unknown[f]	1123	68 (30), 81 (55), 82 (30), 109 (55), 124 (100)	oily, plastic, earthy	6	7	NQ
2,6-dimethylphenol	1130	MS, LRI	roasted, phenolic, chemical	5	7	16.48 ± 2.60
unknown[f]	1136	55 (60), 79 (65), 91 (95), 122 (85), 126 (100)	earthy, plastic, cucumber	5	6	NQ
unknown	1142	43 (30), 81 (18), 91 (27), 109 (100), 138 (40)	raw vegetable, carrot	5	7	NQ
1,2-dimethoxybenzene	1147	MS, LRI	earthy, moss, woody, mouldy	5	7	7.78 ± 1.48
3-ethylphenol[f]	1153	MS, LRI	moss, earthy, woody, smoke	5	6	5.75 ± 0.38
unknown	1157	77 (75), 79 (95), 122 (80), 135 (100), 136 (100)	moss, cucumber	3	4	NQ
2,4-dimethylphenol[f]	1160	MS, LRI	carrot, green, violet, vanilla	5	6	Tr
2,5-dimethylphenol[f]	1167	MS, LRI		7	7	28.60 ± 3.36
1-methyl-1(*H*)-indene	1172	MS	plastic, phenolic	6	6	1.51 ± 1.48
3-methoxybenzaldehyde	1176	MS	burnt, amine	6	6	4.02 ± 0.88
3,4-dimethylphenol	1182	MS, LRI	chemical/burnt, smoked, roasted	6	6	11.98 ± 7.90
2,3-dimethylphenol	1184	MS, LRI	burnt, smoke, plastic	6	7	0.98 ± 1.92
4-methylguaiacol	1192	MS, LRI, STD	phenolic, smoke, plastic	5	7	33.66 ± 2.16
2-(2-butoxyethoxy)ethanol	1198	MS, LRI	fruity, plastic	6	6	Tr
naphthalene	1211	MS, LRI, STD	spicy, smoke, cold ashes	6	7	NQ
2,5-diformylthiophen[f]	1220	MS	burnt, smoke, green, earthy	4	5	5.11 ± 0.88
2,4,6-trimethylphenol	1229	MS, LRI	roasted, earthy, burnt, smoke	4	5	4.40 ± 0.42
4-methoxybenzaldehyde	1235	MS, LRI	gasoline, green, cucumber	4	7	Tr
4,7-dimethylbenzofuran	1240	MS	smoke, moss, spicy	6	6	1.01 ± 1.44
2,3-dimethoxytoluene	1247	MS, LRI	aniseed/green, smoke, NC	6	6	9.10 ± 4.92
3-ethyl-5-methylphenol	1260	MS	green/honey, smoke, NC	6	5	1.09 ± 1.54
(*E*)-2-decenal	1266	MS, LRI	plastic, green, cheese	6	6	Tr
thymol	1272	MS, LRI, STD	spicy, chemical, medicinal	7	8	4.84 ± 2.16
3,5-dimethoxytoluene	1282	MS, LRI	spicy, gasoline, chemical	7	7	11.08 ± 0.46
4-ethylguaiacol/2-undecanone[f]	1287 1296	MS, LRI MS, LRI, STD	peanut, vanilla, camphor, phenolic	5 5	6 4	97.35 ± 9.24 Tr
unknown	1300	58 (86), 115 (50), 134 (80), 145 (100), 160 (55)	sweet, leather, phenolic	4	4	NQ
2,3-dihydro-1(*H*)indene	1308	MS, LRI	burnt rubber, medicinal, resinous	5	7	5.14 ± 4.90
undecanal[f]	1319	MS, LRI	leather, rubber	5	4	Tr

Table 1. (Continued)

