Characterization of aroma-active compounds in canned tuna by fractionation and GC/Olfactometry

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Abstract

Odour-active compounds from two canned tunas (albacore and skipjack) were isolated using solvent extraction followed by solvent-assisted flavour evaporation and normal phase chromatography separation. Aroma-active compounds were identified by gas chromatography/olfactometry-mass spectrometry (GC/O-MS). Many sulfur-containing compounds (2-methylthiophene, 2-methyl-3-furanthiol, 1-acetyl-1-pyrroline, dimethyl sulfide, dimethyl trisulfide, 2-furfurylthiol, methional) were identified contributing to meaty, chicken-like aroma. The majority of the odour-active compounds, however, were saturated and unsaturated aldehydes such as hexanal, nonanal, (*Z*)-4-heptenal, (*E*,*Z*)-2,6-nonadienal, (*E*,*E*)-2,4-decadienal, and acids. Most of these compounds were identified in both skipjack and albacore species, but their aroma intensities were different. Results demonstrated that normal phase chromatography is a useful tool to help compound identification in complex mixture.

Introduction

Many factors can affect the aroma profile of canned tuna, including processing conditions [1], fish species [2,3], and storage conditions [4,5]. Oxidation of unsaturated fatty acids in fish generates saturated and unsaturated aldehydes [6], and some of these compounds have been reported as useful markers for fishy off-flavours in fish and fish products [7]. Besides lipid oxidation, off-flavours may originate from environmental pollutants, microbial spoilage, or endogenous enzymatic decomposition [8,9]. The objectives of this study were to identify the odour-active compounds responsible for the canned tuna aroma.

Experimental

Materials

Two types of commercially canned tuna (skipjack and albacore species) were provided by an industrial collaborator (Bumble Bee Foods, San Diego, CA). Each of the species was procured from five different fish suppliers/regions, including Europe, Asia, and America. All samples were stored at 4 °C until use.

Tuna aroma isolation with Solvent-Assisted Flavour Evaporation (SAFE)

For each tuna species, one can of tuna sample (125 g) from each supplier/batch was blended with liquid nitrogen into fine powders and all five samples were mixed together (625 g totally). The tuna powder was mixed with 200 mL of saturated salt water and then extracted with 200 mL of freshly distilled diethyl ether. The mixture was shaking vigorously for 1 hour at room temperature in a Teflon centrifuge bottle. The organic phases were separated by centrifuge at 5500 rpm for 10 min at 5 °C. The organic phase was saved and the sample was extracted two more times. The organic phases from three extractions were combined and distilled using solvent assisted flavour evaporation (SAFE) (Glasblaserei Bahr, Manching, Germany) at 50 °C under vacuum. The distillates

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were dried over anhydrous sodium sulfate and concentrated to 1mL at 40 °C using a Vigreux column, then concentrated to 0.5 mL using a gentle nitrogen.

Normal Phase Chromatography and Gas Chromatography/Olfactometry-Mass Spectrometry (GC/O-MS)

To facilitate the GC/O analysis, aroma extracts were separated by fractionation prior to GC-O analysis. A column packed with 5 g of silica gel was washed with 100 ml methanol, then 100 ml diethyl ether, and then with 100 ml pentane. After sample loading, pentane (fraction 1), 50 ml pentane: diethyl ether (98:2, fraction 2), pentane:diethyl ether (95:5, fraction 3), pentane:diethyl ether (90:10, fraction 4) and diethyl ether (fraction 5) were sequentially applied to elute the aroma compounds from the column at a flow rate of 3 ml/min. All elutes were slowly concentrated to 10 ml and then to 100 µL with a stream of nitrogen for GC–O and GC–MS analysis.

The GC-O and GC-MS analysis were performed using an Agilent 6890 GC-MS (5973N, Agilent, Willmington, DE), and a Gerstel olfactory detection port (Gerstel, Baltimore, MD). All the samples were analysed on a DB-Wax column (30 m, 0.25mm ID, 0.5 µm film thickness). One microliter of fractionated aroma extract was injected into the GC in splitless mode. The oven temperature was programmed initially at 40 °C for 1 min, then increased to 70 °C at a rate of 8 °C/min, then increased to 200 °C at a rate of 3 °C/min and increased to 230 °C at a rate of 8 °C/min with 15 min holding. The column carrier gas was helium at a flow rate of 2 mL/min. The flow was split between MS and ODP at 1:1 ratio to provide one stream for MS identification and another stream to the sniffing port for odour detection simultaneously. The olfactometry analysis was achieved by five experienced panellists for all samples. The odour intensities were evaluated on a five-point intensity scale, where 1 meant a volatile has a slight sensory impact, 3 was for moderate, and 5 was for extreme impact. The intensity was the average from all panellists. Compounds' identification was achieved by comparing mass spectral data from the MS spectra database and confirmed by comparing Kovats retention indices of standards under the same conditions or those reported in the literature, in addition to odour description.

