8550 J. Agric. Food Chem. 2009, 57, 8550–8556
DOI:10.1021/jf901656k

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Iron Is an Essential Cause of Fishy Aftertaste Formation in Wine and Seafood Pairing

Takayuki Tamura,* Kiyoshi Taniguchi, Yumiko Suzuki, Toshiyuki Okubo, Ryoji Takata, and Tomonori Konno

Product Development Research Laboratory, Mercian Corporation, Jonan 4-9-1, Fujisawa, Kanagawa 251-0057 Japan

Fishy aftertaste is sometimes perceived in wine with fish and seafood pairing. However, what component of wine clashes with seafood or what compound contributes to the unpleasant fishy aftertaste in the mouth remains an open problem. First, intensities of unpleasant fishy aftertaste of wine and dried scallop pairings were rated by sensory analysis. Second, components of the wines were analyzed. Strong positive correlations were found between the intensity of fishy aftertaste and the concentration of both total iron and ferrous ion. Moreover, the intensity of fishy aftertaste was increased by the addition of ferrous ion in model wine and suppressed by the chelation of ferrous ion in red wine. Third, potent volatile compounds of fishy aftertaste, such as hexanal, heptanal, 1-octen-3-one, (*E*,*Z*)-2,4-heptadienal, nonanal, and decanal, were determined by gas chromatography−olfactometry and gas chromatography−mass spectrometry in dried scallop soaked in red wine. The formations of these compounds depended on the dose of ferrous ion in the model wine. These results suggest that ferrous ion is a key compound of the formation of fishy aftertaste in wine and seafood pairing within the concentration range commonly found in wine.

KEYWORDS: Wine; ferrous ion; iron; fishy aftertaste; seafood

INTRODUCTION

The typical combinations of red wine with meat or dry white wine with fish are partially explained by interactions between wine components and food ingredients. Food proteins reduce the bitterness and astringency of tannic red wine and the sourness and astringency of dry white wine on the basis of the senses of taste and touch (*1*).

In addition, red wine paired with seafood is not recommended in some literature because red wine clashes with fish, creating a ferrous taste (*2*), fishy and metallic odors, and bitterness in the mouth (*3*). On the other hand, sherry is recommended in the literature as a potent acceptable partner of kippers (*3*) and mackerels (*4*) besides white dry wine. However, these recommendations are not based on scientific understandings of wine and food combinations, but personal or empirical opinions. It is still an open problem what component of wine clashes with seafood or what compound contributes to the unpleasant fishy aftertaste in the mouth.

On the other hand, a large number of studies have been made on the development of unpleasant flavors in stored seafood. Rancid odor is generated by developments of carbonyl compounds during storage on ice for several days, although pleasant and faint green top notes dominate fresh fish (*5*−*7*). These compounds are produced from oxidation of polyunsaturated fatty acids by lipoxygenase or autoxidation. However, in terms of generation rate, the formation mechanism of these compounds will be different from that of fishy aftertaste in wine and seafood pairing.

We describe here two experiments, which had the following aims. Experiment 1 aimed to evaluate what component of wine clashes with fish and seafood by sensory analysis. Experiment 2 aimed to explain the formation mechanism of fishy aftertaste in wine and seafood pairing by characterization and quantification of volatile compounds released from seafood soaked in wine.

MATERIALS AND METHODS

Wines. Thirty-eight commercial full- and medium-bodied red wines from France, Italy, Australia, Chile, Japan, Spain, the United States, Argentina, Hungary, New Zealand, and South Africa, 26 commercial dry and semisweet white wines from France, Italy, Japan, the United States, Germany, Spain, Chile, New Zealand, and South Africa, 2 sherries, and 1 each of port, madeira, and botrytized wine were purchased in Kanagawa, Japan. A red wine containing 8.0 mg/L of iron was selected from wines additionally purchased.

Seafood. Dried scallop was prepared as follows: boiled scallop (*Patinopecten yessoensis*) without shell was purchased from a retail store in Kanagawa, Japan, and was soaked in a 15% sodium chloride solution for 15 h at 4 °C, then surface-wiped with paper, and sun-dried for 3 days. Dried scallop was sealed in a plastic bag and stored at 4 °C until use.

Chemicals. The following pure samples of the compounds were obtained commercially: ferrous sulfate heptahydrate, potassium sulfate, ferric sulfate *n*-hydrate, copper sulfate pentahydrate, manganese sulfate pentahydrate, zinc sulfate heptahydrate, potassium hydrogen tartrate, 10% tartaric acid solution, hexanal, and (*E*,*E*)-2,4-decadienal (Wako Pure Chemical Industries, Osaka, Japan); heptanal, octanal, nonanal, decanal, and 1-octen-3-one solution (50 wt % in 1-octen-3-ol) (Sigma-Aldrich,

*Author to whom correspondence should be addressed (telephone +81 466 35 1515; fax +81 466 35 1523; e-mail tamura-t@mercian.co.jp).

Steinheim, Germany); (*E*,*E*)-2,4-heptadienal and (*E*,*E*)-2,4-nonadienal (Tokyo Chemical Industry, Tokyo, Japan); ethylenediaminetetraacetic acid (EDTA) dihydrate, disodium salt (Dojindo Laboratories, Kumamoto, Japan).