compound	LRI (DB5)	means of identification or mass fragments of its mass spectrum[a]	odorant descriptors given by judges	intensity[b]	no. of judges[c]	concentration[d] (mean ± SD)
4-vinylguaiacol	1330	MS, LRI, STD	medicinal, woody, spicy, smoke	6	8	40.82 ± 11.12
2-methylnaphthalene	1340	MS, STD	moss, plastic	6	7	3.68 ± 1.28
unknown	1352	43 (65), 55 (55), 121 (50), 145 (100), 146 (75)	minty, eucalyptus, citronella	4	4	NQ
2,3-dimethoxybenzaldehyde	1362	MS	spicy, aromatic plant	3	4	2.78 ± 2.10
syringol	1365	MS, LRI	spicy, smoke	5	5	28.78 ± 19.42
eugenol	1370	MS, LRI, STD	vanilla, clove, burnt rubber	6	7	47.60 ± 7.04
4-propylguaiacol	1382	MS, LRI, STD	clove, marine, vanilla, spicy	7	7	21.25 ± 2.84
1,2,3-trimethoxy-5-methylbenzene	1400	MS, LRI	burnt rubber, earthy, spicy	4	5	0.85 ± 0.60
(*Z*)-isoeugenol	1423	MS, LRI, STD	clove, spicy, coffee, burnt	6	8	19.94 ± 5.06
4-methylindanone	1444	MS, LRI	burnt, plastic, pine	6	5	3.92 ± 1.36
1,6-dimethylnaphthalene	1452	MS	green, burnt, spicy	5	4	NQ
unknown	1465	91 (70), 131 (73), 141 (77), 156 (100), 178 (80)	green, moss, woody, spicy	5	5	NQ
(*E*)-isoeugenol	1473	MS, LRI, STD	clove, fruity, cinnamon, fat	7	8	48.26 ± 13.48
dodecanol	1490	MS, LRI	raw carrot, medicinal	6	7	Tr
unknown	1500	162 (100), 166 (25), 167 (25), 174 (75), 179 (40)	green, woody, spicy	6	8	NQ
2,3,5-trimethoxytoluene	1527	MS, LRI	solvent, fruity, rubber	5	6	10.89 ± 6.44
dibenzofuran	1545	MS, LRI	rotten, rubber, fat, moss	6	5	3.22 ± 0.96
unknown[f]	1575	41 (60), 57 (100), 175 (75), 181 (73), 190 (55)	aromatic plant, roasted	5	8	NQ
1-hexadecene	1600	MS, LRI	burnt rubber, fat, oily, soup	6	7	3.29 ± 2.52
4-allylsyringol	1615	MS, LRI	burnt rubber, medicinal	6	4	3.81 ± 1.54
unknown	1665	41 (80), 55 (80), 79 (100), 81 (65), 91 (85)	woody, earthy, NC	5	6	NQ
8-heptadecene	1680	MS, LRI	leather	6	4	9.91 ± 1.70
hexadecanal	1808	MS, LRI	leather, burnt rubber, NC	5	4	34.82 ± 31.00
(*Z*)-9-octadecenol	1880	MS	cooked, leather, bread, wood	5	5	11.66 ± 6.34
unknown	1915	43 (78), 55 (65), 57 (100), 71 (70), 85 (50)	burnt rubber, leather, cooked	3	4	NQ
(*Z*)-9-octadecenal	1995	MS, LRI	cooked meat, sulfury, leather	5	4	13.58 ± 9.20
unknown	2190	39 (80), 43 (95), 55 (95), 57 (100), 82 (80)	marine, fresh, leather	3	4	NQ

[a] Means of identification: MS, mass spectrum (identified thanks to the mass spectra of the compounds); LRI, linear retention index (when the LRI of the compound identified corresponds to the LRI in the literature); STD, standard (when the retention time, spectrum, and odor description of an identified compound correspond to the retention time, spectrum, and odor description of the injected standard of this compound). For mass fragments, the proportion of the mass fragment is given in parentheses. When only MS or LRI is available for the identification of a compound, it must be considered as an attempt of identification. The odor given corresponds to the odor detected by the judges for its retention time but not surely to the compound that we try to identify. [b] Intensity is rounded to the nearest whole number. An intensity between 3 and 3.5 is rounded to 3 and an intensity between 3.5 and 4 is rounded to 4 (1 = very weak odor intensity, 9 = very strong odor intensity). [c] Number of judges who detected an odor. [d] In microgram equivalents of dodecane per 100 g of smoked salmon. The mean and the standard deviation are given for each identified and quantifiable compound. Each concentration is the mean of three aromatic extracts injected corresponding to three individual fillets smoked at 32 °C. Tr, trace; NQ, not quantified.[e] NC, not common descriptors. [f] Possibility of coelution.

Products of Strecker degradation were also detected in smoked salmon, such as 3-methylbutanal and benzeneacetaldehyde even if Strecker degradation is not the only origin of these molecules (*17*). 3-Methylbutanal is found at trace level with a weak impact (a frequency of detection of four judges with an intensity of 4) and benzeneacetaldehyde, which provides green aromatic notes perceived by seven panelists with an intensity of 5. Therefore, Maillard reaction and Strecker degradation products could strongly affect the overall smoked salmon aroma by varying the smoky flavor with green, roasted, nutty, earthy, and resinous aromatic notes.

Odorant Compounds of Smoked Salmon: Other Cyclic and Aliphatic Compounds in Smoked Salmon. Numerous cyclic compounds were also perceived in smoked salmon flesh. We can differentiate groups of derivatives of cyclopentenone, benzene, toluene, and benzaldehyde. They have been previously described in wood smoke in various studies (*19*, *20*, *41*). Cyclopentenone derivatives are known to be formed from cellulose pyrolysis and provide aromatic notes such as burnt/sweet and green (*18*). 2,3-Dimethyl-2-cyclopentenone was the most smelled by eight judges but with the weakest intensity of 5. 2-Methyl-2-cyclopentenone and 2-hydroxy-3-methyl-2-cyclopentenone were detected by seven and six assessors, respectively, with higher intensities. The cyclopentenone derivative concentrations range from 10 to 22 μg of IS/100 g and appear as the third most common compound family after phenolic and furanic compounds. Benzene derivatives, such as 1,2-dimethoxybenzene and 1,2,3-trimethoxy-5-methylbenzene, have been identified in smoked salmon, but no studies have reported their odors, which were named earthy/moldy/green for the first compound and more burnt and spicy for the second. The assessment of 1,2-dimethoxybenzene is easily established because of its concentration (7.78 μg of IS/100 g), its frequency of detection (seven judges), and its intensity (mark of 5), but for 1,2,3-trimethoxy-5-methylbenzene it is not obvious because of its low concentration, frequency of detection, intensity, and the absence of odorant descriptor in the literature. It is nearly the same case for toluene derivatives. Indeed, except for 3,5-dimethoxytoluene, the odor of which is in accordance with the literature, it was not possible to find previous odorant descriptors for 2,3-dimethoxytoluene (found with green, smoked, and fruity aromatic notes) and 2,3,5-trimethoxytoluene (found with solvent,

