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3,342,876

PROCESS FOR THE ISOLATION OF ALPHA-GLYCERYL ETHERS FROM MARINE OILS

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No Drawing. Filed Aug. 31, 1964, Ser. No. 393,413

6 Claims. (Cl. 260-615)

This invention relates to a process for isolating alpha glyceryl ethers from marine oil sources.

Certain marine oils such as the liver oils and the whole body oils of Elasmobranchs, such as dogfish, *Squalus suckleyi* and of the ratfish, *Hydrolagus colliei* or *Chimaera monstrosa*, are known to be rich sources of substances which belong to the general group of the alpha glyceryl ethers. These ethers are also commonly called alkoxyglycerols and alkoxypropandiols. They have the general formula:



where R is a higher straight chain alkyl or alkenyl group. In marine oils the most commonly occurring glyceryl ether is that in which R is an oleyl group. This substance is commonly called selachyl alcohol, although the term alcohol is a misnomer. It is a liquid at room temperature. There is a fraction also of an ether where R is the palmitoleyl group and which assembles the selachyl alcohol. The natural sources also contain a fraction where R is palmityl. This material, called chimyl alcohol is a solid at room temperature when isolated.

These substances do not occur free in marine oils but invariably as ester combinations with higher fatty acids. These esters are similar in physical properties to the ordinary triglycerides which contain the same fatty acids combined with glycerine.

We have discovered a process whereby the alpha glyceryl ethers may be isolated from their marine oil sources in an acceptable state of purity and suitable for medicinal, edible and industrial uses. As well, the process separates to a sufficient degree the liquid and solid compounds of the natural ether mixtures so that the two forms may be used for such uses as is indicated by their physical, chemical and biological characteristics.

According to our invention the marine oil is first subjected to a process as described in our co-pending application Ser. No. 390,180, filed August 17, 1964, entitled, "A Process for the Preparation and Concentration of Free Hydroxylic Substances from Marine Oils," now abandoned. Thus, the oil is alcoholysed with a lower aliphatic alcohol, the alcoholysis product is dissolved in a non-polar solvent, the solution of alcoholysis product in nonpolar solvent is contacted with a polar solvent which is substantially immiscible with the non-polar solvent so as to form two phases and an extract containing free hydroxylic alpha glyceryl ethers is recovered from the polar solvent phases. This produces an extract which contains alpha glyceryl ethers in methyl esters. To isolate the alpha glyceryl ethers the extract is treated with caustic alkali to convert the methyl esters into soaps after which the alpha glyceryl ethers are extracted from the soap by solvent extraction. An excess of caustic alkali is preferably used to ensure that the methyl esters are completely converted into soaps.

Our raw materials are preferably the liver oils of the dogfish and the ratfish but obviously any other oils of similar chemical constitution may be used. Dogfish and rat-

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fish lever oils can provide from 5 to about 40% of their weight as the free glyceryl ethers. The liver oils are suitably those prepared by the "alkali" reduction method whereby the livers are cooked with steam after the addition of from 2 to 5% caustic alkali until the oil floats freely to the top. This method assures that the resultant oil will be low in free fatty acid as is preferred by our process. The oils should be of good quality and free from objectionable odor.

The alcoholysis of the oil is preferably carried out with the aid of an alkaline catalyst and under such conditions and with a sufficient excess of reagent alcohol as to ensure that the natural forms of the glyceryl ethers are completely freed from their ester combination with fatty acids. Suitable lower aliphatic alcohols for the alcoholysis include methanol, ethanol and isopropanol, methanol being preferred.

The alcoholysis mixture is introduced into a two-phase liquid-liquid extraction system consisting of a polar and non-polar solvent which are sufficiently immiscible and where the non-polar phase may be a volatile hydrocarbon or a non-volatile edible glyceride oil. A suitable glyceride oil is alkali-refined herring or dogfish liver oil. The polar phase is suitably methanol with from 5 to 10% water content. The alcoholysis mixture may be dissolved in the non-polar phase in suitable concentration so that the glyceryl ethers may be preferentially extracted by the polar phase. The extract, which consists of a concentrate of glyceryl ethers in methyl esters, may also include other hydroxylic matter such as cholesterol and vitamin A.