Sensory Analysis. The sensory panel that carried out the different experiments described in this work was composed of seven laboratory staff members, six men and a woman ranging in age from 27 to 55 years. All of them had wine-tasting experience. An attribute, unpleasant fishy aftertaste, was chosen by consensus to describe wine with seafood pairing. Panelists were untrained. Perceived unpleasant fishy aftertaste intensity was rated on an unstructured five-point category scale anchored with none (score = 0) to extremely strong (score = 4). Dried scallop, chopped with a kitchen knife made of ceramics, was served in a plastic dish. The evaluation was performed using a sequential dried scallop−wine tasting, which consisted of placing a small piece of scallop in the mouth, chewing it, and then taking a sip of wine and evaluating the intensity of fishy aftertaste. Drinking water was provided to cleanse the mouth between each dried scallop−wine pairing but not within a dried scallop−wine pairing.

Rating of the Intensity of Unpleasant Fishy Aftertaste of Wine and Dried Scallop Pairings. The intensities of fishy aftertaste of 69 commercial wines with dried scallop were rated. Panelists evaluated 69 wines with dried scallop during four sessions. In the first session, 21 red wines were rated. In the second session, 17 red wines were rated. In the third session, 18 white wines, 2 sherries, and a botrytized wine were rated. In the last session, 8 white wines and 1 each of port and madeira were rated. The wines in each session were arranged in random order and were presented in this order or reverse order. The wines were presented in randomly coded glasses.

Effect of Ferrous Sulfate. The role of ferrous ion in model wine was evaluated in the formation of fishy aftertaste. Model wine was prepared by saturating aqueous ethanol (12% v/v) with potassium hydrogen tartrate and adjusting the pH to 3.2 by the addition of 10% tartaric acid solution (*8*). Ferrous ion was added as ferrous sulfate at 0.05, 0.1, 1.0, and 5.0 mg/L to the model wine described above. Panelists evaluated four model wines with dried scallop in random order in one session. The model wine samples were presented in randomly coded glasses. Rating of the intensity of fishy aftertaste was done as described above. The model wine without ferrous sulfate was used as a negative control.

Effect of Sulfate and Metal Ions. Sulfate and metal ions commonly found in wine were added to evaluate their role in the formation of fishy aftertaste at concentrations within the range of concentrations analyzed in this study (**Table 2**). Freshly made stock solutions of ferrous sulfate, ferric sulfate, copper sulfate, manganese sulfate, zinc sulfate, and potassium sulfate were added to give, separately, 5 mg/L of ferrous ion, 1 mg/L of ferric ion, 2 mg/L of copper ion, 10 mg/L of manganese ion, 10 mg/L of zinc ion, and 1600 mg/L of sulfate (1300 mg/L of potassium ion was added simultaneously) to model wine. Panelists evaluated seven model wines with dried scallop. The model wine samples were presented in randomly coded glasses. Rating of the intensity of fishy aftertaste was done as described above. The model wine without sulfate and metals was used as a control.

Effect of EDTA. The role of ferrous ion in red wine was evaluated in the formation of fishy aftertaste. EDTA was added at 0.0001, 0.001, 0.01, 0.1, and 1.0 mM to commercial red wine containing 0.07 mM iron. Panelists evaluated six red wine samples with dried scallop. The wines were presented in randomly coded glasses in descending order of EDTA. Rating of the fishy aftertaste intensities was done as described above. The model wine without EDTA was used as a positive control.

Chemical Analyses. Wine components were analyzed to see what aspects of composition correlated with the rating evaluated by sensory analysis. The ethanol, methanol, and acetaldehyde contents of wines were measured by gas chromatography (GC-14A, Shimadzu, Kyoto, Japan). Titratable acidity was analyzed as tartaric acid. Sulfur dioxide and the pH of wines were analyzed by the Ripper determination method and the standard pH procedure, respectively. Specific gravity was analyzed by density/specific gravity meter DA505 (Kyoto Electronics Manufacturing, Kyoto, Japan). Total phenolics of wines were estimated according to the Folin−Ciocalteu method expressed as gallic acid equivalents. Total iron was analyzed by atomic absorption spectrometry (SpectrAA 55B, Varian, Palo Alto, CA). Metal ions (Fe^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}) were analyzed by a postcolumn reaction with 4-(2-pyridylazo)resorcinol reagent combined with spectrophotometric detection (Shimadzu, Kyoto, Japan). Cations (potassium, sodium, calcium, magnesium, and ammonia) and anions (phosphate, sulfate, chloride, and nitrate) were analyzed by nonsuppressor ion chromatography with a Shodex IC YK-421 (Showa Denko, Tokyo, Japan) and a Shim-pack IC-A3 column (Shimadzu, Kyoto, Japan), respectively. Organic acids (citric acid, tartaric acid, malic acid, succinic acid, lactic acid, and acetic acid) were analyzed by ion exclusion chromatography with a Shim-pack SCR-102H column (Shimadzu).

