# Low Temperature Deodorizations of Fish Oils with Volatile Acidic and Basic Steam Sources

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Menhaden, cod liver and siscowet lake trout oils were vacuum steam deodorized at 100°C to 210°C using volatile acid (acetic and hydrochloric) and base (ammonium hydroxide) solutions (0.005N-0.25N) as steam sources. Volatiles in oils were analyzed by Tenax GC headspace analysis, and flavor and odor quality was evaluated. Deodorization of oils at 100°C with acidic solutions yielded oils that lacked the burnt/fishy flavors compared to similar oils that were deodorized with either water or alkaline solutions. Acid catalyzed hydrations of fishy aldehydes by deodorizing acids and flavor masking by t, c-2,6-nonadienal appeared to cause the suppression of fishy flavors in fish oils deodorized by acid solutions. Oils deodorized at 210°C exhibited less intense fishy flavors, and lower concentrations of fishy aldehydes, t,t,c-2,4,7-decatrienal, t,c,c-2,4,7-decatrienal, and c-4-heptenal.

Traditional processing of fats and oils employs several unit processes to remove impurities, and these may involve degumming, alkali refining, bleaching, and vacuum steam deodorization (1-4). Volatile flavor compounds are removed principally by a vacuum steam deodorization step, and conventional processing employs temperatures in the range of  $200-275^{\circ}$ C for vegetable oils (4) and 190-230°C for fish oils (5). While these conditions generally remove off-flavors, such elevated temperatures cause formation of artifacts through isomerization and polymerization reactions in fish oils and other oils containing highly unsaturated fatty acids (6-10).

Other strategies for removal of aroma compounds from heat-sensitive fish oils have been explored also. Fernandez and Pigott (11-13) have described a process employing cation exchange resin for adsorbing undesirable flavor compounds at temperatures below 80°C for production of oils with less pronounced fishy flavors. Spinelli et al. (14) have used supercritical carbon dioxide extraction as a means to obtain bland-flavored fish oils, using temperatures ranging from 40-100°C. Takao (15,16), through a patent, has claimed that the addition of polyhydric alcohols to fish oils aids in the production of bland oils with low-temperature vacuum steam deodorizations. Pelura and Chang (8) have concluded that acceptable fish oils can be obtained using deodorization conditions of either 150°C for 5 hr or 175°C for 3 hr. However, flavorless fish oils which are nutritionally unaltered are not yet available commercially.

The volatile compounds which contribute much of the characterizing fishiness to fish oils are the t,c,c- and t,t,c-2,4,7-decatrienals (17,18), whose flavor properties in fish oils are modified by a variety of other carbonyls, including 2-alkenals. As a group, 2-alkenals are susceptible to water-mediated retro-aldol reactions which yield products that are more volatile than the parent compounds

(19,20). Retro-aldol reactions are sensitive to pH, and they are particularly rapid under alkaline conditions. Additionally, carbonyl-amine complexes that have not progressed through the Amadori rearrangement are readily reversed under acidic conditions to yield free aldehydes (21-23).

Therefore, this research was undertaken to explore the chemical effects of incorporating volatile acids and bases into the steam employed in vacuum deodorizations of fish oils. Additionally, it was an objective to determine whether the use of acidic and basic steam sources could assist in the production of bland-flavored fish oils at considerably lower temperatures than those conventionally used for vacuum steam deodorization.

### **MATERIALS AND METHODS**

Fish oil sources and preparation. Refined, undeodorized menhaden oil (Zapata Hayne Corp., Reedville, VA) and pharmaceutical grade cod liver oil (McKesson Corp., Dublin, CA) were obtained commercially. Siscowet lake trout (Salvilinus namaycush siscowets) oil was prepared by heat-rendering (100°C for 10 min) freshly-caught commercial fish (4-6 kg, Bodin Fisheries, Inc., Bayfield, WI) that had been gutted, skinned, deheaded, deboned and minced in our laboratory. The siscowet lake trout oil was filtered through beds (1:1) of Celite (J.T. Baker Chemical Co., Phillipsburg, NJ) and anhydrous sodium sulfate (Amend Drug Chemical Co., Irvington, NJ), but the oil was not subjected to degumming or alkali refining processes.

