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ALKYL ESTERS OF SULFONATED MONO-HYDROXY-BENZOIC ACIDS

James O. Harris, Knoxville, Tenn., assignor to Monsanto Chemical Company, a corporation of Delaware

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9 Claims. (Cl. 260—470)

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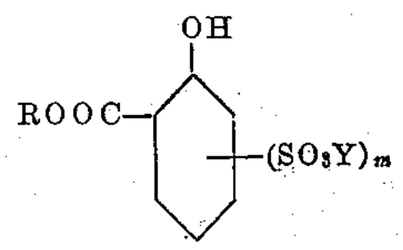
The present invention relates to alkyl esters of sulfonated monohydroxy-benzoic acids and to an improved process of preparing same.

The compounds contemplated by the present invention are represented by the following general formula:



in which R is an alkyl chain of not less than 6 and not more than 18 carbon atoms or mixtures thereof as derived from alcohol obtained by the hydrogenation of coconut oil, commercially known as Lorol; Y is hydrogen, an alkali metal, calcium, magnesium, barium or strontium and *m* is a whole number which may be one or a greater number, indicating that the compounds are mono or polysulfonated. These compounds have properties making them especially suitable for use as detergents, wetting agents, emulsifying agents and the like and they are characterized by a substantial absence of odor and taste.

Heretofore, alkyl esters of monocarboxylic aromatic sulfonic acids and salts thereof have been prepared by sulfonating monocarboxylic aromatic acids, esterifying the resulting sulfonated products and then neutralizing the esters thus formed by means of various alkaline compounds. This method of operation has proved to be quite successful in practically all cases except the corresponding derivatives of monohydroxy-benzoic acids.

For example, when sulfonation of ortho-monohydroxy-benzoic acid is carried out in the absence of a solvent, temperatures in excess of 150° C. must be employed, which render the reaction difficult to control with the result that considerable decomposition and side reactions take place. This process, therefore, results in low yields and also in the production of a crude product which presents a time-consuming and troublesome purification problem.

Ortho-monohydroxy-benzoic acid may be sulfonated at lower temperatures in an inert solvent, but the product invariably contains unreacted SO_3 which cannot be readily removed. This disadvantage and the high product costs involved render such a procedure commercially impractical.

Ortho-hydroxy-benzoic acid may also be

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treated with 2–5% oleum to yield sulfo-ortho-hydroxy benzoic acid, but the objection to this method is that, due to the extreme solubility of the acid in water, the product yield is inordinately low.

With regard to the step of esterifying sulfo-ortho-hydroxy benzoic acid, all attempts to carry out this reaction have resulted in low yields of a product containing relatively large amounts of unreacted materials which not only cause discoloration of the product but render it very difficult to dry.

For example, attempts have been made to react sulfo-ortho-hydroxy benzoic acid with "Lorol" under atmospheric pressure in the presence of catalysts such as sulfuric acid, phosphoric acid and gaseous HCl; under reduced pressure in the presence and absence of catalysts; in the presence of toluene to remove water from the reaction by azeotropic distillation; and in the presence of a mutual solvent for the reactants, but in all instances it was found that the neutral equivalent fell within the range of 220 to 265 (theory 386) indicating that the reaction was only partially complete. In addition, it was found that when the esterification proceeded no further than this, the salt of the acid could not be drum dried without discoloration.

I have found that by sulfonating the lower alkyl esters of hydroxy benzoic acids with sulfur trioxide in sufficient quantity to at least produce monosulfonation and then subjecting the sulfonated product to alcoholysis by means of an aliphatic alcohol having from 6 to 18 carbon atoms in the alkyl chain, the above disadvantages are substantially completely eliminated. For example, I have made the surprising discovery that by using sulfur trioxide as the sulfonating agent, the esters of hydroxy-benzoic acid such as salicylic acid and the corresponding meta and para-isomers thereof can be sulfonated in good yields and at a lower temperature than the free acids without materially affecting the ester group. Moreover, I have discovered that I can obtain the desired high molecular weight esters in excellent yields and without the formation of troublesome by-products and unreacted starting materials which are encountered in the esterification of the free sulfo-hydroxy benzoic acids.

