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SEPARATION OF VINYL ESTERS OF LONG CHAIN FATTY ACIDS FROM THE CORRESPONDING FREE FATTY ACIDS

William S. Port, Edmund F. Jordan, Jr., and Daniel Swern, Philadelphia, Pa., assignors to the United States of America as represented by the Secretary of Agriculture

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The invention herein described, if patented in any country, may be manufactured and used by or for the Government of the United States of America for governmental purposes throughout the world without payment to us of any royalty thereon.

This invention relates to a method for the separation of vinyl esters of long chain fatty acids from mixtures of them and the corresponding free fatty acids, and has among its objects obtaining of the esters in satisfactory yields and substantially pure form by a simple procedure.

In some processes for the production of vinyl esters of long chain fatty acids, such as vinyl palmitate or vinyl stearate, distillation of the reaction products yields a vinyl ester substantially free of impurities other than the corresponding free fatty acids, and this invention is particularly concerned with the purification of the vinyl esters in such production.

In general, according to the invention, the mixture of the vinyl ester and fatty acid is dissolved in a suitable inert solvent, preferably acetone, this solvent being one in which an inorganic salt of the acid is insoluble. A compound which reacts with the acid to form the insoluble salt, preferably sodium hydroxide, is added, preferably in concentrated aqueous solution and in an amount at least equivalent to, and not exceeding by more than about 5 percent, the free fatty acid present in the mixture, as determined by the acid number of the mixture used. The salt which is thus formed and precipitated is separated from the solution as by filtration, the vinyl ester being recovered from the remaining solution as by evaporation of the solvent, or preferably by cooling to cause separation of the vinyl ester therefrom.

The method is applicable to the purification of vinyl esters produced from purified fatty acids such as substantially pure palmitic or stearic acid, and also from commercial mixtures of long chain fatty acids such as double or triple-pressed stearic acid, and the 50 to 97% grades of long chain fatty acids. It can also be advantageously utilized in the purification of vinyl esters produced from mixtures of fatty acids obtained from substantially completely hydrogenated fish oils, hydrogenated vegetable oils, such as castor oil, corn, cottonseed, hempseed, linseed, olive, peanut, perilla, poppyseed, rapeseed, soybean or tung oil; hydrogenated tallow and lard, and other hydrogenated fats and oils containing a high percentage of saturated, aliphatic monocarboxylic acids having 16, 18 or more carbon atoms, as well as

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fatty acids from unhydrogenated oils low in unsaturated acids.

Although acetone is the preferred solvent and aqueous sodium hydroxide the preferred compound for reaction with the free fatty acid, other inert solvents such as methyl ethyl ketone or methyl isobutyl ketone may be used. Compounds yielding calcium, barium, magnesium or lead cations can also be effectively utilized in place of the sodium hydroxide, and the hydroxide of these cations is but one of the many anions that may be used, others being, for example, oxides, carbonates and bicarbonates. Nor is the method restricted to the use of an aqueous solution of the salt forming ionic compound. Thus, sodium ethoxide in ethanol, or dry calcium oxide or carbonate may be used.

The following examples are given as illustrative embodiments of a manner in which the invention may be practiced.

Example I

The mixture of vinyl palmitate and palmitic acid was obtained by the following procedure:

Mercuric acetate, 20.5 g. was mixed with 2060 g. (24 moles) of freshly distilled vinyl acetate kept under an atmosphere of nitrogen. After a portion of the salt had dissolved, 1.8 ml. of 100% sulfuric acid was added dropwise and with agitation. This caused complete solution of the mercuric acetate and resulted in the formation of a straw-colored solution. Palmitic acid, 1026 g. (4 moles), was added and the mixture was heated until the palmitic acid was dissolved, after which the resulting solution was refluxed for 3 hours in a nitrogen atmosphere. The sulfuric acid was then neutralized by the addition of 9.1 g. of finely ground sodium acetate trihydrate. The excess vinyl acetate was recovered by distillation at atmospheric pressure, and the acetic acid was then distilled off by slowly lowering the pressure to 25 mm. and raising the pot temperature to 125° C.

The distillation residue was flash-distilled (boiling point 145° C. at 0.7 mm.) in an alembic flask modified so as to permit continuous or intermittent introduction of the distilland during the process in order to avoid excessive heating of the vinyl ester. The alembic flask was immersed in an oil bath maintained at 215°–225° C., and addition of the distilland was regulated so that the temperature within the alembic flask was 205°–210° C. The yield of vinyl palmitate and palimitic acid so obtained, having an acid number of 15.5, was 874 g., or 78 percent.

Separation of the vinyl palmitate from the mixture in accordance with the present invention was accomplished as follows:

830 g. of the vinyl palmitate-palmitic acid mixture was dissolved in 2490 ml. of acetone at room temperature (about 25° C.), and the resulting solution was treated with 42.42 ml. of 5.69 N sodium hydroxide solution (a 5% excess over the free fatty acid), added dropwise with vigorous stirring. After one hour, the precipitated soap was filtered off and washed with 830 ml. of acetone on the filter.

The combined filtrate and washings were cooled to −20° C. and allowed to stand overnight at this temperature. The vinyl palmitate precipitate thus obtained was filtered off, washed with 1000 ml. of acetone at −20° C., and dried. The yield was 689 g. (63% based on the palmitic acid used, or 88% based on the crude ester obtained by flash distillation). The product melted at 26.9°–27.2° C., and had an acid number of approximately 1.

Example II

The procedure of the foregoing example was repeated using 1138 g. of stearic acid in place of the palmitic acid. The reaction product was flash distilled at 192°–196° C., at 0.8 mm. at a bath temperature of 240°–255° C. The yield of vinyl stearate and stearic acid so obtained, having an acid number of 24.7, was 617 g. or 49.7%.

599 g. of this vinyl stearate-stearic acid mixture was dissolved in 1800 cc. acetone and treated with 47.70 ml. of 5.68 N sodium hydroxide solution, added dropwise with vigorous stirring at room temperature. After one hour's stirring, the soap which had separated was filtered off and washed with 600 cc. acetone. The combined filtrate and washings were cooled to 0° C. and allowed to stand overnight at this temperature.

The yield of vinyl stearate thus obtained having an acid number of approximately 1, was 326 g. corresponding to 28 percent based on the stearic acid used or 62 percent based on the crude ester obtained by flash distillation.

We claim:

1. The process of separating a vinyl ester of a long chain fatty acid from a mixture containing the ester and the corresponding free acid, comprising forming a solution of the mixture in acetone, adding an amount of sodium hydroxide at least equivalent to, and not exceeding by more than about 5 per cent, the free fatty acid present in the mixture, separating the resultant precipitate of the sodium salt of the acid, and recovering the vinyl ester from the solution.

2. The process of claim 1, wherein the ester is selected from the group consisting of vinyl palmitate and vinyl stearate.

3. The process of claim 2, wherein the ester is recovered by cooling the solution to a temperature to cause separation of the ester from the solution.

4. The process of claim 3, wherein the cooling is at about −20° C.

5. The process of separating a vinyl ester of a long chain fatty acid from a mixture of the ester and the corresponding free acid, comprising forming a solution of the mixture in an inert solvent in which an inorganic salt of the acid is insoluble, adding a compound which reacts with the acid to form the insoluble inorganic salt of the acid, separating the precipitated salt, and recovering the vinyl ester from the remaining solution.

WILLIAM S. PORT.
EDMUND F. JORDAN, JR.
DANIEL SWERN.

No references cited.