Aqueous, acidified and alkaline fish oil emulsions. Some fish oil samples for vacuum steam deodorizations were prepared by homogenizing 50 ml of a selected aqueous acid solution mixture (0.025N-0.25N acetic acid; J.T. Baker Chemical Co., Phillipsburg, NJ, or 0.005N-0.01N hydrochloric acid, HCl, Hi-Pure Chemical Inc., Nazareth, PA) or aqueous alkaline solutions (0.025N-0.25N) of ammonium hydroxide (Hi-Pure Chemical, Inc.) with 200 ml of oil for 5 sec at the low setting in a Waring Blendor (Dynamic Corp., New Hartfort, CT) under air or a blanket of nitrogen. Control aqueous emulsions (pH 7.4) were prepared with a blender using 50 ml of deionized water and 200 ml of oil.

Vacuum steam deodorization system. A modified laboratory, batch-type steam deodorizer similar to that described by Schwab and Dutton (24) and Heide-Jensen (25) was employed. The steam stripping chamber consisted of an elongated Pyrex flask constructed from a modified commercial (2 liter) percolator reservoir that had been sealed to provide a rounded bottom to accommodate small oil samples (200-300 ml). An elongated configuration (37 cm) provided a large wall surface area which allowed for greater thin-film deodorizing opportunities than the system originally described. Four sequential cold traps cooled by ethanol-dry ice were employed for collection of volatiles and water.

Deodorizations at 4-7 mm Hg were performed over a range of temperatures from 100-210°C, and deodoriza-

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tion times ranging from 0.5 hr (at 210°C) to 2 hr (at 100°C). Some samples included dilauryl thiodipropionate (Evans Chemetics, W.R. Grace, Lexingtion, MA) at levels of 200-500 ppm (26) added before deodorization. After deodorizations, the system was brought to ambient pressure with nitrogen before cooling. An antioxidant mixture consisting of 100 ppm butylated hydroxyanisole (BHA) and 100 ppm *tert*-butyl hydroquinone (TBHQ) (Eastman Chemical Products, Inc., Kingsport, TN) was added to each batch immediately after distilling (35°C) while taking care to minimize exposure to air.

For removal of residual water and acids, when desired, deodorized oils were passed through beds of powdered anhydrous sodium sulfate/sodium bicarbonate (2:1, wt/ wt; Columbus Chemical Industries, Columbus, WI, and Amend Drug and Chemical Co., Irvington, NJ, respectively) under reduced pressure (ca 500 mm Hg). For removal of residual water and ammonia, oils were passed through beds of powdered anhydrous sodium sulfate/ citric acid monohydrate (2:1, wt/wt; Fisher Scientific, Fairlawn, NJ).

Collection and analysis of headspace volatiles from oils. Volatile compounds in fish oils were quantitatively measured using the dynamic headspace procedure described by Olafsdottir et al. (27), with modifications. Aliquots of oil (15 ml) were added to cylindrical glass 30 ml reservoirs (3 cm  $\times$  10 cm) constructed with 24/40 ST glass joints (female), and assembled with a purging head described in the earlier procedure. Ethyl heptanoate was added as the internal standard at a level of 2.08 ppm of the oil. Headspace volatiles were purged from the oil by introducing nitrogen (270 ml/min for 3 hr at  $75 \pm 5^{\circ}$ C) below the surface of the sample, and volatiles were entrained onto Tenax GC (60-80 mesh, ENKA N.V., Holland). Volatile compounds were eluted from Tenax GC traps with ca 0.5 ml of redistilled diethyl ether (Fisher Scientific, Fairlawn, NJ), and extracts were then concentrated under a slow stream of nitrogen to about 30 ul at room temperature (20°C).

Volatile compounds were analyzed quantitatively by capillary column gas chromatography using a Varian 3700 gas chromatograph (Varian Associates, Inc., Sunnyvale, CA) equipped with an on-column injector system and FID detector. Separation of volatile compounds was achieved using a Carbowax 20M ( $60 \text{ m} \times 0.25 \text{ mm}$ ) fused silica capillary column (J & W Scientific, Inc., Rancho Cordova, CA) operated with helium as the carrier gas. A program rate of 50°C (1 min hold) to 220°C at 4°C/min was used. Chromatographic data were processed with a computing integrator (Model 4200, Spectra Physics, San Jose, CA).

Mass spectra were obtained using a Finnigan 4500 mass spectrometer fitted with the same Carbowax 20M capillary column using a temperature program rate of 50°C (1 min hold) to 220°C at 4°C/min. Identification of peaks in chromatograms was achieved by matching electron impact (70/ev) mass spectral data to those published in *EPA/NIH Mass Spectral Data Base* (28,29), or those of authentic compounds. Coincidence of retention indicies of unknown compounds ( $I_E$ ; 30) with authentic compounds was also employed for compound identification.