Table 2. Volatile Odor-Active Compounds of Smoked Salmon Present in Wood Smoke, Fresh Seafood, or Processed Seafood

compound	occurrence in wood smoke	occurrence in processed seafood	occurrence in fresh seafood
diacetyl	21	38	45
acetic acid	18	14	50
2-pentanol	21	49	50
2,4-hexadienal	18		45
heptanal		38	50
benzonitrile		10	
(*E*,*E*)-2,4-heptadienal		38	29
2-ethyl-1-hexanol		38	29
benzyl alcohol	18	38	50
acetophenone	21	49	29
(*E*)-2-decenal		14	
2-undecanone		38	29
undecanal		48	
dodecanol		51	
hexadecanal		14	

fruity, and chemical aromatic notes). Nevertheless, their presence in smoked salmon was checked by MS spectra and LRI in accordance with the literature. Benzaldehyde and benzaldehyde derivatives exhibit green and spicy pleasant odors, like 4-methoxybenzaldehyde (even when found at trace level), which was perceived by seven judges with an intensity of 4, and 2,3-dimethoxybenzaldehyde. 3-Methoxybenzaldehyde gives more burnt/amine notes, but only an MS spectrum was obtained to assess its presence as 2,3-dimethoxybenzaldehyde.

Aromatic hydrocarbons, such as indene derivatives and naphthalene derivatives, were determined. Indene derivatives, such as 2,3-dihydro-(1*H*)-indene or 4-methylindanone, give a rubber, plastic, and resinous aroma to the smoked flesh. Naphthalene and its derivatives could be interpreted as polycyclic aromatic hydrocarbon contaminants through the smoking process or environmental contaminants through the rearing of the salmon. Naphthalene is responsible for a spicy/smoked odor, whereas 2-methylnaphthalene, described by seven judges with an intensity of 6, and 1,6-dimethylnaphthalene carry more green notes with the burnt/smoke overall odor. Even if naphthalene and its derivatives must be avoided in smoked salmon, they seem to play a role in the smoked aroma. Naphthalene and 1,6-dimethylnaphthalene could not be quantified because of problems of separation from other compounds. However, their odors were assessed by seven and four judges, respectively, with intensities of 6 and 5. Hexadecene was the most smelled aliphatic alkene, whereas 8-heptadecene was perceived by only half of the total number of judges with a leather odor and an intensity of 6. Nevertheless, 8-heptadecene concentration is about 9.91 μg of IS/100 g and that of hexadecene is about 2. Therefore, the odor threshold values of these two similar aliphatic hydrocarbons are very different and an increase in the carbonated skeleton can strongly influence the perception of the odor of the molecule.

It is interesting to note that certain compounds found in smoked salmon have been reported in wood smoke (*21*) or in fresh seafood (*29*), sometimes in both, or also in processed seafood (*38*). They are heterocyclic, such as benzonitrile, or aliphatic compounds, alcohols (2-pentanol, dodecanol), aldehydes (2,4-alkadienals, heptanal), ketones (2-undecanone), and acids (acetic acid). Carbonyls and alcohols, which have low odor threshold values, are detected at trace level except for hexadecanal, which is significantly abundant (34.82 μg of IS/100 g). These ubiquitous compounds are compiled in **Table 2** and illustrate the difficulty in assessing the origins of the odorants in smoked salmon. Indeed, the odorant compounds can derive from common lipid oxidation in unsmoked fish flesh, from lipid oxidation due to the smoking process conditions or from the wood smoke.

It is also important to note that the smoking process favors fatty acid degradation because some compounds not present in fresh salmon and known to derive from fatty acids are present in smoked salmon. This is the case for (*Z*)-9-octadecanol and (*Z*)-9-octadecanal with cooked odors, but more woody/pleasant for the first and more sulfury/leather for the second. Their concentrations are, respectively, 11.66 and 13.58 μg of IS/100 g. They have nearly the same weak frequency of detection (four/five judges), so they may not have a strong effect on the overall aroma. Nevertheless, their intensity is marked for both compounds at 5.

Odorant Compounds of Smoked Salmon: Chromatographic Coelutions and Impact on the Odors. Unexpected odors for several compounds, such as 2,4- and 2,5-dimethylphenol, were detected by the judges. They are identified in the odorant areas of the chromatogram that correspond to green and floral aromatic notes, whereas burnt, spicy/smoky notes were expected as for 2,3- and 3,4-dimethylphenol. This phenomenon can be explained by coelution with (*E*)-2-nonenal, which carries similar green and vegetal odors, observed at the same retention time in unsmoked salmon. It is also the same type of coelution between (*E*)-2-decenal and thymol, where (*E*)-2-decenal, with a plastic, green, and cheesy odor, has a retention time close to that of thymol, marked by spicy and chemical notes. Moreover, 10 of the 14 unknown compounds were assessed with green, floral, woody, and spicy notes. These odors are more similar to the descriptors of odorants of fresh salmon. It can be proposed that these odorants, which often have a low odorant threshold, are the unknown compounds of smoked salmon aroma but cannot be measured because of their very low quantities and so are hidden by the signal given by the important odorless volatiles of smoked salmon. The extraction method could also explain a part of the unknown compounds by the treatment of the sample.