The extract of glyceryl ethers is saponified and the ethers are separated from the soap by treatment with ethylene dichloride. This treatment is improved by the addition of small amounts of phosphates. Particularly useful phosphates are sodium dihydrogen phosphate, disodium hydrogen phosphate and sodium tripolyphosphate.

The vitamin A which is present in the marine oil sources of the glyceryl ethers can be moved either from the base oil by a process such as molecular distillation before beginning our process, or it can be removed after the extraction; chiefly in the alcohol form, by a suitable modification of the extraction procedure. This consists in the separation of the first fractions which contain the bulk of the vitamin A. The first contacts are suitably carried out in smaller volume than the later contacts. This portion of the extract may be used as a commercial source of vitamin A. The first extracts are made with about 2 to 3 volumes of ethylene dichloride to each volume of soap and extraction is continued with up to 6 volumes of the solvent for each contact. The extracts are distilled either as produced or after bulking, to recover and re-use the solvent. The ethers are thus secured as a semi-liquid material consisting of the liquid selachyl alcohol with smaller quantities of the liquid palmitoleyl ether and the solid chimyl alcohol. The product will also contain varying but small quantities of cholesterol, soaps, vitamin A, and traces of methyl esters. The first fractions are richer in the liquid glyceryl ethers, the latter fractions are richer in the solid glyceryl ethers, and there is a regular progression from an almost completely liquid mixture at the commencement to an almost completely solid material toward the end of the series. It is possible, therefore, to commence the separation and purification procedure by selecting those fractions which provide the most suitable starting point for the type of material desired.

To effect further purification and separation, the crude material is dissolved in a suitable volatile solvent and the

solution cooled. There separates in succession, fractions which are rich in individuals of the component glyceryl ethers and the impurities. From acetone at 20% concentration, by settling or filtration, soaps come out at room temperature, chimyl alcohol at $-5^{\circ}\text{C}.$, selachyl at about $-20^{\circ}\text{C}.$, with highly unsaturated soaps and a small quantity of polyunsaturated ethers and some cholesterol remaining in the filtrate. The first crude chimyl alcohol fraction, containing much soap is filtered with the addition of a filter aid. After filtering in the warm to remove the filter aid the chimyl alcohol is then recrystallized out of a 10 to 30% solution in 95% ethanol by holding the solution at around -5° to $-10^{\circ}\text{C}.$

While it is convenient to carry out this process in a batch fashion, it is clear that a continuous extraction process may be set up following known procedures. However, in a continuous process, the alcoholysis product may be introduced either into the polar or non-polar solvent or into a mixture of both types of solvent.

It is secured as a white powder with a soft unctuous feel. The material is about 99% saturated glyceryl ethers, containing small quantities of the C18 and C14 homologues in addition to chimyl itself (C16). It is substantially free from unsaturates. A good quality of selachyl alcohol, suitable for some purposes, may be recovered directly out of the acetone solution of the crude ethers after removal of the chimyl alcohol by crystallization. A purer quality, lower in polyunsaturated products, is secured by crystallization out of acetone at $-20^{\circ}\text{C}.$ In either case the product should be deodorized by conventional steam-deodorization or by removing a small head-cut in a thin-film high vacuum still. The most satisfactory purification includes a final distillation of the selachyl alcohol itself at high vacuum from a thin film and over a short path. This gives a material with a bland odor, which is almost colorless and which is fluid at room temperature.

