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ESTERS FROM SPERM OIL

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This invention relates to esters from sperm oil.

Sperm oil obtained from the blubber and the head cavities of the sperm whale contains as the principal component thereof about two thirds of esters of unsaturated fatty acids with unsaturated fatty alcohols and about one third of glycerides of the said unsaturated fatty acids. As unsaturated fatty acid, preferably oleic acid, as unsaturated fatty alcohol, oleic alcohol is present. Besides this, sperm oil contains a smaller part of cetyl alcohol, a saturated alcohol, in form of an ester. The fatty alcohol esters of unsaturated fatty acids constitute valuable raw materials for the production of cosmetic and pharmaceutical creams and ointments. They have been hitherto obtained by the esterification of the appropriate fatty acids and fatty alcohols as for example derived from sperm oil by alkali splitting or sodium reduction, constituting a labor, time and energy consuming procedure.

One object of the invention comprises among others the obtaining of substantially neutral unsaturated fatty alcohol esters from sperm oil in a much more simple and direct manner than hitherto practiced.

It was found in accordance with the invention that it is possible to subject a sperm oil to an ester splitting reaction under conditions at which the glycerides contained in the sperm oil are split while the non-glyceride esters remain substantially unaffected by the splitting reaction. In accordance with the invention this desideratum is accomplished by heating the sperm oil in the presence of water at a temperature sufficient to split the glycerides in said sperm oil and insufficient to appreciably split non-glyceride esters in said sperm oil. It is then only necessary to remove the components of the split glyceride and recover the substantially neutral fatty alcohol ester of unsaturated fatty acids.

The glyceride splitting reaction in accordance with the invention may be carried out by way of batch process or in a continuous operation including one by way of counter-current flow of reactants. In certain cases it may be of advantage to carry out the glyceride splitting reaction in accordance with the invention in presence of organic solvents, as gasoline-fractions or lower aliphatic alcohols, as well as in the presence of materials conventionally known and used as fat splitting agents such as metal oxides, metal soaps

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or materials containing sulfonic acid or sulfuric acid ester groups.

The process in accordance with the invention is carried out at a temperature of about 100 to 270° C. When the reaction is performed at temperatures of 100–200° C., the above mentioned splitting agents may be added in catalytic amounts to enlarge the velocity of the reaction. The more the operating temperature rises to the upper limit of 270° C., the more the splitting reaction begins to extend to appreciable amounts of the fatty alcohol fatty acid esters. Within certain limits this ester splitting is not objectionable provided it does not affect too large a portion of the esters which are desired to be preserved in accordance with the invention.

The amount of water present should be of course in all cases sufficient to yield the required OH groups and hydrogen required for the splitting of the amount of glycerides present in the sperm oil product treated in accordance with the invention. It is preferred to have an excess of water available for the practice of the invention and in amount to permit the formation of an aqueous layer containing dissolved glycerine and an oily layer comprising the desired ester together with the split-off fatty acid component of the glyceride and, as the case may be, relatively small amounts of fatty alcohols as might have been produced by an incidental splitting of relatively minor amounts of the ester in the treatment of the sperm oil in accordance with the invention when applying, for example, relatively high temperatures.

The time of contact of the reagents used in the practice of the invention would be sufficient to obtain a substantially complete splitting of the glycerides present in the sperm oil product subjected to the treatment. This may be either determined by analysis of periodically withdrawn samples or may be predetermined as to any given set of reaction conditions and thereafter applied as so determined to the practice of the novel process involving the same or similar conditions. The pressure to be used in the practice of the invention is a function of the temperature and of the vapor characteristics of the liquids being present. If low-boiling solvents are present, or if temperatures above 100° C. are used, the pressure is above atmospheric pressure. If the process is carried out in a closed pressure receptacle as for example

an autoclave or similar vessel this pressure is a direct function of the temperature to which the given system of reactants is subjected. Where a type of structure used in the practice of the invention is one which is not necessarily of the pressure closed or autoclave or similar type, the pressure to be used in the practice of the invention should be one equivalent to an assumed autoclave pressure for the given materials at the given temperature and where therefore reference is made herein to a pressure in excess of atmospheric or an expression of similar import is used, there is meant thereby a pressure calculated on this basis.