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Oil stability assessments. Twenty-ml portions of deodorized oils were placed into 60 ml clear glass bottles (85 mm  $\times$  30 mm) that were then placed uncapped in an aluminum tray at 21°C under light (950 lux). These oil samples were assessed for flavor quality by the authors immediately after processing and at selected intervals over a 28 day storage period. The remainder of each batch of deodorized oil was held under vacuum (5 mm Hg) in a glass desiccator at 4°C in the dark until needed.

Oil samples were first assessed for odors, and then tasted. The large end of a disposable Pasteur pipette was dipped into an oil, and then a drop of oil was placed on the tip of the tongue to minimize flavor carryover by coating the lips with oil (31).

Hydroperoxide concentrations measured by the method of Buege and Aust (32) were used as a general index of oil quality. Values are reported as micromoles of hydroperoxide per mg of oil.

Chlorine atom content of fish oils deodorized with steam containing hydrochloric acid was measured by instrumental neutron activation analysis (INAA; 33-35) at the University of Wisconsin-Madison Reactor Laboratory. Samples were irradiated for 10 min in a thermal neutron flux of  $1 \times 10^{13}$  neutrons/cm<sup>2</sup>-sec in the reflector region of the reactor. After a 30 min delay, the samples were counted for 180 sec at 4 cm distance on the axis of an intrinsic-Germanium  $\gamma$ -ray detector coupled to a Tracor Northern TN-11 computer-based multichannel  $\gamma$ -ray spectrometer. Photopeak areas were determined by the classical method for both the 1643 and 2167 keV  $\gamma$  rays emitted by 37.3 min<sub>38</sub>Cl after standardizing the data with known samples run simultaneously. Chlorine content was determined in ppm (36).

### **RESULTS AND DISCUSSION**

Deodorization trials. Initial trials were carried out at 100°C for 2 hr using 0.025N acetic acid as the steam source for the deodorization of cod liver oil. Compared to trails where distilled water was substituted for the acetic acid solution, the acid-distilled samples were markedly less fishy-flavored and exhibited mild green, plant-like aromas. When 200 ppm dilauryl thiodipropionate (DLTDP; 200-500 ppm) was added to cod liver samples before deodorizations for a presumed hydroperoxide decomposing action (37), more pronounced green flavor notes were observed in both acid and water-deodorized oils. Thus, it appeared that acidic steam provided conditions that more efficiently removed compounds causing fishy flavors at low temperatures than water, and that DLTDP treatments also contributed to more green and less distinct fishy flavors.

Similar low temperature (100°C) deodorization trails with 0.025N ammonium hydroxide as the steam source yielded oils that were markedly more fishy than either water or acid-deodorized cod liver oils, and the oils caused a burning-stinging sensation on oral tissue when tasted. Thus, it appeared that alkaline steam did not efficiently remove compounds causing fishy flavors in cod liver oil, and that residual concentrations of ammonium hydroxide remained in the oils that were high enough to be detected when tasted. However, neither acetic acid nor ammonium odors per se were perceived in the headspace of deodorized oils. Trials at 100°C were then carried out using solutions containing a mixture (1:1) of 0.025N acetic acid and 0.005N HCl as the steam source to provide more ionizable volatile acid in the deodorization medium. The acid mixture yielded mild, green, very slightly fishy flavors similar to acetic acid deodorizations. However, when 0.01N HCl was used, the green flavors were accompanied by very sharp, burning sensations on oral tissue that was caused by residual HCl in the oil.

Trials were then conducted using acidic or alkaline percolation beds to explore the removal of residual acids and bases from deodorized oils. Satisfactory removal of HCl was achieved by passing samples of deodorized oils through beds (1:1, vol:vol) composed of sodium bicarbonate and powdered anhydrous sodium sulfate (2:1, wt:wt) under slightly reduced pressure (ca 500 mm Hg). Likewise, ammonia (ammonium hydroxide) was removed from deodorized oils by passing samples through beds of anhydrous sodium sulfate and citric acid monohydrate (2:1, wt:wt). After these finishing treatments, neither HCl nor ammonia were detectable by taste in the oils.

Sequential deodorizations employing alternating acid or alkaline steam sources for various times to 2 hr each were evaluated to investigate possible beneficial effects of pH extremes in the low-temperature batch deodorizations of fish oils. Based on sensory properties of oils, however, sequential low-temperature deodorizations did not provide improved oil quality, and the flavor quality of deodorized oils reflected the final deodorization treatment of the series. Fish oils that were last deodorized with ammonium hydroxide consistently exhibited distinct fishy/burnt flavors that are characteristic of the 2,4,7decatrienals (17,18). When acetic acid or mixtures of acetic acid and HCl were employed in the final deodorization, mild, green, and slightly fishy flavors were observed in the oils.