In identifying and analyzing the alpha-glyceryl ethers one of the most distinctive features of their structure is the presence of neighbouring or "vicinal" hydroxyl groups. These may be assayed by taking advantage of their ability to react readily with periodic acid. For purposes of comparison with data to be given in the examples, the theoretical figures for the four glyceryl ethers which are found in greatest abundance in the products obtained by our process are as follows:

Alkyl group	Iodine value (as percent iodine absorbed)	Vicinal hydroxyl groups (as mg. per gm. of substance)
Oleyl (selachyl alcohol).....	74.1	99.3
Palmitoleyl.....	80.7	108.1
Stearyl (batyl alcohol).....	Nil	98.7
Palmityl (chimyl alcohol).....	Nil	107.5

EXAMPLE 1

An example of the manner in which our process may be carried out is as follows:

(A) Preparation of the concentrate

In a suitable reaction vessel, a batch of 2431 pounds of filtered, alkali-refined dogfish liver oil, with an unsaponifiable content of 19.5%, was mixed with 720 pounds of anhydrous methanol. To this was added 4.89 pounds of anhydrous flake potassium hydroxide (0.2% of oil weight) and the mixture agitated at $60^{\circ}\text{C}.$ Within less than an hour the two separate phases had become one uniform phase. Heating was continued for four hours. After standing overnight the mixture was passed through a vacuum

evaporator at around $70^{\circ}\text{C}.$ The stripped methanolysis mixture was then allowed to stand for several hours when a black viscous phase of glycerine, alkali and soap separated out and was removed. This was found to weigh 80 pounds. The methyl ester phase had a residual methanol content of 1.4%. The weight of this phase was 2559 pounds. From the above batch was taken a quantity of 1228 pounds (135 gals.) for an extraction which was carried out as follows: A glyceride oil phase, consisting of 120 gals. of alkali-refined dogfish liver oil, was added and mixed with the methanolysis mixture. The mix was then contacted with 150 gals. of 90% aqueous methanol, the ratio of polar solvent to non-polar mix being 0.6. The mixture was heated to $50^{\circ}\text{C}.$, agitated gently for fifteen minutes, then allowed to settle for 2 hours. Phase separation was then complete. This procedure was then complete. This procedure was then repeated for a total of 6 contacts to give 425 pounds of concentrate which was found by analysis to contain 170 pounds of unsaponifiable matter which is 71% of the unsaponifiable content of the raw material. The concentration of unsaponifiable matter in the product was 40%.

(B) Preparation of the crude glyceryl ethers

From a similar preparation with an unsaponifiable content of 37.6% and a saponification value of 100 mg. of KOH per gram, a batch of 273 pounds was taken. To this was added, in a suitable container provided with agitation, 33.1 pounds of potassium hydroxide and 33 pounds of water. After allowing to react for 16 hours, the resulting soap was disintegrated in about an equal volume of ethylene dichloride and the resulting slurry transferred to a heated agitated extractor. Solvent was added to make a total addition of 300 gallons. The mass was heated to $130^{\circ}\text{F}.$ for 25 minutes then cooled to room temperature. 9 pounds of disodium phosphate, dissolved in 55 pounds of hot water, were then added and the whole mixture subjected to gentle agitation for a few minutes. Unsaponifiables were extracted from the soap curd by 7 successive extracts with ethylene dichloride, using 300 gals. of solvent for each contact. The mixed mass was heated to $140^{\circ}\text{F}.$ then cooled to $70^{\circ}\text{F}.$ before drawing off. The results for seven steps of the extraction procedure are tabulated as follows:

Extract number	Weight of unsaponifiable matter extracted in pounds	Percent of total content of unsaponifiable extracted
1.....	30.4	29.7
2.....	17.5	17.0
3 to 7 combined.....	37.9	36.9
1 to 7 combined.....	85.8	83.6

Fractions 1 and 2 were brown liquids with some solid material. Fraction 7 was solid and intermediate fractions show increasing proportions of solid as the extraction progressed. Later fractions were lighter in color. The crude glyceryl ether preparations thus secured were used in the further preparation of specific products according to commercial demand.