As above stated, when proceeding in accordance with the invention an aqueous glycerine containing layer and an oily ester-fatty acid layer are obtained. The former layer may be worked up in the usual manner for the recovery of glycerine therefrom. The latter layer is treated for the removal of fatty acids therefrom which may be accomplished for example by neutralization with aqueous alkalis or by way of joint removal with any fatty alcohols that may be present by way of extraction with suitable solvents. Satisfactory solvents for this purpose are, for instance, the lower aliphatic alcohols such as methanol. It is also possible to remove the free acids by distillation and thereby obtain a substantially neutral ester. This distillation has the advantage that a re-esterification is obtained of such fatty alcohols that may have been produced by the incidental ester splitting above referred to.

Within the referred embodiment of the invention, however, the removal of free fatty acid acidity is accomplished by heating the oily component or layer obtained in the glycerine splitting reaction in accordance with the invention with appropriate amounts of fatty alcohols and preferably of the type desired as ester component for the ultimate product, to thereby esterify the free fatty acids present in the oily ester layer. For this purpose there may be used also fatty alcohols of other sources, for instance pure oleic alcohol, cetyl alcohol, lauryl alcohol and others.

The practically neutral esters obtained in accordance with the invention are suitable for the production of ointments, creams or other cosmetic or pharmaceutical preparations. The fatty acids or fatty alcohols which may be obtained as by-products as well as the esters themselves may be also used in conventional manner for the production of saturated or unsaturated fatty alcohols or other products and may be thus, for example, subjected for this purpose to treatment with nascent or catalytically activated hydrogen, solvents, adsorbents or to distillation under reduced pressures.

In the hitherto used methods of treating sperm oil such as by reduction with the aid of sodium or by hydrogenation under high pressure in the presence of catalysts, the glycerine was lost. When splitting with alkalis the glycerine was obtained in such diluted conditions that its recovery was uneconomical. It was furthermore necessary to subject the resulting soaps for their further treatment to a splitting reaction such as by the use of acids. These disadvantages are eliminated in the practice of the invention. The reaction product obtained in the practice of our invention, i. e. fatty acids, glycerine, the alcohol esters and as the case may be fatty alcohols, may be directly worked up after separation without any further treatment to yield the desired end product hereby the kind and type of the latter determines the method to be used.

The following examples are furnished by way of illustration but not of limitation.

Example 1

10,000 kg. of sperm oil (acid number 0.5 saponification number 138) and 5,000 kg. of water are heated in an autoclave to 210° C. for seven hours. The autoclave is provided with a stirring arrangement. The reaction mixture upon cooling to 90° C. is separated into an oil component and an aqueous component. The latter contains 5.8% by weight of glycerine which corresponds to about 2.9% by weight calculated on the basis of the sperm oil used.

The oil component freed from the glycerine (acid number 68, saponification number 138) contains about 32.8% by weight of free fatty acids. The oil is then extracted in an extraction column filled with Raschig rings with three times the amount by volume of 95% methanol at room temperature in counter-current flow. After removal of the methanol from the extract and the extraction residue, 36.5% by weight of free fatty acids (acid number 186; saponification number 192) and 62.3% by weight of a practically acid-free oil (acid number 2.5; saponification number 120; iodine number 73; unsaponificable matter 48.5%) both calculated by weight of originally used sperm oil, are obtained.