Odorant Compounds of Unsmoked Fresh Salmon. Fifty-eight odorant areas were detected in unsmoked fish extract by GC-O, and 49 were identified by GC-MS in **Table 3**. Among them, 13 were perceived by at least seven of the eight assessors. Carbonyl compounds resulting from lipid oxidation are very present and contribute strongly to the overall fishy odor as *n*-alkanals, 2-alkenals, and 2,4-alkadienals.

Odorant Compounds of Unsmoked Fresh Salmon: *n*-Alkanals. All *n*-alkanals are produced from *n*-6 or *n*-9 polyunsaturated fatty acids (PUFA) present in fish flesh (*6*, *7*, *11*). Indeed, aldehydes from butanal to undecanal could derive from oleic acid (*n*-9 PUFA), detected in a large amount in salmon but with a weak odor of plastic/earth. *n*-Alkanals from hexanal to undecanal were identified in unsmoked flesh. They were detected by at least six judges, except decanal and undecanal, which were perceived by only four judges. Each alkanal was smelled very differently by the judges. Products of lipid oxidation with higher carbon atom number are also present in unsmoked fish flesh. As a result, hydroperoxides and carboxylic acids are created. Thus, tetradecanoic acid (with marine/fatty, cheese aroma) found in fresh salmon at a concentration of 5.83 μg of IS/100 g could be formed from hydrolysis of triglycerides but also from tetradecanal. Although the tetradecanal concentration is not very high (0.37 μg of IS/100 g), it was smelled by seven assessors with an intensity of 5. Following the same scheme of oxidation, hexadecanoic acid

Table 3. Identification and Odorant Characteristics of Volatile Odor-Active Compounds of Unsmoked Salmon