Table 1. Correlation between the Fishy Aftertaste Intensities of Wine and Dried Scallop Pairing and Wine Parameters (n = 69)

parameter	*rs*	*P value*
ethanol	−0.036	0.75
methanol	0.319	0.008
acetaldehyde	−0.158	0.187
titratable acidity	−0.149	0.21
free SO_2	0.216	0.07
total SO_2	0.111	0.36
pH	0.336	0.005
specific gravity	0.033	0.83
extract	0.010	0.97
total phenolics	0.397	0.001
total iron	0.706	<0.001
ferrous	0.691	<0.001
ferric	0.330	0.006
copper	0.020	0.48
manganese	0.409	0.85
zinc	0.355	0.003
potassium	0.268	0.03
sodium	0.086	0.49
calcium	−0.071	0.55
magnesium	0.158	0.19
ammonia	0.210	0.08
phosphate	−0.019	0.87
sulfate	0.248	0.04
chloride	0.061	0.51
nitrate	−0.120	0.32
citric acid	−0.173	0.15
tartaric acid	0.210	0.08
malic acid	−0.306	0.01
succinic acid	0.343	0.004
lactic acid	0.424	<0.001
acetic acid	0.281	0.02

Solid Phase Microextraction (SPME) Coupled with Gas Chromatography−Mass Spectrometry (GC-MS) and GC−Olfactometry (GC-O) Analysis. *Extraction of Volatile Compounds by SPME.* Dried scallop (2 g) was ground and soaked in wine and then stirred at room temperature for 5 min. The mixtures were filtered by filter paper. The supernatants (2 mL) and internal standard (0.1 mg/L of methyl hexanoate) were sealed in glass vials (20 mL). A Supelco SPME fiber holder and a StableFlex/polydimethylsiloxane fiber (Supelco, Bellefonte, PA) were used, and the fiber length was set to 1 cm for analysis. Then the SPME fiber was inserted into the headspace above the solution and exposed at 70 °C for 1 h. Volatile compounds were desorbed by inserting the fiber into the GC injector set at 250 °C for 10 min.

GC-MS and GC-O Analysis. GC-MS analysis was carried out on an Agilent 6890N with an Agilent 5973 mass spectrometer. Compounds were separated on a DB-5 capillary column (30 m × 0.25 mm, 1.0 μm film thickness, J&W Scientific, Folsom, CA) under the following conditions: injection port temperature, 250 °C; oven temperature, 40 °C for 1 min, raised at 5 °C/min to 130 °C, followed by 20 °C/min to 230 °C, and held for 6 min. Carrier gas was helium, and it was maintained at a constant flow of 1.6 mL/min. The MS was operated at an ion source temperature of 230 °C.

At the exit of the capillary column, the effluent was split into the MS and a sniffing port. Humid air was constantly added to the effluent at the sniffing port. Analyses were performed by three assessors experienced in

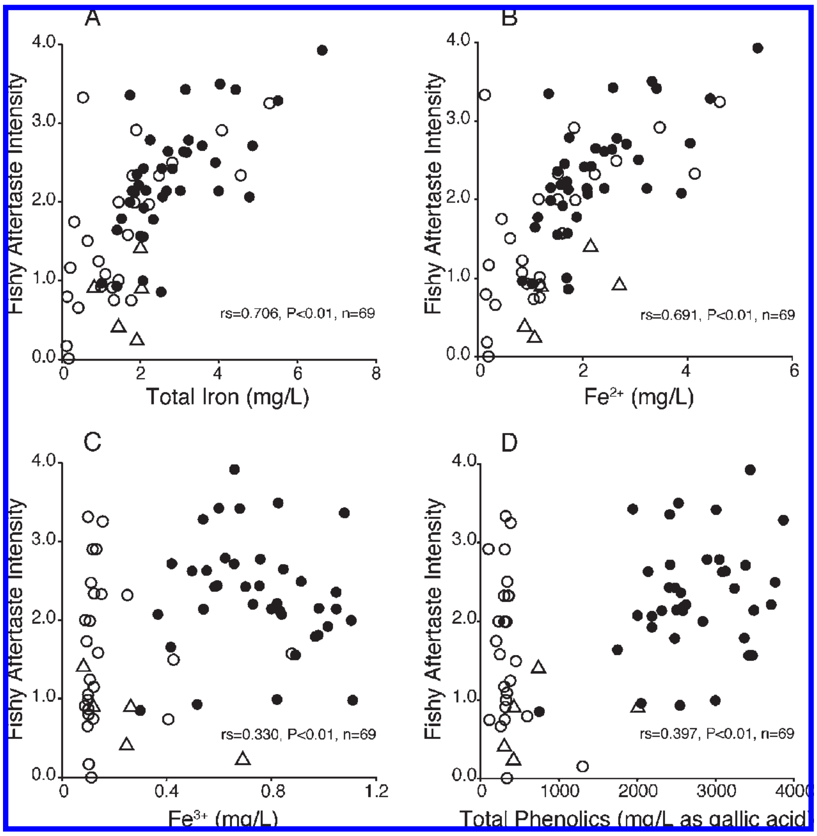

Figure 1. Relationships between the intensity of unpleasant fishy aftertaste of wine and dried scallop pairing and (**A**) total iron, (**B**) Fe^{2+}, (**C**) Fe^{3+}, and (**D**) total phenolics in commercial red wines (solid circle), white wines (open circle), and other types of wines (triangle).