The free fatty acids obtained as above set forth may be utilized by converting the same to soaps or washing agents. The neutral oil obtained in the above procedure is principally composed of the esters of unsaturated fatty acids with cetyl- and oleyl alcohols. If desired or necessary the same may be subjected to a treatment with a bleaching earth such as by filtration or other conventional manner to be thereafter used in pharmacy or cosmetics as, for example, in the production of readily resorbable ointments.

Example 2

8,200 kg. of sperm oil as it is obtained from the blubber and the head cavities of the sperm whale and having an acid number of 1.3, a saponification number of 139, an iodine number of 85, containing 34% by weight of unasponifiable matter and 3.1% by weight of glycerine (corresponding to an approximate 30% content of triglycerides) are heated together with 3,200 kg. of water in pressure receptacles for eight hours with continuous stirring at a temperature of about 200° C. The glycerides are split into fatty acids and glycerine while the unsaturated fatty alcohol fatty acid esters remain substantially untouched. The reaction mixture is cooled to about 85° C. Whereupon 8,170 kg. of oil component are separated from 3,100 kg. of aqueous glycerine component containing about 8.4% by weight of glycerine. The aqueous glycerine is thereafter concentrated by evaporation and the residue is distilled in vacuo for the production of a glycerine conforming to pharmacopoeia standards resulting in about 213 kg. of pure glycerine. The substantially glycerine free oil component containing free fatty acids and fatty alcohol esters of unsaturated fatty acids has a saponification number of 139 and an acid number of 71. The oil component is thereafter subjected in vacuo at a pressure equivalent to 1 mm. Hg to fractionated distillation. The following three fractions of the given boiling ranges were obtained:

Fraction I.—32% by weight with a boiling range of 156–225° C.

Fraction II.—9.5% by weight of boiling range 225–240° C.

Fraction III.—58.5% by weight of boiling range 240–298° C.

Fraction I is practically completely composed of free fatty acids (acid number 190, saponification number 203). Fraction II is essentially composed of a mixture of free fatty acids and esters (acid number 21, saponification number 122.5). This fraction may be again subjected to the fractionated distillation with the next distillation charge. Fraction III constitutes a substantially colorless and practically odorless oily ester (acid number 2.1, saponification number 114.5) which may be used for the purpose herein indicated including those set forth in Example 1.

Example 3

1000 kg. of sperm oil (saponification number 140), 500 kg. of water and 10 kg. of zinc oxide are heated in an autoclave under agitating for seven hours to 195° C. whereby a pressure of about 16 atmospheres was formed. The reaction mixture is cooled to 95° C. and separated by a centrifugal separator into an oily and a water layer, containing 8.2% by weight of glycerine. There are obtained 988 kg. oil, containing 35% by weight free fatty acids, 350 kg. of oleyl alcohol are added to the oil, the mixture is heated slowly up to 200° C. while passing a stream of nitrogen through the mixture to remove the water, formed during the reaction. After 3 hours the esterification is complete and no more water is formed. 1295 kg. of ester are obtained. The ester is cooled to 0° C. whereby solid parts are formed. The solid parts are removed by passing the product through a filter press. The obtained oily liquid has a specific gravity of 0.870 g./cm.^{3} at 20° C., a viscosity of 3.8° Engler/20° C., a solidification point below +5° C., an iodine value of 85, an acid number below 1, a saponification number of 112, and a hydroxyl number of 15. The oil is very well suited for the manufacture of skin protecting preparations.

Example 4

100 kg. of a partially splitted sperm oil, obtained according to Example 1, containing 32.8% of free fatty acids, is mixed in an iron vessel, being equipped with an agitator, with 65 kg. of a 10% NaOH solution. After 30 minutes, 200 liters of a gasoline fraction and 20 liters of isobutyl alcohol are added to the emulsion of oil and soap solution. The agitating is continued for 30 minutes, then the mass is allowed to stand for one hour without agitating. The gasoline layer is separated from the layer of the soap solution and the latter washed with 100 liters of a fresh gasoline fraction. Then the soap solution is completely freed from the residual gasoline by careful heating. The excess of alkali in the solution is neutralized by adding oleic acid. By atomizing the solution in a stream of hot air, soap powder is produced.