Other variables that were investigated included the fine dispersion of the same acidic or basic water solution that was to be employed in the deodorization into the oils (25% by volume). Variable results were obtained with 0.025N acetic acid and a mixture of 0.025N acetic acid and 0.005N HCl (1:1) with regards to the flavor quality of cod liver oil. Deodorized oils from this treatment were not always equivalent of those receiving only acidic deodorizations, but lowered flavor qualities were traced to the use of a blender cup with a worn blade bearing assembly that contributed metal ions to the emulsions. Shaking the oil and acetic solutions in a glass separatory funnel overcame the variability observed, however. Dispersion of 0.025N ammonium hydroxide in fish oil (25% by volume) also did not appear to significantly alter the effects of subsequent deodorization with a steam source of the same composition.

Potential chloropropanediol production in HCldeodorized oils. The use of HCl in deodorizing steam potentially could cause the formation of harmful artifacts in fish oils. It has been shown that chloride ions react at elevated temperatures with triglycerides to yield chloropropanediol esters (38-42) that are potentially toxic substances (39). Chloropropanediol esters have been found in contaminated cooking oils that apparently had contact with HCl at elevated temperatures during processing to remove aniline, an intentional adulterant (39). Samples of various fish oils were analyzed for chlorine atom content using neutron activation analysis to gain some insight into the degree of residual chlorine present in HCldeodorized fish oils (Table 1). A slightly elevated content in the oil was observed in cod liver oil deodorized with 0.01N HCl for 2 hr compared to the nondeodorized control. However, washing the sample of 0.01N HCldeodorized oil sequentially with three equal volumes of distilled water reduced the chlorine atom content of the oil to essentially that of the initial oil which indicates that the chlorine in the sample was in the chloride ion form. Thus, it appears that at low deodorization temperatures (near 100°C), HCl-acidified steam does not cause the formation of significant quantities of chloropropanediols. However, usage of HCl in steam sources for oil deodorizations should be cautiously approached, especially if higher deodorization temperatures are employed.

#### TABLE 1

Concentration of Chlorine in Fish Oil Samples Deodorized with HCl Solutions and Analyzed by Neutron Activation Analysis

Sample description	Chlorine atom content (ppm)
A. no deodorization treatment	33.70
B. 0.01N HCl deodorization <sup>a</sup>	36.20
C. 0.01N HCl deodorization + H <sub>2</sub> O washed	33.38

<sup>a</sup>Deodorizations at 100°C for 2 hr total time.

Source and temperature effects on oil flavors. Cod liver, laboratory-rendered siscowet lake trout, and commercially-refined, nondeodorized Menhaden oils deodorized under a variety of conditions, did not have the same flavor qualities after equivalent processing. Differences in minor constituents and polyunsaturated fatty acid compositions seem to be probable contributors to these variations. For example, cod liver oils contain notable amounts of iron and vitamins A and D compared to fish body oil (43). The siscowet trout oil was body oil that was not refined, and it exhibited a light-salmon color presumably contributed by carotenoids. The Menhaden oil was obtained from whole fish, and was refined which should have substantially lowered phospholipids and other minor components. Thus, differences in oxidations of lipids and formation of influential flavor compounds caused by minor components in the oils (18,44) appear to provide the basis for flavor variations observed.

A variety of deodorization times at 100°C were evaluated, and oils processed for 2 hr or longer at this temperature had similar flavors. When higher temperatures were employed (to 210°C), relatively bland-flavored oils were obtained from our apparatus with deodorization times as short as 0.5 hr. Pelura and Chang (8) have reported that deodorization times of 3-5 hr at 175-200°C were required to obtain acceptable deodorized fish oils. Since minimization of thermal damage to n-3 lipids was desired, deodorization times for most experiments were 2 hr or less.

More detailed investigations of selected 0.025N acetic acid and water deodorizations of fish oils were then undertaken. In these trials, data were also collected for individual volatile flavor compounds, and the influence of abusive storage conditions (950 lux, 21°C, air exposures) were determined. Additionally, higher deodorization temperatures (130, 150, and 210°C) were also included to provide information about conditions between low (100°C) and conventional high temperature (230°C) steam deodorizations for fish oils (5).