compound	LRI (DB5)	means of identification[a]	odorant descriptors given by judges	intensity[b]	no. of judges[c]	concentration[d] (mean ± SD)
diacetyl	600	LRI	butter	4	6	Tr
1-penten-3-ol	688	MS, LRI, STD	chemical, plastic	2	4	Tr
2-hydroxy-3-pentanone	710	MS, LRI	floral, dusty	3	4	$23.50 \times 10^{-3} \pm 4.76 \times 10^{-3}$
hexanal	805	MS, LRI, STD	cut grass, fruity, plastic	4	6	$380.74 \times 10^{-3} \pm 78.82 \times 10^{-3}$
unknown	835	43 (50), 44 (50), 45 (100), 57 (30), 70 (12)	roasted, burnt rubber	4	5	Tr
(*E*)-2-hexenal	865	MS, LRI, STD	eucalyptus, mushroom	5	6	1.06 ± 0.47
p-xylene	875	MS, LRI	solvent, phenolic	6	8	$1.24 \pm 43.21 \times 10^{-3}$
m-xylene	885	MS, LRI	plastic, phenolic	6	7	1.32 ± 0.38
o-xylene	900	MS, LRI	cooked vegetable	5	8	$117.66 \times 10^{-3} \pm 28.43 \times 10^{-3}$
heptanal	914	MS, LRI, STD	cooked potato, fat	7	7	2.13 ± 0.18
(*Z*)-4-heptenal	915	MS, LRI, STD	cooked vegetable, fishy	7	6	$673.37 \times 10^{-3} \pm 95.50 \times 10^{-3}$
methional	925	MS, LRI, STD	cooked potato	7	6	$670.53 \times 10^{-3} \pm 0.1$
2-acetyl-1-pyrroline	935	LRI	roasted, roasted bread/nuts	5	6	Tr
benzaldehyde	980	MS, LRI, STD	fruity, floral	4	5	$547.53 \times 10^{-3} \pm 86.30 \times 10^{-3}$
1-octen-3-ol	990	MS, LRI, STD	mushroom	5	6	$186.72 \times 10^{-3} \pm 24.76 \times 10^{-3}$
phenol	992	MS, LRI, STD	phenolic, sulfury, leather	6	7	$789.25 \times 10^{-3} \pm 0.16$
octanal	1009	MS, LRI, STD	cooked potato, fat, fishy, wax, citrus	6	6	2.23 ± 0.37
thiophenecarboxaldehyde	1012	MS, LRI	sulfury, earthy	5	4	Tr
(*E*,*E*)-2,4-heptadienal	1019	MS, LRI, STD	roasted	5	4	2.04 ± 0.25
2-ethyl-1-hexanol	1038	MS, LRI, STD	mushroom, cucumber, cooked vegetable	4	4	$1.20 \pm 92.26 \times 10^{-3}$
limonene	1042	MS, LRI	pine/chemical, floral/fresh	2	4	Tr
benzyl alcohol	1057	MS, LRI, STD	herbaceous, wet wood, floral	3	4	$200.43 \times 10^{-3} \pm 49.57 \times 10^{-3}$
benzeneacetaldehyde	1062	MS, LRI, STD	moss, spicy	3	4	$446.42 \times 10^{-3} \pm 70.45 \times 10^{-3}$
(*E*)-2-octenal	1076	MS, LRI, STD	moldy, pungent, cucumber/moss	4	5	$937.70 \times 10^{-3} \pm 66.89 \times 10^{-3}$
3,5-octadien-2-one	1098	LRI	plastic	5	5	1.54 ± 0.24
nonanal	1110	MS, LRI, STD	hospital, cucumber, vegetal	6	6	5.09 ± 0.17
(*E*,*E*)-2,4-octadienal	1111	MS, LRI, STD	phenolic, roasted/cucumber, cooked, fat	6	7	2.32 ± 0.38
unknown	1121	45 (45), 81 (30), 85 (100), 97 (15), 114 (100)	cooked meat, fat, green	5	7	NQ
menthatriene	1130	MS, LRI	green, cucumber, floral	5	7	$813.10 \times 10^{-3} \pm 0.19$
unknown	1144	40 (80), 43 (65), 57 (100), 119 (88), 133 (70)	roasted, burnt	5	5	NQ
unknown	1153	40 (100), 57 (75), 71 (75), 133 (90), 151 (50)	cut grass, spicy	3	4	NQ
(*E*,*Z*)-2,6-nonadienal	1160	MS, LRI, STD	floral, cucumber	6	7	$525.63 \times 10^{-3} \pm 60.09 \times 10^{-3}$
(*E*)-2-nonenal	1173	MS, LRI, STD	moss, woody, floral	6	6	Tr
decanal	1213	MS, LRI, STD	plastic, fishy, cardboard	4	4	2.89 ± 0.74
benzothiazole	1258	MS, LRI	green, plastic, fruity	4	7	$1.24 \pm 404.31 \times 10^{-3}$
(*E*)-2-decenal	1266	MS, LRI	cooked, plastic	3	5	$370.42 \times 10^{-3} \pm 66.15 \times 10^{-3}$
decanol	1280	MS, LRI	plastic, fatty,	4	4	Tr
unknown	1289	40 (100), 41 (88), 44 (88), 55 (95), 57 (95)	green, vanilla	6	6	NQ
2-undecanone	1296	MS, LRI, STD	nutty, green, fruity	4	6	$208.79 \times 10^{-3} \pm 48.57 \times 10^{-3}$
undecanal	1319	MS, LRI, STD	herbaceous, aniseed, fruity	4	4	1.31 ± 0.23
(*E*,*Z*)-2,4-decadienal	1319	MS, LRI, STD	fishy, medicinal	5	7	$349.06 \times 10^{-3} \pm 76.35 \times 10^{-3}$
1-methylnaphthalene	1325	MS, LRI	vegetal, cooked, green	5	5	$458.17 \times 10^{-3} \pm 0.16$
(*E*,*E*)-2,4-decadienal	1330	MS, LRI, STD	cooked, oily, solvent	6	6	$817.38 \times 10^{-3} \pm 0.15$
2-methylnaphthalene	1340	MS, LRI	marine, green, solvent	6	5	$309.90 \times 10^{-3} \pm 0.14$
unknown	1390	39 (75), 40 (60), 43 (100), 55 (100), 69 (80)	minty, green, spicy	5	6	NQ
aromadendrene	1441	MS, LRI	cucumber, vanilla, floral	4	7	$131.36 \times 10^{-3} \pm 39.66 \times 10^{-3}$
unknown	1472	41 (90), 43 (70), 55 (100), 69 (75), 83 (70)	rubber, sugar	4	4	NQ
1-pentadecene	1488	MS, LRI	rubber, plastic	3	4	3.45 ± 0.58
unknown	1540	41 (90), 55 (46), 69 (100), 95 (45), 109 (75)	plastic, fishy, earthy	3	6	NQ
tetradecanal	1625	MS, LRI	wet wood, marine, plastic	5	7	$369.71 \times 10^{-3} \pm 84.03 \times 10^{-3}$
unknown	1672	41 (90), 55 (100), 67 (95), 81 (95), 96 (80)	rubber, amine, algae	5	7	NQ
8-heptadecene	1680	MS, LRI	plastic, moss	6	5	23.96 ± 5.85
unknown	1735	43 (80), 55 (65), 57 (100), 71 (80), 85 (55)	sugar, plastic	4	4	NQ
tetradecanoic acid	1770	MS, LRI	marine, fatty, cheese	4	5	5.83 ± 1.18
(*E*)-3-octadecene	1795	MS, LRI	cheese, plastic	5	4	3.62 ± 1.67
hexadecanal	1808	MS, LRI	marine, fat, NC[e]	4	5	18.74 ± 7.87
farnesol	1822	MS, LRI	fruity	4	5	Tr
oleic acid	2130	MS, LRI	plastic, alcoholic, earthy	3	4	Tr

[a] Means of identification: MS, mass spectrum (identified thanks to the mass spectra of the compounds); LRI, linear retention index (when the LRI of the compound identified corresponds to the LRI in the literature); STD, s tandard (when the retention time, spectrum and odor description of an identified compound corresponds to the retention time, spectrum and odor description of the injected standard of this compound). For mass fragments, the proportion of the mass fragment is given in parentheses. When only MS or LRI is available for the identification of a compound, it must be considered as an attempt of identification. The odor given corresponds to the odor detected by the judges for its retention time but not surely to the compound that we try to identify. [b] Intensity is rounded to the nearest whole number. An intensity between 3 and 3.5 is rounded to 3 and an intensity between 3.5 and 4 is rounded to 4 (1 = very weak odor intensity, 9 = very strong odor intensity). [c] Number of judges who detected an odor. [d] In microgram equivalents of dodecane per 100 g of unsmoked salmon. The mean and the standard deviation are given for each identified and quantifiable compound. Each concentration is the mean of three aromatic extracts injected corresponding to three individual fillets smoked at 32 °C. Tr, trace; NQ, not quantified. [e] NC, not common descriptor.