EXAMPLE 2

(A) Separation and purification of alpha-glyceryl ethers

From the crude preparations described in Example 1 there was selected for purification by acetone, a batch which consisted of fractions 3 to 7 combined. This material was low in content of soap, fatty acid and ester and had only a small fraction of the original vitamin A content. The 37.9 pounds of crude glyceryl ethers were dissolved with agitation in 22 gals. of warm acetone in a

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25 gal. tank. The solution was allowed to cool in a room held at minus 5° C. for 20 hours, at which time a precipitate had formed. This was separated by filtration through an 18" vacuum filter fitted with a porous stone filterplate. The filtrate was put through a natural circulation vacuum evaporator to recover solvent and isolate the liquid glyceryl ether fraction. The filter cake, which was a bulky and slightly sticky white mass, was dissolved in 10 gals. of acetone and held for two days at minus 5° C. The white crystals which deposited were filtered out and freed of solvent in a vacuum tray drier at a temperature of about 50° C. The yield and analysis of the products is tabulated below:

	Liquid Glyceryl Ethers	Solid Glyceryl Ethers
Weight, lbs.	26.8	47.7
Recovery (percent)	70.7	20.2
Melting point (° C.)		57
OH content as mg. per gram:		
Total	195.1	
Vicinal	295.5	
Iodine absorption value	373.2	
Vitamin A	None	
Soap (percent)	0.07	
Free fatty acid (percent)	0.27	
Volatiles (percent)	0.15	
Refractive Index, N_D^{20}	1.4687	

¹ By acetylation using the method of Karl Meier (Organic Analysis, vol. 1, edited by Mitchell et al., Interscience, page 16).

² By periodate consumption using the method of Kruty et al. (J.A.O.C.S., 31, 466-9, November 1954).

³ Wijs—½ hour.

⁴ A further 3.4 lbs. of liquid glyceryl ethers was recovered from the filtrate.

The substantial identity of the total and vicinal hydroxyl values in the above table indicates that the hydroxylated substances present are largely glyceryl ethers. The iodine value is in agreement with that which would be shown by a material which is largely selachyl alcohol. The above example illustrates the use of crude glyceryl ethers which were low in soap content through choice of an appropriate fraction in the extraction of the soap made from the alkyl esters. An example which illustrates the further purification of the solids and use of material containing an appreciable percentage of soap is as follows:

(B) Separation and purification of the alpha-glyceryl ethers

A batch of 26.3 kilograms of crude glyceryl ethers prepared as in Example 1 and with a soap content of 3.5% were dissolved in 200 liters of acetone at 48° C. The solution was allowed to cool by standing at room temperature for 16 hours and the solids, consisting of soap and filter aid, removed by filtration at 7° C. The filtrate was cooled to -13° C. and allowed to crystallize for about 48 hours. After addition of filter aid a cake of saturated glyceryl ethers was secured by filtration through a suction filter. The acetone filtrate was treated further to prepare a purified liquid glyceryl ether as described in Example 3. The filter cake with a gross weight of 5.78 kilograms, was mixed with 10 liters of ethanol with the application of heat. This mixture was filtered while warm to remove filter aid. The weight of the filtrate was 13.53 kilos. By analysis the solids content of the filtrate was 29.5%. By calculation, the weight of dissolved material was 3.99 kilograms. The filtrate was cooled in a vessel provided with coils through which cold water was passed and held at 5° C. for 16 hours. The crystals which deposited were removed by filtration at the same temperature. The wet crystals were dried in trays in an oven over steam coils at a 29 inch vacuum. The weight of the product was 1.39 kilo. The filtrate from this filtration was cooled to -5° C. and held at this temperature for 20 hours.