Table 2. Composition of Various Metals, Potassium, and Sulfate in Commercial Wine

	amount in wine (mg/L)	
compound	range	mean
total iron	0.11−6.6	2.3
Fe^{2+}	0.13−5.3	1.9
Fe^{3+}	0.08−1.1	0.5
Cu^{2+}	0−2.4	0.2
Mn^{2+}	0−2.3	0.07
Zn^{2+}	0−0.9	0.35
K^{+}	280−1500	830
sulfate	100−1400	340

sensory analysis. During GC-O, the assessors were asked to give a description of each perceived odor. A description was assigned only if the odorant was detected for at least two of three GC-O evaluations.

Identification of Volatile Compounds. Some of the volatile compounds were identified by comparison of their retention time and mass spectrum with those of the authentic standards, whereas others were identified by comparison of their retention time and mass spectral data with published retentions times (*9*) and the National Institute of Standards and Technology (NIST) mass spectral database, respectively.

Quantification Method. The SPME and GC-MS conditions were set as described above. The quantification was realized by selective ion monitoring mode. The selected and specific ions are 56 for hexanal, 70 for heptanal and 1-octen-3-one, 57 for 1-octen-3-ol, nonanal, decanal, 81 for (*E*,*Z*)-2,4-heptadienal, (*E*,*E*)-2,4-heptadienal, (*E*,*Z*)-2,4-nonadienal, and (*E*,*E*)-2,4-nonadienal, and 74 for methyl hexanoate. The standard curves for individual volatile compounds were built up by plotting the response ratio of target compound and internal standard against the concentration ratio. Determinations were made in triplicate with relative standard derivations ranging from 2 to 11% and with correlation coefficients for all compounds between 0.994 and 0.999.

Volatile Compounds Released from the Dried Scallop Soaked in Red Wine. Volatile compounds released from the dried scallop soaked in red wine, containing 0.14 mM total iron (equivalent to 8.0 mg/L), were compared with the volatile compounds from dried scallop soaked in model wine without ferrous sulfate to find what kinds of compound were produced when the fishy aftertaste was perceived. Analyses were done in triplicate.

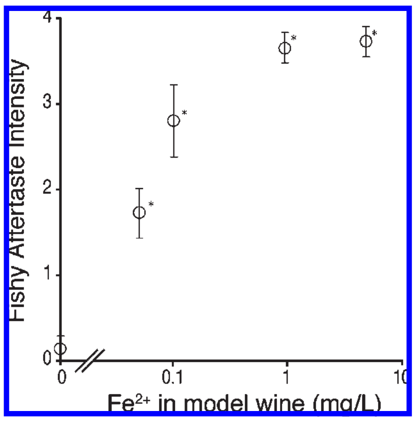

Figure 2. Effect of increasing ferrous ion concentration on the intensity of fishy aftertaste in model wine and dried scallop pairing. Results are expressed as mean ± SEM (n = 7). ∗, $P < 0.01$, compared with the model wine without ferrous sulfate.

Effect of Ferrous Ion. The role of ferrous ion in model wine was evaluated in the formation of volatile compounds. Ferrous ion was added as ferrous sulfate at 0.1, 1, and 5 mg/L to a 10% ethanol solution. Volatile compounds from dried scallop soaked in these model wines were analyzed. The model wine without ferrous sulfate was used as control.

Data Analyses. Statistical analyses were performed using Excel 2000 (Microsoft, Redmond, WA) with the add-in software Statcel 2 (*10*). The correlations between the mean intensity evaluated by sensory analysis and the variables of wine were assessed by Spearman rank correlation.

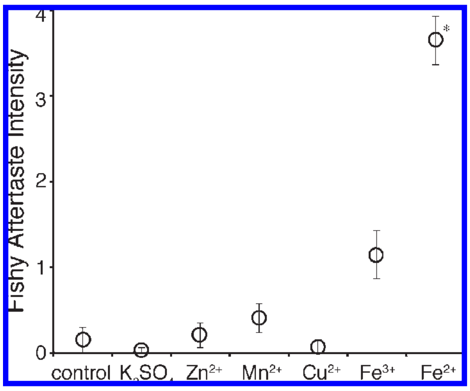

Figure 3. Impact of addition of various metals and sulfate at the concentrations found in commercial wine to model wine on the intensity of fishy aftertaste in model and dried scallop pairing. Results are expressed as mean ± SEM (n = 7). ∗, P < 0.01, compared with control.

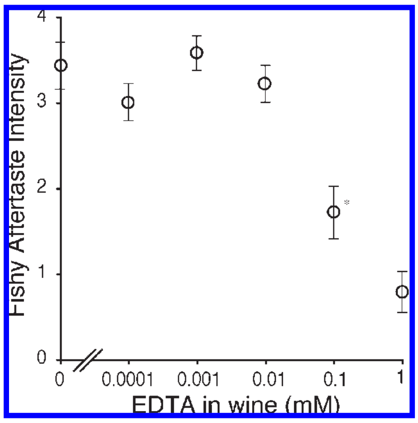

Figure 4. Effect of increasing EDTA concentration on the intensity of fishy aftertaste in red wine, containing 0.07 mM iron, and dried scallop pairing. Results are expressed as mean ± SEM (n = 7). ∗, P < 0.01, compared with untreated red wine.

