

UNITED STATES PATENT OFFICE

2,468,725

PREPARATION OF LONG-CHAIN ESTERS OF
BETA-THIODIPROPIONIC ACID

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No Drawing. Application April 8, 1947,
Serial No. 740,268

5 Claims. (Cl. 260—481)

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This invention relates to a process for the preparation of the higher molecular weight alcohol esters of thiodicarboxylic acids and more particularly to the preparation of such esters of thiodipropionic acid.

The 3-substituted mercaptoaliphatic organic acid esters and more particularly the mercaptopropionic acid esters have been found to be especially effective anti-rancidity agents for use in oils, fats, waxes and the like, as is described in the D. K. O'Leary and in the Gribbins et al. Patents 2,397,960 and 2,397,976 of April 9, 1946. These esters have likewise been found suitable for use in soap for preventing rancidity as is described in the Gribbins Patent 2,416,052 of February 18, 1947. These uses demand esters of high quality that are not only colorless, for off-color is highly undesirable in soaps, food products and the like, but also odorless, for foreign odors are not tolerated in foods or in the better grades of soap and soap products.

An object of the present invention is to provide a process for the preparation of esters of 3-substituted mercaptoaliphatic organic acid esters which are substantially colorless and odorless. A further object is to provide a process for preparing the higher aliphatic alcohol esters of these 3-substituted mercaptopropionic acids and more particularly such esters of 3-substituted mercaptopropionic acid by the alcoholysis of the lower alkyl esters of 3-substituted mercaptopropionic acid, more particularly the methyl ester with higher aliphatic alcohols. Other objects and advantages of the invention will hereinafter appear.

The invention is directed to the preparation of substantially colorless and odorless higher aliphatic alcohol esters of a beta-thioether of an ester of propionic acid having the formula:



in which R is an alkyl group having at least 10 carbon atoms, such for example, as decyl, dodecyl, tetradecyl, cetyl, carnaubyl, ceryl, melissyl, tarchonyl and other straight and branch chain alkyl groups included within the limits of this group and more particularly, those containing from 10 to 24 carbon atoms and in which X is:

1. A hydrocarbon group such as e. g.: the alkyl groups: methyl, ethyl, propyl, butyl, lauryl, and the aryl groups: phenyl, naphthyl, benzyl; and such groups as cyclohexyl;

2. An oxygenated-hydrocarbon group such as e. g.: the alcohol groups: hydroxymethyl, hydroxyethyl, and hydroxybutyl; the ether groups;

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methoxymethyl, methoxyethyl, and ethoxyethyl; the acid groups and the R esters thereof: carboxymethyl, carboxyethyl, carboxypropyl and carboxybutyl; and the aldehyde groups such as aldehydeethyl;

3. A sulfur-hydrocarbon group such as e. g.: mercaptoethyl, mercaptopropyl, mercaptoethyl, mercaptoisobutyl, mercaptohexyl and ethiaethyl.

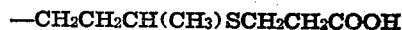
4. A sulfur- and oxygenated-hydrocarbon group such as e. g.: carboxyethiaethyl,



carboxyethiaethdithiaethyl,



carboxythiaisobutyl,



and carboxyethiapropyl,



and

5. A sulfur-, and nitrogen-hydrocarbon group such as e. g.: 3-benzothiazyl, which compounds are more specifically described in the Gribbins et al. patent supra.

In accord with the invention the substantially odorless and tasteless esters above described are prepared by gradually heating a mixture of the lower dialkyl esters of the acids with a higher alcohol until a homogeneous mixture is obtained, an acid catalyst is then added and the temperature raised rapidly to from 150 to 250° C. where it is maintained until substantially no more of the lower alcohol, which is formed by the interchange, distills over, the product is then cooled rapidly to 40 to 50° C. and a sufficient amount of water and caustic soda or alkali dissolved in water added to neutralize the acid catalyst used. Neutralization is carried out as accurately as possible in order not to contaminate the product. After filtering off the precipitated catalyst (a catalyst and neutralizer being selected such that a precipitate is obtained, such for example, as sulfuric acid and barium hydroxide or phosphoric acid and sodium hydroxide) the filtered ester is subjected to a deodorizing treatment by passing it counter-current to the flow of steam at a temperature between 150 and 225° C. and under a vacuum of less than about 40 millimeters, preferably below 20 millimeters.