The crystal crop secured by filtration and drying had a weight of 0.65 kilos. The over-all recovery of purified

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saturated glyceryl ethers was 2.04 kilograms, which is 51% of the weight of lipid material taken. The vicinal hydroxyl value of the raw material was 100 mg. per gram and that of both crops of crystals was 101 mg. per gram. The soap content of both crystal crops was 1.8%. The melting point of Crop I was 53-54° C. and that of Crop II was about 49° C. The residue remaining dissolved in the filtrate after recovery (weight 1.87 kilograms) was liquid at room temperature. Further purification of the solid material by recrystallization from ethanol gave a large fraction with a melting point of 60.2° to 61.0° and a vicinal hydroxyl content of 105.5. Analysis by thin layer chromatography indicated that the non-glyceryl ether impurities, chiefly cholesterol, was less than 1%. Gas-liquid chromatography of the derived acetonides, using diethylene glycol succinate polyester as stationary phase, showed that the homologue composition was 80% chimyl alcohol with 17% batyl alcohol and 3% of the C14 alkyl glyceryl ether. This material may, therefore, be referred to as "chimyl alcohol."

EXAMPLE 3

Purification of liquid glyceryl ethers by low temperature crystallization from acetone

The acetone filtrate from Example 2(B) was concentrated in a vacuum evaporator until the glyceryl ether content was 22.7 grams per 100 ml. of solution. The solution was then cooled to -23° C. and crystals allowed to form for about 16 hours. The resulting slurry was filtered with suction at -18° C. Addition of a small amount of filter aid was necessary to maintain a rapid rate of filtration. The filter cake, containing about 50% acetone, melted at room temperature and was filtered to remove filter aid. The melted cake and the filtrate were stripped of solvent in a vacuum evaporator at about 28" vacuum and at temperature of 70-80° C. The weight recoveries and analysis of the two fractions was as follows:

Analyses of liquid glyceryl ethers

	Starting Material (analysis of a withdrawn sample)	Purified fraction (filtered at -18° C.)	Material in Filtrate (recovered from solvent), impure fraction
Weight, kilograms	15.4	9.3	6.06
Recovery, percent	100	60.6	39.4
Vicinal hydroxyl as mg. of OH per gram	93.7	96.0	90.6
Iodine Absorption Value	92.7	82.7	109.3
Vitamin A as International units per gram	8,500	3,440	16,300
Soap (Calculated as potassium oleate), percent	2.0	1.2	0.8
Fatty acid, percent	0.06	0.05	2.2

The purified fraction is suitable for further purification as shown in Example 4.

EXAMPLE 4

A liquid glyceryl ether material, prepared as in Example 3, is further purified as illustrated by the following example. 9300 grams of purified liquid glyceryl ethers was passed through a 2-inch diameter glass thin-film still with a 0.314 square-foot evaporating area. This was operated at a temperature of 120-159° C. and at a pressure of 100 to 130 microns. Steam was passed through the equipment counter current to the flow of material. The material was passed through at such a rate that approximately 3% was taken off in a head cut and discarded. The residue was then re-cycled to distil it at a temperature of 170-185° C. at 8 to 10 microns. A distillate of 7779 grams was secured as a desired product, the second residue being discarded.

The analytical data on the materials before and after this run are as follows:

Sample	Iodine Value ¹	Vicinal $\frac{3}{4}H$ ²	Refr. Index ³
Before distillation.....	82.7	96.0	-----
After distillation.....	79.4	98.4	1.4696

¹ Wijs $\frac{1}{2}$ hr.

² Krutzy's method.

³ n_D^{20} .

The material before deodorization and distillation had an acrid odor. After processing the odor was bland.

Analysis of the distillate using silica G (according to Stahl) see "Dunnschicht-Chromatographie," E. Stahl, Springer Verlag, Germany, 1962, indicates that non-glyceryl ether impurities, chiefly cholesterol, are about 2½%. Gas liquid chromatography on the derived acetone using diethylene glycol succinate polyester as stationary phase showed that the homologue composition was as follows:

Analysis of liquid glyceryl ether products

Chain length of alkyl group and number of double bonds:	Composition, percent
C14:0	2.0
C14:1	Nil
C16:0 (chimyl alcohol)	2.1
C16:1	16.4
C18:0 (butyl alcohol)	2.2
C18:1 (selachyl alcohol)	77.2
C20:0	No evidence

Total accounted for 99.9

EXAMPLE 5

Isolation of glyceryl ethers from alcoholated glyceride oil after removal of vitamin A by molecular distillation