Generally, temperatures from  $100-150^{\circ}$ C gave oils within a series that were comparable in flavor qualities when deodorized with either water or 0.025N acetic acid. Oils deodorized with water, however, exhibited more pronounced fishy/burnt and less green flavors than those deodorized with acetic acid. Deodorizations carried out at 210°C with water gave less intensely-flavored fish oils than those employing 0.025N acetic acid although both gave very mild flavors.

Stability of oils. Initial hydroperoxide concentrations in deodorized fish oils were below 2.5 micromoles/mg oil for all trials, including those employing 0.025N ammonium hydroxide as the steam source. Data for hydroperoxide concentrations of selected samples of deodorized menhaden oils during storage under light at room temperatures are shown in Figure 1. Lower deodorization temperatures and the presence of DLTDP in samples deodorized under these conditions gave slightly higher initial hydroperoxide values than higher temperatures and omission of DLTDP. Thermal decomposition of hydroperoxides has been reported to result from exposure of oil to 150°C or above (45), but substantial decomposition of hydroperoxides also occurred during the 100°C deodorizations. Initial hydroperoxide concentrations of nondeodorized fish oils range from 0.75-9.30 micromoles/mg oil. DLTDP in oils deodorized at high temperatures (210°C) did not result in slight elevations of hydroperoxides noted at low temperatures (100°C), but it has been reported recently that DLTDP does not appear to be an efficient hydroperoxide-decomposer at the concentrations employed (26). Rates of hydroperoxide formations in all deodorized fish oils were markedly similar, and only menhaden oil deodorized at 210°C with 0.025 acetic acid and DLTDP (Fig. 1) appeared to exhibit noticeably slower formation of hydroperoxides.

The array of volatile compounds from oxidizing fish oils is complex, but certain compounds provide the characterizing flavor notes (18). Thus, selected data for measurements of some of these aroma compounds in deodorized fish oils are discussed here. Concentrations of compounds in cod liver oil containing DLTDP immediately after deodorization at 100°C for 2 hr were surprisingly high (Fig. 2) in view of the very mild, green, fresh fishlike flavor observed. The sample contained 700 ppb t,c,c-2,4,7-decatrienal which contributes strongly to fishy/ burnt, cod liver oil flavors, and it contained 1510 ppb of t,c-2,6-nonadienal which contributes most of the green, plant-like flavor to freshly deodorized fish oils (18). Holding the oil under light resulted in the maintenance of a reasonably mild flavor through about 10 days, at which time it became distinctly fishy/burnt in flavor. When cod liver oil was deodorized with 0.025N acetic acid (Fig. 3) or water (Fig. 4), initial concentrations of the decatrienals and t,c-2,6-nonadienal were much lower than observed for the sample containing DLTDP and deodorized with 0.025N acetic acid. Notably, both of these samples had as much or greater degrees of fishy flavors as the acetic acid/DLTDP sample, but they lacked the pronounced green flavor of that sample.

These puzzling results along with other data suggest that some unexpected effects or interactions between flavor compounds and possibly the medium were occurring. Initially, it seemed that these effects might be caused entirely by high concentrations of the potent green compound, *t*,*c*-2,6-nonadienal, which was capable of blending, masking, or ameliorating the flavor of the fishy/burnt cod liver oil-like 2,4,7-decatrienals. When the concentration of *t*,*c*-2,6-nonadienal decreased greatly in the 0.025N acetic acid/DLTDP sample after 12 days of holding (Fig. 2), the flavor of the oil became objectionably fishy/burnt. At the same time, the concentration of *c*-4-heptenal correspond-

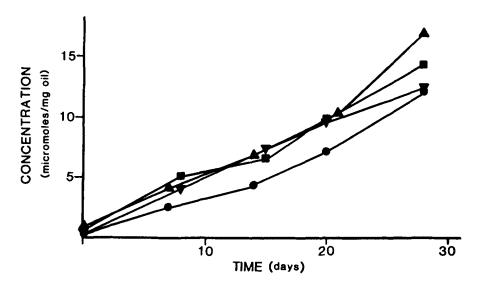


FIG. 1. Hydroperoxide concentrations of various samples of oxidizing Menhaden oils that were steam deodorized under different conditions and exposed to light (950 lux) and air at room temperature (21°C) over 28 days of storage ( $\blacktriangle$ , 100°C/acetic acid/DLTDP;  $\blacksquare$ , 150°C/water;  $\lor$ , 210°C/water;  $\diamondsuit$ , 210°C/acetic acid/DLTDP).