The example which follows illustrates a preferred embodiment of the invention in which parts are by weight unless otherwise indicated.

Example.—Stoichiometric amounts of dimethyl thiodipropionate and a mixture of alcohols, prin-

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cipally lauryl alcohol obtained by the catalytic hydrogenation of fats and oils under elevated temperatures and pressures were charged to a reaction vessel and heated to a temperature of about 50° C. An 85% solution of phosphoric acid in water was added (1% acid based on the ester) and the temperature raised as rapidly as possible to 200° C. where it was maintained for approximately two hours. The reaction started at 150-160° C. (made evident by the evolution of methanol) and proceeded quite rapidly until about about 75% complete. At this point the pressure was reduced to about 200 millimeters of mercury absolute to facilitate complete methanol removal. When the reaction was completed (no more distillate coming off) the product was cooled rapidly to 40 to 50° C. and the proper amounts of water and sodium hydroxide dissolved in water added to neutralize the phosphoric acid catalyst to $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. The product was then cooled to room temperature and filtered.

The above product was further deodorized by subjecting it to a countercurrent steam scrubbing operation maintained at a temperature of approximately 190° C. (although temperatures between 150 and 300° C. may be used) wherein a liquid stream of the ester was continuously passed into the top of a reaction vessel and continuously withdrawn from the bottom, superheated steam passing through the vessel countercurrent to the flow of ester, the deodorization being conducted at a pressure below 100 mm. and preferably as in this example, between 15 and 20 mm. Hg absolute pressure. The product obtained in accord with this process was substantially odorless and colorless and wholly acceptable for comestible uses.

The other higher aliphatic alcohol esters of the other 3-substituted dicarboxylic acids may be similarly prepared to give products that are both odorless and tasteless by reacting these alcohols with the methyl esters of the acids and subsequently if necessary removing the final traces of odor by the countercurrent flow steam distillation process.

We claim:

1. A process for the preparation of a substantially odorless and tasteless monohydric alcohol, ester of beta-thiodipropionic acid the alcohol containing ten to twenty-four carbon atoms, which comprises heating methyl beta-thiodipropionate with a monohydric alcohol containing ten

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to twenty-four carbon atoms in the presence of an acid catalyst while withdrawing the methanol as formed, the reaction being conducted at a temperature below 250° C.

2. The process of claim 1 in which the product is deodorized by subjecting it to countercurrent scrubbing with steam, the scrubbing operation being conducted at a temperature between 150° C. to 225° C. and at a pressure below 100 mm. Hg absolute.

3. A process for the preparation of a substantially odorless and tasteless stearyl alcohol ester of beta-thiodipropionic acid, which comprises heating methyl beta-thiodipropionate with stearyl alcohol in the presence of an acid catalyst while withdrawing the methanol as formed, the reaction being conducted at a temperature below 250° C.

4. A process for the preparation of a substantially odorless and tasteless higher alcohol ester of beta-thiodipropionic acid, the higher alcohol consisting of a mixture of higher alcohols, predominately lauryl alcohol, obtained by the catalytic hydrogenation of fats and oils under elevated temperatures and pressures, which comprises heating methyl beta-thiodipropionate with the aforesaid higher alcohol in the presence of an acid catalyst while withdrawing the methanol as formed, the reaction being conducted at a temperature below 250° C.

5. A process for the preparation of a substantially odorless and tasteless monohydric alcohol ester of beta-thiodipropionic acid, the alcohol containing 10 to 24 carbon atoms, which comprises heating a lower dialkyl ester of beta-thiodipropionic acid with a monohydric alcohol containing 10 to 24 carbon atoms in the presence of an acid catalyst while withdrawing the lower boiling alcohol formed, the reaction being conducted at a temperature below 250° C.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,122,716	Graves	July 5, 1938
2,298,186	Woodhouse et al.	Oct. 6, 1942

Certificate of Correction

Patent No. 2,468,725.

May 3, 1949.

WILLIAM F. GRESHAM ET AL.

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 2, lines 4 and 5, for the word "aldehydroethyl" read *aldehydoethyl*;
line 16, for "carboxythiaisobutyl" read *carboxyethiaisobutyl*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 11th day of October, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.