Alkali-refined dogfish liver oil was processed in a wiped-surface, thin-film, high-vacuum distillation unit. All wetted surfaces were made of stainless steel. The processing unit consisted of two degassers with remote condensers followed by a 12" diameter still with a short path condenser. This unit operated as a continuous still with automatic temperature control on the two degassers and distillation unit. Variable speed pumps with indicating flowmeter were used for feeding the input materials and transferring the processor products. Vitamin A esters were removed from the dogfish liver oil by distillation with the still operating at temperatures between 550–580 deg. F. under a pressure of 14–20 microns as measured by a thermocouple vacuum gauge on the still vacuum line. In Run 1 the input rate was 12.85 kilos/hr. with the still at 550 deg. F. In Run 2 the still bottoms from Run 1 were recycled through the distillation units at 15.9 kilos/hr. with the still operating at 580 deg. F. The results of this process were as follows:

Fraction	Weight, kilos	Vitamin A potency of material as U.S.P. units per gram
First run, I:		
Feed (start).....	25.7	3,700
Degassing loss.....	0.07	12,000
First distillate.....	0.69	86,000
+First bottoms.....	25.0	1,000
Re-run, 2—Feed is bottoms of first run:		
Second distillate.....	2.2	13,000
Final bottoms (by difference).....	22.8	Trace

From these data it is calculated that the recovery of vitamin A was 62.4% in the first distillate and 30.1% in the second distillate, a total of 92.5%. The weight of feed which passed into the distillate was 11.5% of the feed weight. The unsaponifiable content of the feed material was assayed at 19.5% and that of the final bottoms was 17.4%. The glyceryl ether content of the unsaponifiable matter was estimated gravimetrically after separation by preparative scale thin-layer chromatography using 0.50 mm. layer of silica gel G (according to Stahl) and ethyl ether/petroleum ether/acetic acid 20/80/1 by volume, as eluting agent. This was found to be 84% for the feed material and 94% for the final bottoms. The rest of the unsaponifiable matter in both cases was almost entirely cholesterol. The glyceryl ether content calculated as percentage of the whole material remained unchanged at 16.4% for both the raw feed and the final bottoms. Since there is no change in glyceryl ether content of the bottoms resulting from the high-vacuum processing of the dogfish liver oil, it is clear that this material may be used as a raw material as in Example 1, without further modification of the process.

EXAMPLE 6

The separation of vitamin A from the glyceryl ethers by making use of the higher extractability of the vitamin A by ethylene dichloride from the solid saponification product of concentrate isolated from the methanolysis product is illustrated by the following example.

A quantity of dogfish liver was subjected to methanolysis in the presence of alkaline catalysts, dissolved in a glyceride oil and extracted with methanol as described in Example 1. There was obtained 545 pounds of concentrate which was found to have a saponification value of 103 mg. of potassium hydroxide per gram and a content of 32.9% glyceryl ethers. This was then treated with 92 pounds (30% excess) of 89% potassium hydroxide, 18 pounds of disodium hydrogen phosphate and 70 pounds of water. After completion of the reaction the solid mass was broken up and extracted with increasing volumes of ethylene dichloride with the results shown in the following table:

Extract No.	Gallons of Solvent used	Weight of Extract (kilograms)	Weight of glyceryl ethers* (kilograms)	Vitamin A potency of extract Int. Units/gram	Units of Vitamin A extracted per contact million units
1.....	130	4.45	2.96	58,100	358
2.....	130	6.93	5.90	28,200	195
3.....	130	3.76	3.38	19,700	74
4.....	130	4.69	4.36	10,670	50
Total 1-4.....	520	19.83	16.60	-----	577
5.....	260	4.00	3.78	7,260	29
6.....	260	9.53	9.02	2,520	24
7.....	260	6.87	6.52	Negligible	Negligible
8.....	260	7.02	6.07	Negligible	Negligible
9.....	350	7.46	7.09	Negligible	Negligible
10.....	350	2.27	3.20	Negligible	Negligible
11.....	350	4.01	3.80	Negligible	Negligible
Total 5-11.....	2,090	42.26	40.08	-----	53
Total 1-11.....	2,610	62.09	56.68	-----	630

*As determined by analysis of each fraction.