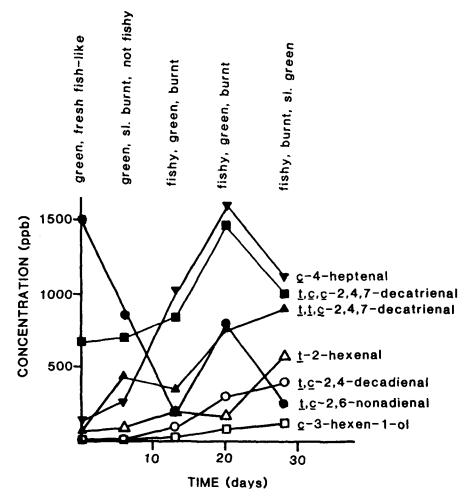


FIG. 2. Concentrations of compounds associated with fishy flavor development in oxidizing low-temperature (100°C for 2 hr) acetic acid (0.01N) steam deodorized cod liver oil containing 200 ppm dilauryl thiodipropionate.

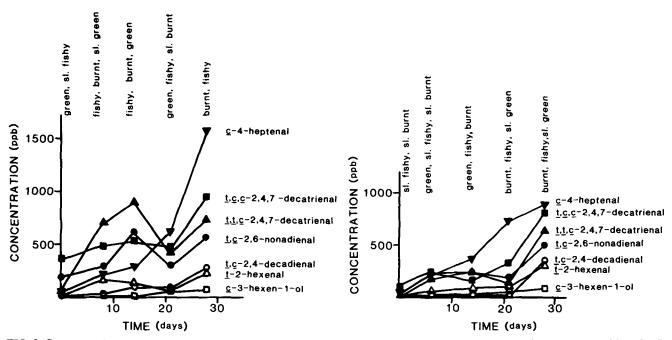


FIG. 3. Concentrations of compounds associated with fishy flavor development in oxidizing low-temperature  $(100^{\circ}C \text{ for } 2 \text{ hr})$  acetic acid (0.01N) steam deodorized cod liver oil.

FIG. 4. Concentrations of compounds associated with fishy flavor development in oxidizing low-temperature ( $100^{\circ}$ C for 2 hr) steam deodorized cod liver oil.

ingly increased because it is formed from the retro-aldol reaction of t,c-2,6-nonadienal (19). In fish oils, c-4-heptenal enhances the burnt characteristics and fishy flavors of the 2,4,7-decatrienals (18).

Subsequently, it was discovered that the mild green flavors in fish oils deodorized with acetic acid solutions compared to those deodorized with water appeared to result from both an enhanced formation of t,c-2,6-nonadienal (Figs. 3 and 4) and residual deodorant acids in the oils. Josephson *et al.* (22) have observed that fishy flavors are suppressed in vinegar pickled fish, and lemon juice is frequently used to suppress fishiness associated with fish and other seafoods. While the citric acid in lemon juice neutralizes trimethyl amine in marine fish, the effect of acidity on fishy flavors appears to extend beyond that action.

In a report on the retro-aldol reaction of t,c-2,6nonadienal, Josephson and Lindsay (19) have discussed the chemistry of the hydration of aldehyde groups of alkenals and related compounds. Under acidic conditions, carbonyl groups of 2-alkenal compounds are hydrated to form a pool of compounds which would not be sensorially active and which must be dehydrated to exhibit significant vapor pressure. The equilibrium between the volatile nonhydrated and hydrated form in acidic deodorized fish oils has not been investigated. However, hydrated aldehydes in acidified oils appear to be readily dehydrated and swept from samples during purging with nitrogen for Tenax GC collection. Thus, the apparently contradictory results of sensory analysis and measurements of fishy compounds illustrated in Figure 2 can be rationalized in part by this concept. Similarly, some of the reduction of fishiness in fish oils observed by Fernandez and Pigott (11-13) may have resulted from the release of protons from the cation exchange resin which would lead to acidic conditions in the oils.

Fishy/burnt flavors were characteristic of lowtemperature deodorizations with 0.025N ammonium hydroxide, and these occurred even though notable concentrations of t,c-2,6-nonadienal where present with low concentrations of the 2,4,7-decatrienals (data not shown). In the absence of protons to catalyze aldehyde hydrations, the fishy flavors of the 2,4,7-decatrienals are fully available for sensorial detection. Additionally, the alkaline conditions of oils deodorized with 0.025N ammonium hydroxide rapidly promote the retro-aldol degradation of t,c,-2,6-nonadienal to c-4-heptenal (19) which further intensifies the fishy/burnt character of the oils (18).