Results and discussion

Normal phase chromatography separates the tuna extract into five fractions. The number in each fraction represented the odour intensity ranging from 1 to 5, where 5 was the strongest odour, and 1 was the weakest.

Table 1. Odour-active compounds in canned tuna detected by GC-O and Normal Phase Fractionation.

Compounds	*RI (DB-wax)*	*ID*	*Odour*	*Skipjack*						*Albacore*					
				F1		F3	F4	F5	All	F1	F2	F3	F4	F5	All
Dimethyl sulfide	842	1,2	cabbage	3					3						0
2,3-Butanedione	982	1,2	buttery		2	2	2	3	9				1	4	5
Methyl thioacetate	1014	1,2	roasted	1	1		2		4	2					2
Dimethyl disulfide	1029	1,2,3	fishy						0			2			2
2,3-Pentanedione	1046	1,2,3	buttery		2				2	3			1	2	6
Hexanal	1067	1,2,3	grassy		3				3		2				2
2/3-Methylthiophene	1079	1,2,3	roasty	2					2	3					3
Heptanal	1169	1,2,3	oily		3	1			4						0

Table 1 (continued)

Compounds	*RI (DB-wax)*	*ID*	*Odour*	*Skipjack*						*Albacore*					
(*Z*)-4-Heptenal	1228	1,2,3	meaty	4		3	4	3	14	3	3	3	3		12
Octanal	1287	1,2,3	soapy	2	2	2	2		8	2					2
1-Octen-3-one	1301	1,2	mushroom	2	2	2		2	8	3	3	3		2	11
2-Methyl-3-furanthiol	1309	1,2	meaty	3	2	2			7	3	4			2	9
2-Acetyl-1-pyrroline	1340	1,2	popcorn						0		3			1	4
Ethyl thioacetate	1360	1,2	sulfury		2	1		2	5	4	3				7
Dimethyl trisulfide	1380	1,2	onion	4					4	5					5
Nonanal	1389	1,2,3	fruity						0			1			1
(*E*)-2-Octenal	1426	1,2,3	oily		2				2						0
2-Furfurylthiol	1430	1,2,3	coffee		4		3		7	4	5	4	2	4	19
Acetic acid	1445	1,2,3	vinegar				4		4					3	3
1-Octen-3-ol	1450	1,2,3	mushroom			4			4				3		3
Methional	1454	1,2	nutty				3		3		4				4
(*Z*)-1,5-octadien-3-ol	1486	1,2,3	earthy						0		1	1			2
(E, E)-2,4-Heptadienal	1497	1,2,3	earthy	2					2						0
(*Z*)-2-Nonenal	1501	1,2,3	oily		3			2	5						0
Benzaldehyde	1520	1,2,3	nutty		4				4						0
Isobutyric acid	1564	1,2,3	sweaty				3		3				2		2
(*E*,*Z*)-2,6-Nonadienal	1581	1,2,3	cucumber			5			5						0
2-Undecanone	1592	1,2,3	oily			3			3			2			2
2-Ethylthiophene	1597	1,2,3	fishy				3		3			2			2
(*E*,*E*)-2,4-Octadienal	1619	1,2,3	mushroom		2				2						0
Butanoic acid	1628	1,2,3	sour			5	5		10			4	3	3	10
(*E*)-2-Decenal	1639	1,2,3	oily				1		1						0
2-Acetylthiazole	1663	1,2,3	popcorn						0	3					3
Isovaleric acid	1670	1,2,3	sweaty			5		3	8			4	4		8
Valeric acid	1744	1,2,3	sour			2			2						0
(*E*)-2-Undecenal	1756	1,2,3	green						0						0
β-Damascenone	1816	1,2,3	sweet						0					2	2
(*E*,*E*)-2,4-Decadienal	1819	1,2,3	oily			4			4						0
Hexanoic acid	1856	1,2,3	sour			4	4		8			3			3
Heptanoic acid	1965	1,2,3	sour						0		2				2
Furaneol	2049	1,2,3	candy						0				3	2	5
Octanoic acid	2070	1,2,3	sour		2				2			3			3
p-Cresol	2097	1,2,3	horse			4	4		8			4	3		7
Sotolon	2229	1,2,3	sweet				3		3						0
Vanillin	2572	1,2,3	vanilla						0					3	3

1: compounds were identified by the aroma descriptors; 2: compounds were identified by retention indices compared with pure compound standard;3: compounds were identified by the MS spectra.

The major odour compounds identified in canned tuna were sulfur-containing compounds, aldehydes, ketones, alcohols and short-chained fatty acids. The sulfur-containing compounds are generated via Maillard reactions during cooking and generally contribute to meaty, chicken-like aroma. The aldehydes, ketones as well as some alcohols are generated via lipid oxidation, and they contribute to fishy, oily off-flavour in the products. This research provided directions for future research and actionable steps to improve flavour quality of canned tuna fish.

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