Dose dependencies of ferrous ion in model wine, EDTA in red wine, and multiple comparison of the addition of metals and potassium sulfate with the control were analyzed by Steel's test for multiple comparisons. Simple comparisons of the concentrations of volatile compounds were determined by Student's t test. The dose dependency of ferrous ion on the formation of volatile compounds was analyzed by one-way ANOVA with Dunnett's multiple-comparison post hoc test. Differences were considered to be significant when $P < 0.01$.

RESULTS AND DISCUSSION

Relationships between the Intensity of Fishy Aftertaste of Wine and Dried Scallop Pairing. The relationships between the intensity of fishy aftertaste and variables of wines are shown in **Table 1**. Strong positive correlations were found between the intensities of fishy aftertaste and the concentrations of both total iron (**Figure 1A**) and ferrous ion (**Figure 1B**). However, other variables including ferric ion (**Figure 1C**) indicated a weak correlation with the intensity (**Table 1**). In addition to this, iron in wine was dominated by ferrous ion (**Table 2**). These results show that ferrous ion in wine correlated with the intensity of fishy aftertaste.

Effect of Ferrous Ion in Model Wine in the Intensity of Fishy Aftertaste. When a range of ferrous ion found in wine (**Table 2**) was added to model wines as ferrous sulfate, the intensity of the fishy aftertaste depended on the dose of ferrous sulfate (**Figure 2**). This does not exclude the possibility that sulfate in wine has an essential effect, although a relatively weak correlation between sulfate and intensity is shown in **Table 1**. Next, sulfate in wine was tested. Sulfate and potassium were added to the model wine as potassium sulfate at concentrations similar to those found in commercial wine (**Table 2**). Little fishy aftertaste was detected in model wine with potassium sulfate and dried scallop pairing (**Figure 3**). Therefore, sulfate did not play an essential role in fishy aftertaste formation. These results show that ferrous ion in model wine played a role in the formation of fishy aftertaste in model wine and dried scallop pairing.

Effect of Metal Chelation of Red Wine in the Formation of Fishy Aftertaste. When EDTA, a metal chelating agent, was added to red wine containing 0.07 mM total iron (equivalent to 3.8 mg/L) at 0.1 mM and higher, the intensity of fishy aftertaste was suppressed (**Figure 4**). This does not exclude the possibility that other chelated metals in red wine have essential effects, although relatively weak correlations between the concentrations of these metals and the intensity are shown in **Table 1**. Next, metals found in wine were tested in model wine. Zinc ion, manganese ion, copper ion, ferrous ion, and ferric ion were added to the model wine at concentrations similar to or significantly above those found in commercial wine (**Table 2**). Weak fishy aftertastes were detected in dried scallop and model wines with metals except ferrous ion (**Figure 3**). In other words, the fishy aftertaste was observed only in the presence of ferrous ion (**Figure 3**). These results show that ferrous ion in red wine is a potent key compound in the formation of fishy aftertaste in red wine and dried scallop pairing.

Volatile Compounds Released from Dried Scallop Soaked in Red Wine. Dried scallop soaked in model wine without ferrous sulfate exhibited a pleasant flavor of dried scallop. On the other hand, an unpleasant fishy odor was perceived when dried scallop was soaked in red wine containing 0.14 mM iron (equivalent to 8.0 mg/L). GC-O and GC-MS analyses revealed potent volatile compounds released from dried scallop soaked in wine (**Table 3**). In particular, the concentrations of six volatile compounds, hexanal, heptanal, 1-octen-3-one, (*E*,*Z*)-2,4-heptadienal, nonanal, and decanal, were different between the scallop soaked in red wine and the scallop soaked in model wine without ferrous sulfate (**Table 3**). On the other hand, those of 1-octen-3-ol, octanal, (*E*,*E*)-2,4-heptadienal, and (*E*,*E*)-2,4-nonadienal were not different between them (**Table 3**). These results show that hexanal, heptanal, 1-octen-3-one, (*E*,*Z*)-2,4-heptadienal, nonanal, and decanal were produced from dried scallop soaked in red wine. These compounds were selected for further evaluations.

Effect of Ferrous Ion in the Formation of Volatile Compounds. Concentrations of selected compounds, 1-octen-3-one, nonanal, (*E*,*Z*)-2,4-heptadienal, and heptanal, released from dried scallop soaked in model wine with multiple concentrations of ferrous ion are shown in **Figure 5**. The formations of volatile compounds depended on the dose of ferrous ion (**Figure 5**). These results show that ferrous ion in model wine played a role in the production of selected volatile compounds in the model wine and dried scallop pairing.

General Discussion. This study is the first trial intended to evaluate the fishy aftertaste that is sometimes generated in wine and seafood pairing.

