Adsorptive Bleaching and Molecular Distillation of Menhaden Oil

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Abstract

Some of the major barriers to wide acceptance of fish oils as sources of polyunsaturated triglycerides, fatty acids, and fatty acid derivatives have been the problems associated with color, odor, flavor, and other impurities. Adsorptive bleaching and molecular distillation were investigated as methods to obtain natural triglycerides from menhaden oil that do not have undesirable flavors and odors. Results of these studies have shown that certain activated clays will satisfactorily reduce the color of commercial menhaden oil but will not remove the odor and flavor. Molecular distillation was found to be more effective in improving the odor and flavor of the oil than adsorptive bleaching with activated clays but somewhat less effective in reducing the color. When used jointly with bleaching, molecular distillation yields menhaden oil of high quality, suitable for use both in animal and human nutrition and in medical research. Spectral data in the 400–700 mμ range were used to evaluate the success of the refining process.

Introduction

Raw commercial fish oils are composed of major amts of triglycerides; of minor amts of free fatty acids, vitamins, phospholipids, steroids, and hydrocarbons; and of very small amts of lipid-protein degradation products, pigments, and suspended mucilaginous and colloid-like matter. Choice of a refining process for fish oils is dependent upon which substances are to be removed, which in turn is dependent upon the ultimate use of the refined product. Fish oils are currently refined commercially to produce oils suitable for certain industrial applications. However, these refined oils are not of sufficiently high quality for certain areas of research. High quality fish oils of the type demonstrated in this work have been used, for example, in medical research (1–4), in poultry nutrition studies (5), and in food science (6) where the unique polyunsaturates of fish oil are important.

"Winterization" or cold-pressing (precipitation at low temp) results in the removal of stearine. Cold-pressing, however, does little to improve the color and odor of fish oil since the pigments and the degradation products are not selectively removed. Some color is removed by occlusion of the pigments in the solid stearine fraction, but this is only to a slight extent. The primary purpose of the process is to produce an improved drying oil at a low cost.

The alkali-refinement process, which generally utilizes a winterized oil, removes free fatty acids. In addition, certain chromophores may be removed or degraded by the alkali treatment. This process can produce light-colored fish oils that are currently used in certain industrial applications, especially in the manufacture of alkyd resins. Although the color of an alkali-refined fish oil is acceptable, the odor and flavor is still not satisfactory for medical and nutritional research.

Adsorptive bleaching is often used commercially to improve fish oils by removing colored matter and natural pigments. In addition to the removal of colored compounds, adsorptive bleaching improves the brightness of oils by removing the suspended mucilaginous and colloid-like matter. Many adsorbent materials are commercially available for this purpose, including both domestic and foreign clays, activated carbon, and alumina. An adsorbent that is good for bleaching one oil, such as cottonseed oil, is not necessarily good for bleaching fish oils. The presence of different chromophores in different oils can account for such observations. In practice, bleaching is usually preceded by other refining techniques (7).

Fish oils that are refined by the methods discussed above do not possess the low levels of color and odor that are required for medical and nutritional studies. Also, the flavor of an oil used in such studies should be as bland as possible. We have found that the extent of the flavor of refined menhaden oil closely corresponds to its level of odor. Low color, in addition to low odor, would also be desired in fish oils used in other areas.

Molecular distillation is another method of refining fish oils. Distilled fish oils should be low in free fatty acids, improved in color and odor, and contain little or no polymeric matter. Also, distilled fish oils should have improved stability toward autoxidation compared to oils refined by other methods, because of the removal of low mol wt proöxidant compounds. The chemical properties of distilled triglycerides would not necessarily be changed by this method of refining. Molecular distillation as a method for refining natural oils has been used very little in the United States, with the exception that concd vitamin A from fish-liver oils was produced by this method prior to and during World War II (8).