For a more complete understanding of the present process, reference is made to the following examples which illustrate the preferred embodiments of the present invention.

Example I

156 grams of methyl salicylate was charged into a reactor mounted upon a balance and equipped with a mechanical stirrer, sulfur trioxide delivery tube and a thermometer. Sulfur trioxide was then introduced into the ester at a rate of approximately 0.5 gram per minute until the resulting sulfo methyl salicylate solidified, at which time the reaction had gone substantially to completion. This product was melted by heating to 110° C. and then poured into an esterification vessel containing 4.5 grams of HCl gas dissolved in 185 grams of "Lorol" which was heated to a temperature of from 60° to 70° C. The mixture thus produced was heated to 110° C., and stirred for 15 minutes under atmospheric pressure and then under reduced pressure for about 30 minutes. At the end of the reaction, a sample of the product (sulfo "loralkyl" salicylate) was titrated and the neutral equivalent was found to be 333.

The remainder of the product was neutralized to form sodium sulfo "loralkyl" salicylate by means of a sufficient amount of 4% caustic soda to yield a slightly alkaline slurry. This slurry, after removal by decantation of a substantial amount of water, was drum dried and a stable light colored product was obtained.

Example II

1580 grams of methyl salicylate was charged into a reactor mounted upon a balance and equipped with a mechanical stirrer, sulfur trioxide tube and thermometer. At the completion of this operation, sulfur trioxide was introduced into the methyl ester in an amount and at the rates given in the following table, which table also shows how the temperature of the reaction varied as the sulfur trioxide was progressively added:

Time	Temperature	Weight Including Reactor	SO_3
Hrs.	*°C.*	*Grams*	*Grams*
0	25	2,675	
½	47	2,720	45
1	111	2,990	270
1½	105	3,180	190
2	104	3,400	220
2⅚	107	3,507	107
		Total	832

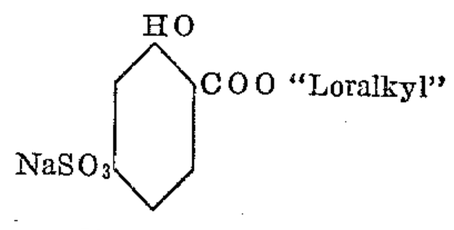
At the end of the reaction, the neutralization equivalent of the product was determined and found to be 164.

2320 grams of sulfo-methyl salicylate, including practically all of the above product together with a relatively small proportion of sulfonated product prepared in another batch, was placed in a suitable reactor containing 13 grams of HCl dissolved in 1629 grams of "Lorol" which included a relatively small proportion of added octanol and dodecanol. The resulting mixture was then heated with stirring for 3½ hours at a temperature of from 100° C. to 105° C. and at the end of the alcoholysis reaction, the product was neutralized with a caustic solution prepared by mixing 700 c. c. of approximately 50% NaOH with 3200 c. c. of water. The slurry of "loralkyl" sodium sulfo-salicylate thus obtained was then dried upon steam heated rolls under a steam pressure of from 90–100 lbs./in.^{2} and screened through ¼ mesh hardward cloth.

2835 grams of a light colored stable product

was obtained, which corresponded to a yield of 78% of theory.

The products obtained by the procedures described in Examples I and II have the following structural formula



The corresponding compounds of the meta and para isomers may be prepared by employing meta-hydroxy-benzoic acid and para-hydroxy-benzoic acid respectively in the process described in the above examples. Other ester-salts may also be produced by reacting the sulfonated lower alkyl esters of ortho-, meta- and para-hydroxy benzoic acid with a straight or branched chain aliphatic alcohols having from 6 to 18 carbon atoms, or mixtures of at least two of these alcohols. Moreover, although the monosulfonated derivatives are preferred, it is to be understood that the polysulfonated esters are also within the scope of the present invention.