This study elucidates one new property of iron in wine by sensory analysis; ferrous ion is a key compound in the formation of fishy aftertaste in wine and seafood pairing within the concentration range commonly found in wine, in addition to causing color change (*11*, *12*), accelerating the oxidation (*11*−*13*), and causing cloudiness (*14*, *15*). We arrived at this conclusion as follows. First, the addition of ferrous sulfate in model wine increased the intensity of fishy aftertaste (**Figure 2**); second, the chelation of ferrous ion of red wine suppressed the intensity of

Table 3. Identification and Quantification of Potent Odorants in Dried Scallop Soaked in Red Wine, Containing 0.14 mM Iron, and Model Wine without Ferrous Sulfate

RI[a] on DB-5	odor description [b]	compound	model wine (mg/kg)	red wine (mg/kg)
797	fat, green	hexanal[c]	5.9	10.5*[f]
900	chemical	heptanal[c]	1.7	3.5*
977	metallic	1-octen-3-one[c]	0.09	0.528*
980	mashroom	1-octen-3-ol[c]	8.3	10.0
996	fishy	(*E*,*Z*)-2,4-heptadienal[d]	nd[e]	4.2*
1002	green	octanal[c]	1.9	4.3
1010	fat	(*E*,*E*)-2,4-heptadienal[c]	3.3	5.4
1104	oily	nonanal[c]	1.1	4.2*
1206	green	decanal[c]	0.22	0.9*
1217	green	(*E*,*E*)-2,4-nonadienal[c]	4	4.8

[a] Retention index. [b] Odor description assigned during GC-O. [c] Identified by comparison of their retention time and mass spectrum with those of authentic standards. [d] Identified by compariton of their retention time and mass spectrum with retention time and MS databases. [e] Not detected. [f] *, $P < 0.01$.

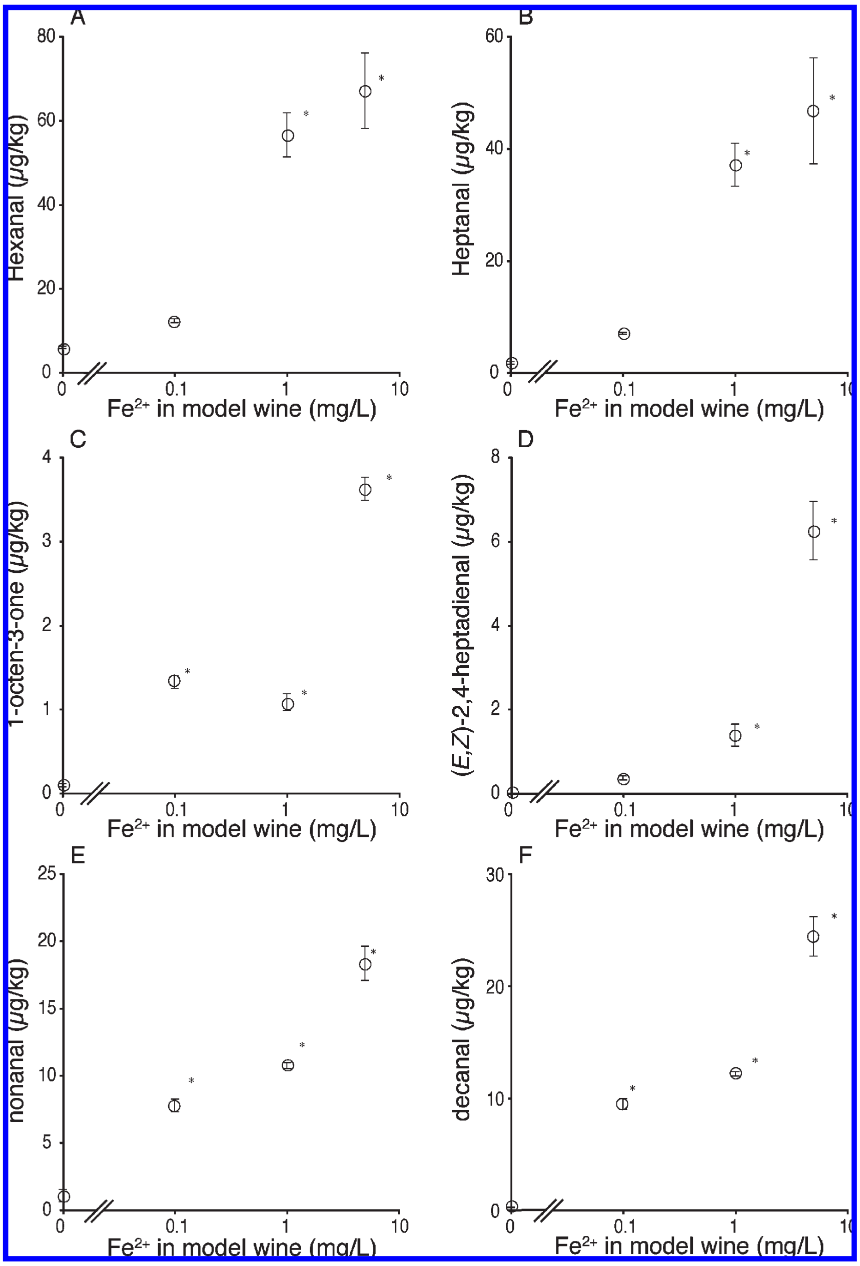

Figure 5. Concentrations of selected volatiles released from dried scallop soaked in model wine with multiple concentrations of ferrous ion: (**A**) hexanal; (**B**) heptanal; (**C**) 1-octen-3-one; (**D**) (*E*,*Z*)-2,4-heptadienal; (**E**) nonanal; (**F**) decanal. Results are expressed as mean ± SEM ($n = 5$). ∗, $P < 0.01$, compared with the dried scallop soaked in model wine without ferrous sulfate.

fishy aftertaste (**Figure 4**); and, third, potassium sulfate and other metals, ferric ion, copper ion, manganese ion, and zinc ion, in model wine did not increase the intensity of fishy aftertaste (**Figure 3**).