With a general aim towards developing a method to produce high quality triglycerides from menhaden oil suitable for human nutrition and medical research, the objectives of this investigation were to determine: (a) how well menhaden oil responds to adsorptive bleaching with activated earths, carbons, and other chemicals; (b) whether or not molecular distillation alone can produce an oil free of objectional odors and flavors; and (c) the effects on menhaden oil by a combination of adsorptive bleaching and molecular distillation.

Experimental and Discussion

The experimental work on menhaden oil involved the following approach: Making a reasonable choice of conditions for adsorptive bleaching studies based principally on commercial practices; the screening of 17 commercial adsorbents for their effectiveness; the study of the bleaching variables of temp, pressure, time, and adsorbent concns; and the application of molecular distillation to bleached and unbleached menhaden oil.

Adsorptive Bleaching

The fish oil used in this investigation was commer-

TABLE I

Percentage Transmission of Winterized Menhaden Oil Bleached with Various Adsorbents for 30 Min at 80C and 15 mm Hg

Adsorbent Earths [a] (4% wt/wt)	Percent Transmittance 400 mμ	460 mμ	550 mμ	620 mμ	665 mμ	700 mμ
Canada	11.1	77.5	98.4	99.0	99.0	99.0
Louisiana-2	6.3	68.0	95.4	97.4	98.1	98.7
Louisiana-1	7.2	66.5	94.3	96.1	96.8	98.3
Texas	2.8	57.2	94.0	97.0	97.0	99.3
California-1	3.0	37.7	91.9	95.5	94.8	97.0
Florida-3	1.9	18.7	95.6	98.8	97.3	99.2
Illinois	1.7	14.6	93.4	97.1	92.9	97.5
Florida-2	1.1	8.0	89.3	93.6	91.7	95.0
California-2	0.0	0.2	83.5	92.8	85.5	96.1
Florida-1	0.0	0.0	78.0	87.7	43.0	95.3
Georgia-2	0.0	0.0	69.6	77.7	26.3	89.4
Georgia-1	0.0	0.0	67.7	74.6	19.3	89.4
Carbons (3% wt/wt)						
Darco	0.0	4.6	94.2	98.7	98.5	99.3
Nuchar-2	0.8	1.3	92.0	98.5	98.5	98.7
Nuchar-1	0.0	0.0	89.7	96.9	96.8	97.8
Norit	0.0	0.0	87.2	97.5	95.6	99.2
Other (4% wt/wt)						
Activated alumina	0.0	0.0	71.4	83.0	41.2	93.0
Untreated oil	0.0	0.0	60.0	64.8	7.2	82.0

[a] Listed by geographical location of adsorbent production.

cial winterized menhaden (*Brevoortia tyrannus*) oil. Various commercially available adsorbents were investigated for their effectiveness in reducing the color of this oil. These adsorbents included natural and activated clays, activated carbons, alumina, and a diatomaceous-earth filter aid. The adsorbents used in this investigation were generously supplied by various manufacturers and dealers interested in the work.

To evaluate the color of bleached menhaden oil by a means that is both accurate and reproducible, visible spectral data were collected using an automatic recording spectrophotometer (Beckman Model DK-1). The method used was patterned after the AOCS Spectrophotometric Method (Tentative Method Cc 13c-50), whereby the percent transmission of the oil was measured directly, using 1 cm cells and carbon tetrachloride as the reference standard.

All bleaching experiments were carried out using a mechanical shaker and a constant temp bath controlled to ±0.1C. Samples of menhaden oil weighing 25 g were placed into 100 ml round-bottom flasks fitted with vacuum adapters. The appropriate amts of adsorbents were added, and the system was controlled at the desired conditions for bleaching. All samples were mechanically treated in the same manner.

The effects of temp, pressure, and contact time were studied in order to establish the best set of bleaching conditions to evaluate the various adsorbents. The temp, pressure, and contact time were varied from 22–93C, 15–760 mm Hg, and 10–60 min, respectively.