In the production of sulfonated lower alkyl esters of ortho-, meta-, and para-hydroxy benzoic acid, the alkyl esters and sulfur trioxide are reacted together in substantially stoichiometric proportions, the actual amount of SO_3 employed depending upon the degree of sulfonation desired. In general the reaction may be carried out at a temperature ranging from about 23° C. up to a temperature at which substantial decomposition of the desired sulfonated product is avoided, but in the production of the sulfonated methyl ester, the reaction temperature is desirably maintained within the range of about 23° C. up to about 125° C. and preferably within the range of from 90° C. to 115° C.

In practice, the sulfonation of the methyl ester is initiated at room temperature by introducing SO_3 into the liquid ester and within a relatively short time, the heat of reaction raises the temperature to about 90° C. to 100° C. If, after 60% to 70% of the theoretical amount of gaseous SO_3 has been added, the reaction mixture has not reached this temperature, heat is applied until that is accomplished. As soon as approximately 90% of the SO_3 has been introduced, the reaction is completed by heating the reaction mixture to at least 110° to 115° C. but not above 125° C. while adding further amounts of SO_3.

The alcoholysis reaction is executed using substantially equimolecular proportions of the sulfonated lower alkyl esters of hydroxy benzoic acid and an aliphatic alcohol having from 6 to 18 carbon atoms. The reaction temperature may vary from the melting point of sulfonated alkyl ester up to a temperature at which substantial decomposition of the alcoholysis product is avoided.

In preparing sulfoloralkyl salicylate, "Lorol" is saturated with HCl gas, heated to about 60° C. to 70° C. and then mixed with sulfomethyl salicylate which is at a temperature of 100° C. to 115° C. The reaction mixture is then heated to about 110° C. with stirring for about 2 hours. If the neutral equivalent has not reached 330–340 at the end of this time, the reaction is continued for another half hour under reduced pressure of about 100 mm. of mercury.

The manner of mixing the reactants is not critical, but it is preferred to add the molten sulfonated methyl ester to the alcohol as improved yields are thereby obtained.

In place of HCl, up to 5% by weight of other mineral acids such as sulfuric and phosphoric acid may be employed in the alcoholysis reaction.

The neutralization step is conveniently carried out by adding the alcoholysis product to a sodium hydroxide solution with stirring until the resulting slurry has a pH of about 8–9, whereupon the product is dried, preferably by means of a drum drier using a steam pressure of from 80 to 100 lbs./in.^{2}. When drum drying the neutralized product, it is desirable to adjust the solids content of the slurry to at least 18% but preferably not above about 27% by weight.

In place of sodium hydroxide, other alkalies such as sodium carbonate, sodium oxide, potassium hydroxide, potassium carbonate, potassium oxide, calcium hydroxide, calcium oxide, calcium carbonate, magnesium oxide, magnesium carbonate, barium oxide, barium hydroxide, barium carbonate, strontium oxide, strontium hydroxide and strontium carbonate may be employed.

The expression "Lorol" within the meaning of the present specification is intended to cover mixtures of alcohols prepared by hydrogenating coconut oil, which mixtures have an average molecular weight of about 186 (basis, dodecyl alcohol) and contain alcohols having 6 to 18 carbon atoms. The following is a typical mixture of alcohols produced by the above method.

	Per cent
Hexyl alcohol	2
Octyl alcohol	9
Decyl alcohol	10
Lauryl alcohol	45
Myristyl alcohol	20
Cetyl alcohol	7
Stearyl alcohol	5
Oleyl alcohol	2

The expression "loralkyl," therefore, represents the alkyl radicals derived from the above mixture of alcohols.

The expression "lower alkyl" as used in the specification and claims is intended to cover alkyl groups containing from 1 to 5 carbon atoms.