At the moment, ferrous ion in wine is an essential cause of the formation of fishy aftertaste. Tannin in red wine, however, is believed to clash with fish (*3*), although there is no evidence to support this opinion. Likewise, it is not supported by our findings because significant correlation was not observed between the concentration of total phenolics and the intensity of fishy aftertaste (**Figure 1D**). On the other hand, our conclusion could explain some opinions regarding wine and seafood pairing. First, the opinion that white wine with high acidity is recommended with sardines (*3*) could be explained by the acids' properties of iron chelation. Second, the opinion that fino and manzanilla sherries are ideal partners of kippers (*3*) could be explained by their relatively low contents of ferrous ion (other type wines in **Figure 1B**). Third, the opinion that red wine and fish pairing required care formed in the past, when red wines were more tannic than they are today (*3*), could be explained by the observation that the iron content has been considerably reduced with the general use of stainless steel (*15*). Finally, as mentioned earlier, the opinion that red wine creates a ferrous taste in the mouth could be explained by the metallic character of 1-octen-3-one, which is a potent compound responsible for the metallic odor found in oxidized butterfat (*16*, *17*). In addition to this, the metallic sensation of ferrous sulfate solution is likely due to the development of a retronasal smell, possibly following a lipid oxidation reaction in the mouth (*18*).

In daily life, it is difficult to predict the iron content in a bottled wine without opening it. It is a still a problem for the customer because the content of iron is not related to wine type (**Figure 1A**,**B**) or the country of origin (*14*, *15*, *19*). In fact, iron content depends on the winemaking process (*14*, *15*, *19*), that is, the iron content of the soil, the dust on the berry, contamination during harvesting, transportation, and crushing, and absorption or adsorption by yeasts during fermentation.

Next, we propose a formation mechanism of fishy aftertaste as follows. Ferrous ion in wine can promote instantly hexanal, heptanal, 1-octen-3-one, (*E*,*Z*)-2,4-heptadienal, nonanal, and decanal by the breakdown of preformed lipid hydroperoxides derived from unsaturated fatty acids in fish and seafood. We reached this conclusion as follows. First, these compounds increased with soaking in red wine (**Table 3**); second, these compounds were described as unpleasant characters (**Table 3**); third, the formations of these compounds depended on the dose of ferrous ion in model wine (**Figure 5**). In addition, ferrous ion can catalyze lipid oxidation via the breakdown of already existing lipid hydroperoxides (*20*). Furthermore, these compounds are found and generated in other foods related to oxidation by iron, such as 1-octen-3-one and hexanal from porcine liver (*21*), hexanal and heptanal from food emulsions enriched with long-chain polyunsaturated fatty acids (*22*), and (*E*,*Z*)-2,4-heptadienal and decanal from fish oil enriched mayonnaise (*23*).

From the viewpoint of lipid oxidation, other variables in wine such as phenolic compounds and pH remain as candidates for modulators. The phenolic compounds are sometimes pro-oxidative in omega-3-enriched oil-in-water emulsions and virgin olive oil, by reducing ferric ions to ferrous ions (*24*, *25*). In addition, at pH 4, the volatile compounds caused by autoxidation of fish oil in mayonnaise-like emulsions are highest (*20*, *26*).

Nevertheless, further investigation is needed for a more thorough understanding of the mechanisms, including the basis of the generation rate and why the fishy aftertase is more easily perceived with wine with dried scallop compared with wine with other fish and seafood.

ACKNOWLEDGMENT

We thank Yumiko Takahashi, Hiroko Konno, Emi Kaneko, and Chiaki Takaishi for technical assistance, the sensory panels at the Product Development Research Laboratory for their participation despite the unpleasant pairings and sensory work, and an anonymous reviewer for helpful comments and discussions of the manuscript.