As temps were increased above 80C, the visible spectra indicated that desorption occurred in bleaching for 30 min at 15 mm Hg. The lower the temp used for adsorptive bleaching of fish oils, the less chance there would be for alteration of the polyunsaturated fatty acid moieties in the glyceride oil. There was no appreciable advantage found in extending bleaching contact time beyond 30 min. Vacuum bleaching was found to be more effective than was bleaching at atmospheric pressure. The best general conditions for adsorptive bleaching were eventually set at 80C and 15 mm Hg for 30 min.

TABLE II

Typical Molecular Distillation Data for Menhaden Oil Using a Model CMS-14 Centrifugal Molecular Still

Fraction	Temperature, C		Pressure, microns	Flow rate,[b] gal/hr		Yield, vol %
	Preheat line	Distilland [a]		Distillate	Distilland	
Degas [c]	60	50	20	—	—	—
Forerun	98	190	17	0.198	3.658	4
Main	105	180	16	0.951	1.585	92
Pot residue	—	—	16	—	—	4

[a] Distillation temps are measured at a point where the distilland just leaves the distilling surface; hence, it closely approximates the boiling point.

[b] Total throughout is the sum of flow rates for distillate and distilland; controlled by variable speed pump.

[c] Degassing cycles prior to removal of forerun fraction.

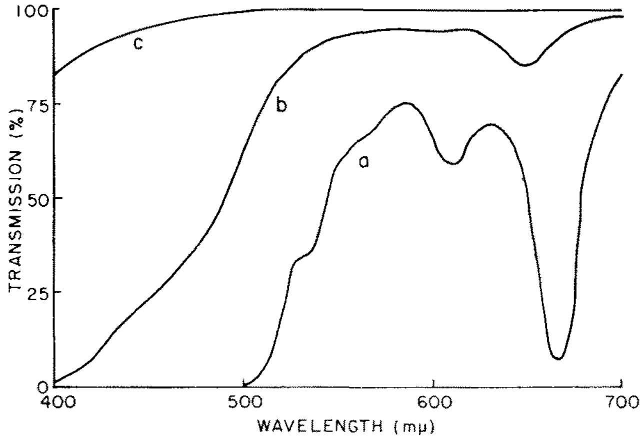

FIG. 1. Visible spectra of untreated and treated winterized menhaden oil: *a*, untreated oil; *b*, molecularly distilled oil; *c*, molecularly distilled, bleached oil.

The various adsorbents were evaluated under these set conditions. The percent transmittance of the bleached oil at particular wavelengths is given in Table I.

The better clays easily remove the pigments that absorb in the 550–700 mμ range of the spectra. The 400–550 mμ range, however, was found to be the most useful range for the establishment of optimum conditions for bleaching menhaden oil. Clay concns up to 15% (by wt) were investigated, but the data shown in Table I are given at the more practical 4% concn. Winterized menhaden oil responded poorly to activated alumina. A diatomaceous-earth filter aid, which was used with all adsorbents, showed no bleaching effect by itself.

Activated carbons were found to be effective for the removal of pigments that absorbed in the spectral range above 500 mμ. The carbons, however, had very little bleaching power for pigments absorbing below 500 mμ, even when concns as high as 12% (by wt) were used. Activated carbons were found to be effective in reducing the odors in the oil; for this reason, the use of 1–2% carbon is recommended.

Molecular Distillation

The same commercial winterized menhaden oil used in the bleaching work was subjected to molecular distillation. The equipment used for this purpose was a 5-gallon batch, centrifugal-type molecular still (Consolidated Vacuum Corporation, Model CMS-14) (9). This equipment was chosen for use in this investigation because of the short contact time (fraction of a second) of the oil with the heated distilling surface. This variable is of particular importance in the case of fish oils, since they contain a high percentage of heat-labile fatty acid moieties.

Prior to actual distillation, the still charge was degassed overnight by continuous cycling over the rotor at 60C under vacuum. The feed line and rotor temps were then increased and the oil flow across the distilling surface was controlled such that a 3–4% forerun fraction was removed in one cycle of the still charge. It is very important to remove the forerun fraction, since this fraction contains the bulk of the highly odoriferous constituents in the oil. Failure to remove these constituents completely in the forerun fraction will result in a lower quality product.