Relationship of deodorized fish oils and food quality. When deodorized fish oils were incorporated into standard mayonnaise, fishy flavors were suppressed to the extent that even moderately fishy-flavored oils could not be detected in substitutions up to 50% of the oil. These results are also in agreement with Fernandez and Pigott (13), who found that acceptable salad dressings could be prepared with fish oils that were deodorized by a procedure involving an ion exchange medium. When a freshly deodorized cod liver oil (0.025N acetic acid at 100°C for 2 hr) was incorporated into a standard cheddar-based processed cheese at 5% of the formulation, an extremely fishy product resulted. This cheese was much more fishy than a comparable cheese manufactured with menhaden oil that had been freshly deodorized at 210°C for 0.5 H. This menhaden oil exhibited a virtual absence of fishy flavors, and contained very low concentrations of compounds contributing to fishy flavors (Fig. 5). However, when placed in the relatively high pH environment of processed cheese (pH = 5.6; 46), sufficient concentrations of the 2,4,7-decatrienals and c-4-heptenal that were either preformed or developed in processing were present to produce a distinct fishy flavor.

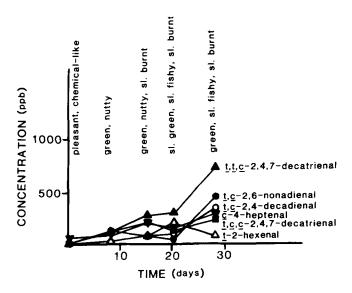


FIG. 5. Concentrations of compounds associated with fishy flavor development in oxidizing high temperature (210°C for 0.5 hr) steam deodorized menhaden oil.

There has been great interest in the development of an analytical test for the flavor quality of fish oils, and data in the current study have been evaluated in this regard. Measurement of the 2,4,7-decatrienals and c-4-heptenal might provide a useful index of fishy flavors (Figs. 2-5) because in most instances these compounds increase reasonably linearly. However, the complicating effects of flavor modifications by t,c-2,6-nonadienal and residual acids in oils make the universal value of these measurements uncertain. Further research is needed to more clearly define the flavor properties and relationships of these compounds in fish oils and foods as well as the effects of other potential fishy-flavored compounds encountered in fish oils (18). Data are also shown (Figs. 2-5) for t,c-2,4-decadienal, t-2-hexenal, and c-3-hexen-1-ol, which do not contribute to distinctive fishy flavors, but which contribute to general oxidized painty background flavors in more extensively oxidized fish oils (18). Use of these compounds as indirect indices of fish flavor quality, however, do not appear promising.

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## REFERENCES

- 1. Carr, R.A. J. Am. Oil Chem. Soc. 53:347 (1976).
- 2. Cowan, J.C. Ibid. 53:344 (1976).
- 3. Duff, A.J. Ibid. 53:370 (1976).
- 4. Zehnder, C.T. Ibid. 53:364 (1976).

- Chang, S.S., in Fish Oils: Their Chemistry, Technology, Stability, Nutritional Properties, and Uses, edited by M.E. Stansby, AVI Publ. Co., Westport, CT, 1967, pp. 206-221.
- Devinat, G., L. Scamaroni, and M. Naudet, *Rev. Fr. Corp Gras.* 27:283 (1980); from Food Sci. Technol., Abstr., 13, 3N173 (1981).
- Elder, S.R., Fette Seifen Anstrichsm. 84:136 (1982); from Food Sci. Technol. Abstr., 14, 12N595 (1982).
- 8. Pelura, T.J., and S.S. Chang, J. Am. Oil Chem. Soc. (Abst.) 65:500 (1988).
- 9. Norris, F.A., and E.G. Perkins, Ibid. 64:414 (1987).
- Wijesundera, R.C., W.M.N. Ratnayake, and R.G. Ackman, *Ibid.* (Abst.) 65:474 (1988).
- 11. Fernandez, C.C., PhD. dissertation, University of Washington, Seattle, WA (1986).
- Fernandez, C.C., and G.M. Pigott, 46th Annual Instit. of Food Tech. Meeting, (Abstr.), pp. 212, No. 529 (1986).
- Fernandez, C.C., and G.M. Pigott, 47th Annual Instit. of Food Tech. Meeting, (Abstr.), pp. 117, No. 163 (1987).
- Spinelli, J., V.F. Stout, and W.B. Nilsson, US patent 4,692,280 (1987).
- 15. Takao, M., US patent 4,554,107 (1985).
- 16. Takao, M., US patent 4,623,488 (1986).
- Meijboom, P.W., and J.B.A. Stroink, J. Am. Oil Chem. Soc. 49:72 (1972).
- Karahadian, C., Ph.D. dissertation, University of Wisconsin-Madison, Madison, WI, 1988.
- Josephson, D.B., and R.C. Lindsay, J. Am. Oil Chem. Soc. 64:132 (1987).
- Josephson, D.B., and R.C. Lindsay, J. Food Sci. 52(5):1186 (1986).
- Hodge, J.E., in Symposium on Foods: The Chemistry and Physiology of Flavors, edited by H.W. Schultz, E.A. Day and L.M. Libby, AVI Publ. Co., Westport, CT, 1967, pp. 465-491.
- Josephson, D.B., R.C. Lindsay, and D.A. Stuiber, J. Food Sci. 52(1):10 (1987).
- Vernin, G., and C. Parkanyi, in *The Chemistry of Heterocyclic Compounds in Flavours and Aromas*, edited by G. Vernin, Ellis Horwood Limited Publ., Chichester, England, 1982, pp. 151-156.
- 24. Schwab, A.W., and H.J. Dutton, J. Am. Oil Chem. Soc. 25:57 (1948).
- 25. Heide-Jensen, J., Ibid. 40:223 (1963).
- 26. Karahadian, C., and R.C. Lindsay, Ibid. 65:1159 (1988).
- Olafsdottir, G., J.A. Steinke and R.C. Lindsay, J. Food Sci. 50:1431 (1985).
- Heller, S.R. and G.W.A. Milne, *EPA/NIH Mass Spectral Data Base*, vol 1-4, 1975, U.S. Government Printing Office, Washington, DC.