(with marine/fatty, fruity notes) could be formed from hexadecanal, identified as a volatile compound in fresh salmon but without odorant properties. Hexadecanal is the second odorant compound in fresh salmon, detected at a concentration of about 18.74 μg of IS/100 g, but it does not have a strong impact on the overall fresh aroma.

Odorant Compounds of Unsmoked Fresh Salmon: 2-Alkenals. 2-Alkenals, from 2-hexenal to 2-undecenal, are products of oxidation of fatty acids such as oleic acid, but they can also derive from *n*-6 PUFA, like arachidonic acid for aldehydes such as 2-heptenal or 2-octenal and like linoleic acid for (*E*)-2-alkenals from 2-heptenal to 2-nonenal and for (*Z*)-2-alkenals such as (*Z*)-2-octenal and (*Z*)-2-decenal (*41*, *42*). Thus, (*E*)-2-hexenal (with green aromatic notes), (*E*)-2-octenal (with less green and more unpleasant odors), (*E*)-2-nonenal (with moss, woody/floral descriptors), and (*E*)-2-decenal (with cooked, plastic odors) have been characterized in fresh salmon. They have very low odor thresholds because they were smelled by five or six judges with medium intensity marks and because they were in very low quantities. The most perceived and the most intense 2-alkenal identified is (*E*)-2-nonenal, which is at trace level. The concentrations of the other 2-alkenals do not exceed 1 μg of IS/100 g. From 2-hexenal to 2-decenal, the odor becomes less citrus and fruity and more fat-like, moldy, and unpleasant when the size of the carbonated skeleton increases.

Odorant Compounds of Unsmoked Fresh Salmon: 2,4-Alkadienals. 2,4-Alkadienals, such as decadienal and isomers, come from PUFA *n*-6 such as linoleic or arachidonic acid. All of these aldehydes give particular notes to the overall aroma. Indeed, they bring a fatty and a floral/fruity note, which decreases with the increase in the number of carbon atoms in the chain of the aldehyde. Except for (*E*,*E*)-2,4-heptadienal, which was detected by only four judges, the other 2,4-alkadienals were described by at least six judges with concentrations of about 2.04 or 2.33 μg of IS/100 g for (*E*,*E*)-2,4-heptadienal and octadienal, respectively. The concentration of (*E*,*E*)-2,4-decadienal is about 0.82 μg of IS/100 g, 2 times more than the concentration of (*E*,*Z*)-2,4-decadienal (0.35 μg of IS/100 g). Nevertheless, the variation of one judge in the frequency of detection or 1 unit in the intensity is not sufficient to show a trend between the concentration and the odorant perception of these compounds.

Odorant Compounds of Unsmoked Fresh Salmon: Other Carbonyl Compounds. Unsmoked salmon aroma is also very marked by (*Z*)-4-heptenal and methional, which provide a strong cooked potato odor. However, (*Z*)-4-heptenal also brings a slight fishy flavor. These two compounds are very close on the chromatogram and were detected by the same number of assessors; they have the same intensity of 7 and similar concentrations of about 0.67 μg of IS/100 g. Thus, their contribution is essential to the overall aroma of unsmoked salmon. Benzothiazole could also be identified as a Strecker degradation compound (like methional) and brings green, plastic, and fruity aromatic notes. (*E*,*Z*)-2,6-Nonadienal, 2-hydroxy-3-pentanone, 3,5-octadien-2-one have been reported in many seafood products with pleasant odors such as cucumber, fruit, and flower. In fresh salmon, several works have suggested that (*E*,*Z*)-2,6-nonadienal plays an important role in fresh fish-like odors due to its low threshold values (*6*, *7*, *13*). Indeed, it is found in unsmoked salmon at a weak concentration; however, it was perceived by seven judges who described it with an intensity mark of 6.

Odorant Compounds of Unsmoked Fresh Salmon: Aliphatic Compounds. The terpenes recovered in fish such as limonene, menthatriene, aromadendrene, and farnesol usually come from the diet. The environment of the salmon is therefore very important for the final odor because contaminants such as naphthalene derivatives and terpenes can be odorants in small quantities. Farnesol and limonene were measured at trace levels in unsmoked fish flesh, aromadendrene was found at 0.13 μg of IS/100 g, and menthatriene was found at about 0.81 μg of IS/100 g. Nevertheless, they were smelled by between four and seven judges for menthatriene and aromadendrene, but their intensities are not very high and, in general, marked at 4. 1-Penten-3-ol and 1-octen-3-ol have a fruity/chemical and a mushroom odor, respectively. These compounds have already been reported in many seafood products (*29*, *38*). Their low odor threshold makes them odorant at low concentrations. Unsmoked salmon aroma is also constituted by 2-acetyl-1-pyrroline with a roasted/nutty aroma. As in smoked salmon, it was detected at trace level but seems to be very predominant in the overall aroma because six panelists marked it with an intensity of 5.

Odorant Compounds of Unsmoked Fresh Salmon: Cyclic Compounds. Aromatic hydrocarbons, such as naphthalene derivatives, have been found olfactively in fresh salmon and could be considered as environmental contaminants. They were detected by five judges with an intensity close to 5/6 and are present in weak concentrations.