LITERATURE CITED

(1) Jackson, S. Wine, health, and food. In *Wine Science: Principles, Practice, Perception*, 2nd ed.; Academic Press: San Diego, CA, 2000; pp 600−605.
(2) Cooper, D. Wine with food. 2. In *Wine with Food*; Crescent Books: New York, 1980; pp 87−97.
(3) Simon, J. Rules, & how to break them. In *Wine with Food*; Octopus Publishing: London, U.K., 1996; pp 10−19.
(4) Walton, S.; Glover, B. Drinking wine with food. In *The Ultimate Encyclopedia of Wine, Beer, Spirits & Liqueurs*; Lorenz Book: London, U.K., 1998; p 21.
(5) Triqui, R.; Bouchriti, N. Freshness assessments of moroccan sardine (*Sardina pilchardus*): comparison of overall sensory changes to instrumentally determined volatiles. *J. Agric. Food Chem.* **2003**, *51*, 7540–7546.
(6) Prost, C.; Hallier, A.; Cardinal, M.; Serot, T. Effect of storage time on raw sardine (*Sardina pilchardus*) flavor and aroma quality. *J. Food Sci.* **2004**, *69*, S198–204.
(7) Ganeko, N.; Shoda, M.; Hirohara, I.; Bhadra, A.; Ishida, T. Analysis of volatile flavor compounds of sardine (*Sardinops melanostica*) by solid phase microextraction. *J. Food Sci.* **2008**, *73*, S83–S88.
(8) Francis, I. L.; Sefton, M. A.; Williams, P. J. A study by sensory descriptive analysis of the effects of oak origin, seasoning, and heating on the aromas of oak model wine extrants. *Am. J. Enol. Vitic.* **1992**, *43*, 23–30.
(9) Acree, T.; Arn, H. Flavornet. http://www.flavornet.org/, **2004**.
(10) Yanai, H. In *Statcel—The Useful Add-in Software Forms on Excel*, 2nd ed.; OMS: Tokyo, Japan, 2004.
(11) Cacho, J.; Castells, J. E.; Esteban, A.; Laguna, B.; Sagrista, N. Iron, copper, and manganese influence on wine oxidation. *Am. J. Enol. Vitic.* **1995**, *46*, 380–384.
(12) Macias, V. M. P.; Pina, I, C. Factors influencing the oxidation phenomena of sherry wine. *Am. J. Enol. Vitic.* **2001**, *52*, 151–155.
(13) Danilewicz, J.; Seccombe, J. T.; Whelan, J. Mechanism of interaction of polyphenols, oxygen, and sulfur dioxide in model wine and wine. *Am. J. Enol. Vitic.* **2008**, *59*, 128–136.
(14) Ough, C. S.; Amerine, M. A. Other constituents. In *Methods for Analysis of Musts and Wines*, 2nd ed.; Wiley: New York, 1988; pp 275−277.
(15) Ribéreau-Gayon, P.; Glories, Y.; Maujean, A.; Dubourdieu, D. Dry extract and minerals. In *Handbook of Enology, The Chemistry of Wine Stabilization and Treatments*, 2nd ed.; Wiley: West Sussex, U.K., 2006; Vol. *2*, pp 96−102.
(16) Swoboda, P. A. T.; Peers, K. E. Volatile odorous compounds responsible for metallic, fishy taint formed in butterfat by selective oxidation. *J. Sci. Food Agric.* **1977**, *28*, 1010–1018.
(17) Swoboda, P. A. T.; Peers, K. E. Metallic odour caused by vinyl ketones formed in the oxidation of butterfat. The identification of octa-1,*cis*-5-dien-3-one. *J. Sci. Food Agric* **1977**, *28*, 1019–1024.
(18) Lawless, H. T.; Schlake, S.; Smythe, J.; Lim, J.; Yang, H.; Chapman, K.; Bolton, B. Metallic taste and retronasal smell. *Chem. Senses* **2004**, *29*, 25–33.
(19) Pohl, P. What do metals tell us about wine? *TrAC, Trends Anal. Chem.* **2007**, *26*, 941–949.
(20) Jacobsen, C.; Timm-Heinrich, M. Oxidation in fish oil enriched mayonnaise: ascorbic acid and low pH increase oxidative deterioration. *J. Agric. Food Chem.* **2001**, *49*, 3947–3956.
(21) Im, S.; Hayakawa, F.; Kurata, T. Identification and sensory evaluation of volatile compounds in oxidized porcine liver. *J. Agric. Food Chem.* **2004**, *52*, 300–305.

(22) Nielsen, N. S.; Petersen, A.; Meyer, A. S.; Timm-Heinrich, M.; Jacobsen, C. Effect of lactoferrin, phytic acid, and EDTA on oxidation in two food emulsions enriched with long-chain polyunsaturated fatty acids. *J. Agric. Food Chem.* **2004**, *52*, 7690–7699.
(23) Jacobsen, C.; Hartrigsen, K.; Thomsen, M. K.; Hansen, L. F.; Lund, P.; Skibsted, L. H.; Hølmer, G.; Adler-Nissen, J.; Meyer, A. S. Lipid oxidation in fish oil enriched mayonnaise: Calsium disodium ethylenediaminetetraacetate, but not gallic acid, strongly inhibited oxidative deterioration. *J. Agric. Food Chem.* **2001**, *49*, 1009–1019.
(24) Sørensen, A.-D. M.; Haahr, A.-M.; Becker, E. M.; Skibsted, L. H.; Bergenståhl, B.; Nilsson, L.; Jacobsen, C. Interaction between iron, phenolic compounds, emulsifiers, and pH in omega-3-enriched oil-in-water emulsions. *J. Agric. Food Chem.* **2008**, *56*, 1740–1750.
(25) Keceli, T.; Gordon, M. H. Ferric ions reduce the antioxidant activity of the phenolic fraction of virgin oil. *J. Food Sci.* **2002**, *67*, 943–947.
(26) Takai, J.; Endo, Y.; Okuzaki, M.; Fujimoto, K. Autoxidation of fish oil in mayonnaise-like O/W type emulsion. *Food Sci. Technol. Res.* **2003**, *9*, 383–386.

Received December 25, 2008. Revised manuscript received August 12, 2009. Accepted August 14, 2009.