The two gasoline fractions are given together and washed with warm water to remove the soap. Gasoline and isobutyl alcohol are removed by steam distillation. The residual oil is refined by treatment with 3% of bleaching earth. There are obtained 64.8 kg. of an acid-free, nearly colorless ester, being free from glycerol. This ester is suited for the manufacture of medical or cosmetic creams.

Example 5

In an open vessel, consisting of pitchpine wood, 5000 kg. of sperm oil (saponification number 142, iodine number 75) and 1000 liters of condensed water are heated to boiling by introducing steam. A solution of 25 kg. of a Twitchell-splitting-catalyst, an arylsulfonic acid, in 50 liters of water is added and the mixture kept in a weak boiling for 13 hours. Then, the reaction product is allowed to stand during 2 hours without boiling, whereby the reaction mass separates into a water layer, containing glycerine and an oily layer. The glycerine-water solution is separated from the oil layer. From the water, containing 5.6% glycerine, the glycerine is obtained in known manner by evaporating the solution and distilling the raw glycerine under reduced pressure. The oil, containing 29.6% of free fatty acids is separated by extraction with methanol into free fatty acids and neutral oil. The oil has a saponification number of 123 and an iodine number of 78 and is a glycerine-free ester of fatty acids with fatty alcohols. It is suitable for the manufacture of cosmetic and pharmaceutical preparations and is extraordinary resistant against ageing and developing rancidity.

We claim:

1. Method for the production of fatty alcohol esters of unsaturated fatty acid from sperm oil having an acid value below 5, which comprises heating such oil in the presence of water at a temperature sufficient to split the glycerides in said sperm oil and insufficient to appreciably split non-glyceride esters in said sperm oil, and recovering practically neutral fatty alcohol esters of unsaturated fatty acids from the reaction product.

2. Method for the production of fatty aclohol esters of unsaturated fatty acid from sperm oil having an acid value below 5, which comprises heating such oil in the presence of water at a temperature of about 100 to 270° C. to thereby split the glyceride in said sperm oil and recovering practically neutral fatty alcohol esters of unsaturate fatty acids from the reaction product.

3. Method in accordance with claim 2 in which said heating is carried out at atmospheric pressure and a temperature of about 100° C.

4. Method in accordance with claim 2 in which said heating is carried out at above atmospheric pressure at a temperature of about 180–250° C.

5. Method for the production of fatty alcohol esters of unsaturated fatty acid from sperm oil having an acid value below 5, which comprises heating such oil in the presence of water and at a temperature of about 100 to 270° C. to thereby split the glyceride in said sperm oil, separating the oil component of the reaction product from the aqueous, glycerine containing component thereof and recovering practically neutral fatty alcohol esters of unsaturated fatty acids from said oily component.

6. Method in accordance with claim 5 in which said heating is carried out in the presence of at least one fat splitting agent.

7. Method in accordance with claim 6 in which the fat splitting agent is an glyceride splitting aryl sulfonic acid.

8. Method in accordance with claim 6 in which the fat splitting agent is zincoxide.

9. Method in accordance with claim 5 in which said oily component is treated for the removal therefrom of fatty acid acidity.

10. Method according to claim 5 in which said

heating is carried out at a temperature of about 100 to 270° C. and in which said oily component is extracted for the removal of the free fatty acid and of any free fatty alcohol therein, with a solvent for said alcohol and said acid.

11. Method according to claim 5 in which said heating is carried out at a temperature of about 100 to 270° C. and in which said oily component is subjected to distillation for the removal of free fatty acid therefrom.

12. Method according to claim 5 in which said heating is carried out at a temperature of about 100 to 270° C. and in which said oily component

is heated in the presence of a fatty alcohol to thereby esterify the free fatty acid contained therein.

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