Other cyclic compounds were also smelled in fresh flesh in the form of benzaldehyde, benzenemethanol, and benzeneacetaldehyde, which exhibit floral and fruity notes. Their contribution to the fish aroma appears not to be very important because only four/five judges pointed them out and qualified them with intensity no higher than 4. Xylene isomers were strongly perceived by nearly all of the judges. Their intensity at around 5 or 6 seems not to be linked to their concentrations because *o*-xylene was detected at 0.12 μg of IS/100 g, whereas *p*- and *m*-xylene are 10 times more present in unsmoked flesh. These compounds can originate from carotenoid degradation and carry odors defined as plastic/fruity or cooked vegetables according to the geometry of the molecule. They have been reported as odor-active components of many fresh seafood products (*44*, *45*).

The unknown odors were generally marked by pleasant descriptors, but they cannot be identified due to a weak MS signal. Nevertheless, even with a weak signal and low concentrations, these compounds remain very odor-active.

Odorant Compounds of Unsmoked Fresh Salmon: New Compounds of Salmon Aroma. Fresh or processed (boiled, canned) salmon aroma has already been studied. By comparison with these previous works, 16 compounds have been identified in unsmoked salmon that were not identified in the past in this matrix. Nevertheless, some of these compounds were identified in fresh or processed seafood but not especially with odorant properties. Phenol, thiophenecarboxaldehyde, limonene, benzyl alcohol, benzeneacetaldehyde, (*E*,*E*)-2,4-octadienal, tetradecanoic acid, and farnesol have been reported as seafood volatile compounds (*12*, *13*, *29*, *30*, *39*). This is the first time that 2-hydroxy-3-pentanone, menthatriene, aromadendrene, 1-pentadecene, tetradecanal, 8-heptadecene, (*E*)-3-octadecene, and hexadecanal are identified in smoked salmon aroma. The presence of none of these compounds is surprising because alkenes, terpenes, and products of lipid oxidation are commonly found in seafood aroma. They do not have a strong impact on the overall odor because they are not perceived by a high number of judges and have low or medium intensities except for the terpenes and (*E*,*E*)-2,4-octadienal.

Quantitative and Odorant Comparison between Unsmoked and Smoked Salmon: Evolution of Odorant Compounds of Unsmoked Salmon during the Smoking Process. The overall aroma of unsmoked and smoked salmon has already been presented (*28*). Comparison between **Tables 1** and **3** explains the aromatic trends previously observed and sufficiently presents the differences from an "odorant descriptor" point of view. Thus, comparison between the two matrices must be more focused on quantitative and odorant parameters such as the concentration and FDT of the compounds identified. The compounds can be divided into three categories. Indeed, the first possibility is that the FDT of the compound is the same in fresh and smoked salmon. The second possibility is that the FDT varies, and it is possible to link these variations with variations in concentrations. The third category concerns the coelutions of odor-active fresh salmon compounds with weak odor-active or odorless smoked salmon compounds. As a result, odor mixtures, synergic or masked effects, can occur. The smoking process acts very unequally according to the odor-active compounds, and each case must be separately discussed.

Similar Odorants FDT in Smoked and Unsmoked Salmon: Case of Benzaldehyde. Benzaldehyde is perceived by five of the eight assessors in both types of matrix. We can conclude that the smoking process does not affect the odorant perception of these molecules. Nevertheless, the concentrations between the two extracts can be different but the odor descriptors lead to unchanged aromatic notes for both molecules. Thus, even if the concentrations are not the same (benzaldehyde is found in fresh salmon at a concentration of 0.55 μg of IS/100 g of product and at 29.49 μg of IS/100 g in smoked salmon), the smoking process does not create odorant differences for these compounds The variation in the intensity from 4 in unsmoked flesh to 5 in smoked fish is not significant enough to imply an effect of the process on the odor perception of this compound.

Variations in Odorants FDT between Unsmoked and Smoked Salmon and Relationship with Concentration: Cases of 2-Ethyl-1-hexanol, 2-Methylnaphthalene, and Phenol. For some compounds, it is easy to link an increase or a decrease in the frequency of the odorant perception with the variation in its concentration. This is the case for 2-ethyl-1-hexanol, for which the frequency of odorant perception increased from four to six while its concentration increased from about 1.20 to 4.34 μg of IS/100 g of salmon. This observation can be also carried out with 2-methylnaphthalene. The number of assessors who smelled it increased from five to seven between the unsmoked and smoked samples. This can be explained by the creation of aromatic hydrocarbons during the smoking process, which could increase the concentration and odorant perception of 2-methylnaphthalene. Indeed, its concentration was approximately 0.31 μg of IS/100 g of salmon in the fresh matrix and reached 3.68 μg of IS/100 g in the smoked matrix. However, it is important to note that the intensity mark between the two matrices does not vary.

Sometimes, it is difficult to confirm the odorant perception of a compound and to relate it to its concentration. Phenol, for example, was detected in smoked extract by fewer judges than in fresh extract (a decrease from seven to five assessors), whereas its concentration was multiplied by a factor of >100. In general, there is no linear relationship between odorant power and concentration. Besides, for some compounds, the quantification cannot be obvious. Therefore, it leads to higher SD values, which can be related to difference in perception of the judges. It is the case of phenol where the coefficient of variation in unsmoked salmon is 20.27% and that in smoked salmon is 30.89%. Then, the lack of homogeneity of the phenol content in smoked salmon could explain the global decrease of FDT. However, even if a linear relationship between FDT and concentration cannot be proven, global trends can be observed between the evolution of some FDT of compounds with their concentrations.