The total weight of glyceryl ethers present is 81.3 kilograms. The total quantity extracted was 56.6 kilograms or 69.6% of the amount present. The weight extracted in the first 4 contacts is 16.6 kilograms or 20.4% of that present. The fraction of vitamin A extracted in the first 4 contacts is 91.6% of that present.

Fractions 5 to 11 were combined and treated to recover purified glyceryl ethers as in Examples 2 and 3.

EXAMPLE 7

Conversion of ratfish liver oil to isopropyl esters and extraction of glyceryl ethers by aqueous ethanol from glyceride system; sodium isopropylate as alcoholysis catalyst

The alkali-refined ratfish liver oil taken as raw material had a glyceryl ether content of 25.5% and a total unsaponifiable content of 29.8%. To 400 grams of this oil was added 100 ml. of anhydrous isopropanol in a suitable glass reaction vessel. At the same time a solution of sodium isopropylate was prepared separately by dissolving 1.2 grams of freshly cut sodium in 60 grams of isopro-

same assay showed the complete disappearance of glyceryl ether diesters and glyceryl triesters.

A further analysis by thin-layer chromatography using silica gel H (according to Stahl) and a system of chloroform/methanol/acetic acid in the ratios of 96/2/2 by volume, as eluting solvent showed the presence of about 6% of an intermediate reaction product, possibly glyceryl ether monoester.

To effect solvent extraction, 40.16 grams of the isopropyl ester product was dissolved in 80 grams of alkali-refined herring oil. An equal volume (134 ml.) of 90% aqueous ethanol containing (10% volume of water) was added and the two phases gently mixed together for about 1 minute. Prior to mixing, both oil and ethanol phases had been heated to 60 deg. C. The alcohol extract was removed and a second contact with 134 ml. of 90% ethanol was made at the same temperature. Before recovery of the extracts the ethanol phases were allowed to settle for 24 hours at room temperature whereby a further small quantity of glyceride-ester phase, separated from each. Analysis gave the following results:

	Phase Volumes in ml.		Weight of extract recovered from ethanol phase (grams)	Unsap. content of extract, percent	Glyceryl Ether		
	Oil	90% ethanol			Percent of Unsap.	Percent of extract	Calculated weight in extract, g.
First extract.....	136	134	10.5	53.6	85	46.6	4.77
Second extract....	125	146	5.6	45.3	85	38.5	2.17

panol, warming gently with agitation for about a half hour until the reaction was complete. The resulting solution was added to the other flask, the contents heated to 60 deg. C. and agitated for 2 hours under reflux in a slow current of dry nitrogen at this temperature. The reaction mixture formed a dark colored viscous two-phase system on first mixing. It became a single phase and more mobile in a few minutes, with lessening of the dark color. There was no evidence of separation and settling of a separate glycerine phase. The catalyst was inactivated and dissolved glycerine was removed by washing the isopropyl ester reaction mixture several times with approximately equal volumes of warm water (60 deg. C.) containing 10% sodium chloride. The small amount of emulsion remaining at the interface between the water and isopropyl esters was broken by adding sufficient isopropanol to give the water phase about a 15% alcohol content. After removing the final water wash, the ester phase was freed of readily volatile matter by heating under a reduced pressure (25 mm. of mercury) with nitrogen sweep at 70 deg. C.