Distillation of the main body of the oil was accomplished by controlling the feed line and rotor temps and the oil flow across the rotor. A pot residue fraction of approx 4% was retained by nature of the batch-type equipment. The pot residue could be substantially decreased with large-scale continuous operation equipment. Typical batch distillation data on the oil processed in this manner are given in Table II.

Analysis of the distilled oil indicated that there was no destruction of the heat-labile constituents. Free fatty acids and odor constituents of low mol wt were removed in the forerun fraction, and high boiling polymeric substances and the bulk of the pigments were retained in the pot residue. The main fraction was lighter in color and almost free of odor as compared to the undistilled oil. Visible spectra of the winterized oil and molecularly distilled oil are shown in Figure 1.

Combined Bleaching and Distillation

Fish oil that has undergone adsorptive bleaching followed by molecular distillation would be expected to be superior in color, odor, free fatty acid content, and polymeric substances to fish oil that had been processed by only one of these techniques. Experiments were designed to give insight into the nature of such a dual processed fish oil.

Winterized menhaden oil was bleached with the Canadian earth (cf. Table I) at 80C for 30 min, as established in the preliminary experiments. Quantities of oil up to 7 gallons were treated in a 10-gallon stainless steel reactor equipped with stainless steel stirrer. The vacuum of the system was controlled at 100 mm Hg, using a mechanical pump and a suitable moisture trap. An 8% clay concn was used, because it was found to produce a high quality oil product from subsequent molecular distillation.

Figure 1 shows the visible spectrum of winterized menhaden oil bleached with 8% clay, followed by centrifugal molecular distillation of a 5-gallon batch. The product of this treatment is pale yellow, nearly odorless, and very bland in taste. It was found that the odor-flavor character of the treated oil was dependent on how carefully the forerun fraction was removed. The color is influenced by the final temp of the distillation. Attempts to force high distillation rates with unnecessarily high temp result in distillation of yellow-colored substances.

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Processing Ironweed (*Vernonia anthelmintica*) Seed in a Soybean Extraction Pilot Plant[1]

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Abstract

High quality domestic *Vernonia anthelmintica* (ironweed) seed was grown on many experimental test plots at a variety of locations during the 1963 season. Quality appeared to be related to seed density as judged by high oil content of 25 to 32%, the oils having oxirane oxygen values of 3.6 to 4.0% with low acidity, less than 2% calculated as epoxyoleic acid. Larger plantings in 1963 made without benefit of test plot data produced poor quality seed. For processing some of this seed was upgraded to fair quality by air-elutriation. Processing in a small soybean continuous solvent extraction plant was successfully achieved with only minor changes in existing equipment. No enzymatic lipolysis occurred during these operations. The oil obtained was equal in quality to that prepared from the same seed in the laboratory by the best procedures available. Also, the oil was improved in quality by removal of the major portion of its free fatty acids and unsaponifiable material. The chief natural component of the seed oil, trivernolin, was prepared from a substantial quantity of the oil miscella to demonstrate the commercial feasibility of this operation.

Introduction

NEW CROPS RESEARCH at the Eastern Regional Research Laboratory has been directed towards development studies on epoxy-bearing seed oils. A series of reports from this laboratory has appeared related to work on imported *V. anthelmintica* whose seed has held from 18 to 27% oil; about 65–70% of the oil has been composed of the single compound trivernolin, the triglyceride of vernolic (12,13-epoxyoleic) acid. The reports mentioned have reviewed the literature on *V. anthelmintica* (1); described procedures used for the production and purification of the oxygenated fatty components, trivernolin, 1, 3-divernolin, vernolic acid, methyl vernolate and 12, 13-dihydroxyoleic acid (2–5); presented information on a satisfactory gas-liquid chromatographic column for the determination of epoxyoleic acid in seed oils (6), and given accounts of evaluation studies on the stabilizing properties of some *Vernonia* products (7, 8).

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