Coelutions in Smoked Salmon between Odor-Active Compounds from Unsmoked Salmon and Compounds of Smoked Salmon. Another explanation for the FDT decrease of phenol between unsmoked and smoked salmon is the phenomenon of coelution of odorless or odor-active aroma compounds of fresh salmon and smoked salmon. Indeed, there is a proximity of elution between phenol and 1-octen-3-ol. Therefore, their odor can very easily be mixed by the judges. In the salmon aromatic extracts, coelutions can occur under three forms according to the intensity and the odor descriptor of the smoked salmon compound. In the case where the smoked salmon coeluted compound is odorless, it causes only problems of identification. If it is odorant, it can strongly affect the odor. For example, in smoked salmon, dimethylphenols are found but related to unexpected green and fruity aromas. By comparing the aromatic profiles of unsmoked and smoked salmon, we have pointed out that, at the same retention time, there were similar odorant descriptors in fresh salmon but attributed to (*E*,*Z*)-2,6-nonadienal and (*E*)-2-nonenal. In this case, the MS signals of the two aldehydes are two small and hidden by the large signal of dimethylphenols. Nevertheless, thanks to a careful study of the mass spectra through extraction ions from the chromatogram of the SCAN acquisition, we have identified four of the five most important ions of (*E*,*Z*)-2,6-nonadienal [*m*/*z* 39 (25%), 41 (100%), 43 (5%), 69 (40%), 70 (45%)] and four for (*E*)-2-nonenal [*m*/*z* 41 (85%), 43 (100%), 55 (90%), 70 (86%), 83 (68%)] under dimethylphenol peaks. These aldehydes cannot be quantified in smoked salmon due to their too weak concentration. In unsmoked salmon, they have been identified because the noise in the fresh sample is lower than in the smoked sample loaded with many volatile compounds. It leads to mixtures of unexpected odors characterized as spicy by the judges but corresponding to mixtures of green/fruity for the aldehydes and burnt/smoke for the dimethylphenols. It is the same case for (*Z*)-4-heptenal in fresh salmon and 2-methyl-2-cyclopentenone found in smoked salmon. Indeed, 2-methyl-2-cyclopentenone is marked, like the cyclopentenone derivatives, with burnt/sugared aromatic notes in wood smoke but, in smoked salmon, the odorant descriptors become less burnt and more like cooked food. We can suggest an influence of (*Z*)-4-heptenal, which carries cooked vegetable/fishy odors, even if we did not manage to identify this compound under the 2-methyl-2-cyclopentenone peak except on one injection. Finally, the third case is when the smoked salmon coeluted compound is very odorant. As a result, the fresh salmon odorant descriptor can totally disappear (like for nonanal coeluted with guaiacol and 2-undecanone coeluted with 4-ethylguaiacol, where the phenolic odor masks the carbonyl odors).

By the study of the coelutions of smoked salmon chromatogram related to odorant descriptors, it becomes easier to understand how the smoking process influences the evolution of odor-active compounds between unsmoked and smoked salmon.

Creation of Smoked Salmon Odorants from Unsmoked Salmon Precursors. It is also very interesting to note that smoked salmon aroma contains odor-active compounds not detected in fresh salmon but known to derive from odorant or odorless precursors that are present in fresh salmon. Under

smoking process conditions, lipid oxidation continues (*46*). For example, 2,4-hexadienal comes from lipid oxidation and is revealed as odorant in smoked salmon, although it cannot be detected in fresh salmon. Oleic acid oxidation is also noticeable. Oleic acid is present and odorant in unsmoked salmon but is not recovered in the smoked sample, whereas we can observe the creation of the odorants (*Z*)-9-octadecenal and (*Z*)-9-octadecenol. It seems that industrial processes involving heat could affect the odorless (or odor-active) components of fresh salmon, which become the precursors of certain aroma compounds of smoked salmon. This is especially the case for carbonyl compounds (*47*).

Smoked salmon odor is a complex combination between its own odor of smoked salmon, due largely to wood smoke, fresh salmon aroma, and the odors created from fresh salmon components under the conditions of the smoking process. It is sometimes very difficult to suggest a simple origin for an odor-active compound because of the various possible routes of its creation. Moreover, it is not easy to elucidate certain odors that are the result of a combination of several odor-active compounds derived from various origins. The differences between smoked and unsmoked fish flesh involve masking and synergic effects in the odor perception.

Conclusion. Smoked and unsmoked salmon aroma profiles have been carried out, and the odor-active compounds have been individually characterized. The influence of the smoking process has been confirmed and assessed in an odorant way because the aroma compounds have been affected by the process. The concentrations and the odorant occurrences of the odor-active compounds of smoked salmon could be good indicators for the discrimination of all smoking processes. Their study also opens up new possibilities for adapting the process to increase the odors of smoked salmon. Indeed, such modifications of smoking parameters could change the concentrations and the odorant perception of certain aroma compounds of smoked salmon to increase the choice of products for the consumer. Phenolic compounds, in particular, can be followed as indicators of the smoke creation and intensity of the process. When the odorants of smoked salmon and their pathways of creation are known, it will be easier to modify the smoking process. This knowledge could also stimulate the production of smoked salmon with required odors. We can also imagine an application of this study to other smoked products such as fish or meat. However, the overall aroma of smoked salmon is built by complex combinations of odors, which will not be easy to favor without creating polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and its derivatives that we have found in smoked salmon.

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