The total weight of ester reaction product recovered was 426.6 grams with the following analysis:

	Percent
Volatiles	0.21
Content of unsaponifiable matter in ester	26.8
Glyceryl ether content of unsaponifiable matter	85.5
Content of glyceryl ether in ester	22.8
Soap content (calculated as sodium oleate)	4.0

The analysis of glyceryl ether content was made by preparative thin layer chromatography (following Stahl) using silica gel G with eluting solvent; petroleum ether/ethyl ether/acetic acid in the ratios of 90/10/1. The

A concentrate with a glyceryl ether content of 43.1% was made by combining the two extracts to give 16.1 grams of material with a recovery of 75.5% (6.94 grams) of the glyceryl ether present in the ratfish liver oil (9.20 grams in the quantity taken). The soap content of the first extract was 9.1% and of the second extract was 2.7% (as sodium oleate). The glyceryl ether content of the unsaponifiable matter was estimated gravimetrically after separation by preparative-scale, thin layer chromatography using 0.50 mm. layer of silica gel G (according to Stahl), 13% binder and an eluting solvent made of ethyl ether/petroleum ether/acetic acid in the ratios of 20/80/1 by volume. Recovery of crude glyceryl ethers from this concentrate was carried out as follows. To a 4.28 gram-sample of the combined extracts 0.59 grams of potassium hydroxide was added as a 50% solution in water. The mixture solidified after 7 minutes. The mixture was held at 40 deg. C. for a further 16 hours to complete saponification. The resultant solid soap was disintegrated in 8 ml. of ethylene dichloride and the mixture heated to 60 deg. C. To the mixture was added a solution of 0.107 gram of disodium phosphate in 0.65 ml. of water. The solution was cooled to room temperature when it was found necessary to add an additional 1.0 ml. of water to improve the phase separation between the solvent and soap. The extraction was repeated four times with 6.0 ml. volumes of ethylene dichloride, then a further four times with 24 ml. of ethylene dichloride. Each contact involved heating to 60 deg. C. and cooling to room temperature before removing the solvent extract phase. Phase separation was complete in about 15 minutes. The effectiveness of the extraction process is shown by the following data.

Extract Numbers	Weight of material extracted (solvent free), grams	Unsap. content of extracted material, percent	Glyceryl Ether		
			Content in unsap. fraction of extracts, percent	Weight in each extract, grams	Content in the extracted material, percent
1-4 combined.....	0.70	84.3	85.5	0.505	72
5-8 combined.....	1.00	97.9	82.9	0.812	81

The 4.28 gram weight of glyceryl ether concentrate (43.1%) contained 1.85 grams of glyceryl ethers. The recovery of glyceryl ethers from this as crude glyceryl ethers is 1.317 grams or 71% of theoretical.

What we claim as our invention is:

1. A process for extracting alpha glyceryl ethers from a marine oil source which comprises alcoholysing a marine oil low in free fatty acids with a lower alkanol containing from 1 to 3 carbon atoms, in the presence of an alkaline catalyst, until the alcoholysis is substantially complete, dissolving the alcoholysis product in a polar solvent selected from the group consisting of methanol, ethanol and aqueous solutions thereof containing up to 10% water by volume, contacting the resulting solution with an immiscible solvent selected from the group consisting of herring oil, dogfish liver oil and hexane separating the resulting phases and recovering an enriched extract containing mixed alpha glyceryl ethers from the polar solvent phase.

2. A process according to claim 1, wherein said extract is treated with alkali to convert fatty acid esters into soap and the mixed glyceryl ethers extracted therefrom with ethylene dichloride.

3. A process according to claim 2, wherein the mixed glyceryl ethers are recovered from the ethylene dichloride by distillation.

4. A process according to claim 3, wherein the mixed glyceryl ethers recovered from the ethylene dichloride extract are dissolved in acetone and cooled until soap and chimyl alcohol crystallize out and the bulk, of the glyceryl ethers, predominantly selachyl alcohol which is liquid at room temperature remains in the filtrate and is recovered by distillation of the acetone.

5. A process according to claim 4, wherein the selachyl alcohol present in the acetone solution, after separation of the chimyl alcohol phase, is further purified by lowering the temperature causing the alcohol to deposit as a solid.

6. A process according to claim 5, wherein the selachyl alcohol is further purified by high-vacuum thin-film distillation.

References Cited

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