- Heller, S.R., and G.W.A. Milne, *EPA/NIH Mass Spectral Data Base*, Suppl. 1, 1980, U.S. Government Printing Office, Washington, DC.
- 30. Van den Dool, H., and P.D. Kratz, J. Chromatog. 11:463 (1963).
- Stansby, M.E., and G. Jellinek, in *The Technology of Fish Utiliza*tion Contributions from Research, edited by R. Kruezer, Fishing News Ltd., London, England, 1965, pp. 171-176.
- Buege, J.A., and S.D. Aust, in *Methods in Enzymology Vol LII* Biomembranes, edited by S. Fleisher and L. Packer, Academic Press, New York, 1978, pp. 302-310.
- Cashwell, R.J., 1981, UWNR Instrumental Neutron Activation Analysis Manual, Department of Nuclear Engineering and Engineering Physics, University of Wisconsin-Madison, Madison, WI.
- Crouthamel, C.E., in *Applied Gamma-Ray Spectrometry*, 2nd edn., edited by F. Adams and R. Dams, Pergamon Press, New York, 1975, pp. 257-294.
- 35. Willard, H.H., L.L. Merritt and J.A. Dean, in *Instrumental Methods of Analysis Fifth Edition*, D. Van Nostrand Co., New York, 1974, pp. 328-331.
- Brune, D., B. Forkman, and B. Persson, in Nuclear Analytical Chemistry, Chartwell-Bratt Ltd., Sweden, 1984, Chapter 10.
- Ingold, C.K., in *Structure and Mechanism in Organic Chemistry*, 2nd edn., Cornell University Press, Ithaca, New York, 1967, pp. 589-607.
- Davidek, J., J. Velisek, V. Kubelka, G. Janicek, and Z. Simicova, Z. Lebensm. Unters. Forsch. 171:14 (1980).
- Gardner, A.M., M.P. Yurawecz, W.C. Cunningham, G.W. Diachenko, E.P. Mazzola, and W.C. Brumley, Bull. Environ. Contam. Toxicol. 31:625 (1983).
- Velisek, J., and J. Davidek, Sb. UVTIZ, Potravin. Vedy. 3(1):11 (1985).
- Velisek, J., J. Davidek, V. Kubelka, J. Bartosova, A. Tuckova, J. Hajslova, and G. Janicek, *Lebensm. Wiss. Technol.* 12:234 (1979).
- Velisek, J., J. Davidek, V. Kubelka, G. Janicek, Z. Svobodava, and Z. Simicova, J. Ag. Food Chem. 28:1142 (1980).
- Brody, J., in Fishery By-Products Technology, AVI Publ. Co., Inc., Westport, CT, 1965, pp. 47-68.
- Josephson, D.B., PhD. dissertation, University of Wisconsin-Madison, Madison, WI, 1987.
- 45. Frankel, E.N., W.E. Neff, E. Selke, and D.D. Brooks, *Lipids 22*:322 (1984).
- Gupta, S.K., C. Karahadian, and R.C. Lindsay, J. Dairy Sci. 67:764 (1984).

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