The expression "neutral equivalent" is defined by the following relationship.

$$NE = \frac{\text{Weight of acid product}}{\text{Volume of base} \times \text{normality of base}}$$

Neutral equivalent may also be defined as the number of grams of acid (sulfomethyl salicylate or sulfoloralkyl salicylate) neutralized by or equivalent to one mole of sodium hydroxide.

Inasmuch as the above description comprises preferred embodiments of the invention, it is to be understood that the invention is not limited thereto and that changes and modifications may be made therein without departing substantially from the invention which is defined in the appended claims.

I claim:

1. The process of producing aliphatic esters of sulfonated monohydroxy benzoic acid wherein the aliphatic group is attached to the carboxyl group, which comprises reacting, at a temperature not exceeding 125° C., a corresponding "lower alkyl" ester with sulfur trioxide in substantially the theoretical proportions required to produce at least monosulfonation, subjecting the sulfonated product to alcoholysis by means of substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, and then neutralizing the resulting product, said alcoholysis being carried out at a temperature varying from the melting point of said "lower alkyl" ester up to a temperature at which substantial decomposition of said alcoholysis-ester product is avoided.

2. The process of producing aliphatic esters of sulphonated monohydroxy benzoic acid wherein the aliphatic group is attached to the carboxyl group, which comprises reacting, at a temperature not exceeding 125° C., a corresponding "lower alkyl" ester with sulfur trioxide in the proportions required to produce monosulfonation, subjecting the sulfonated product to alcoholysis by means of substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, and then neutralizing the resulting product, said alcoholysis being carried out at a temperature varying from the melting point of said "lower alkyl" ester up to a temperature at which substantial decomposition of said alcoholysis-ester product is avoided.

3. The process of producing aliphatic esters of sulfonated monohydroxy benzoic acid wherein the aliphatic group is attached to the carboxyl group, which comprises monosulfonating a corresponding "lower alkyl" ester with sulfur trioxide at a temperature beginning with room temperature and ending with a maximum of 125° C., subjecting the sulfonated product to alcoholysis by means of substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, and then neutralizing the resulting product, said alcoholysis being carried out at a temperature varying from the melting point of said "lower alkyl" ester up to a temperature at which substantial decomposition of said alcoholysis-ester product is avoided.

4. The process of producing aliphatic esters of sulfonated ortho monohydroxy benzoic acid wherein the aliphatic group is attached to the carboxyl group, which comprises monosulfonating a corresponding methyl ester at a temperature of 90° C. to 115° C., subjecting the sulfonated product to alcoholysis with substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, neutralizing the resulting product with a dilute alkaline solution and then drying the resulting slurry, said alcoholysis being carried out at a temperature varying from the melting point of said sulfonated methyl ester up to that temperature at which substantial decomposition of said alcoholysis-ester product is avoided.

5. The process of producing aliphatic esters of sulfonated salicyclic acid wherein the aliphatic group is attached to the carboxyl group, which comprises monosulfonating methyl salicylate with sulfur trioxide at a temperature within the range of room temperature up to about 107° C., subjecting the resulting sulfomethyl salicylate to alcoholysis by reaction at 100° C.–110° C. with substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, neutralizing the resulting product with a dilute sodium hydroxide solution and then drum drying the resulting slurry.

6. The process defined in claim 5 wherein the alcoholysis reaction is carried out in the presence of up to 5% by weight of a mineral acid.

7. The process defined in claim 6 wherein the alcoholysis reaction is carried out in the presence of hydrogen chloride.

8. The process defined in claim 7 wherein the

alcoholysis reaction mixture is stirred for 15 minutes under atmospheric pressure and then under reduced pressure for about 30 minutes.

9. The process of producing aliphatic esters of sulfonated monohydroxy benzoic acid wherein the aliphatic group is attached to the carboxyl group, which comprises subjecting a corresponding sulfonated "lower alkyl" ester to alcoholysis by reaction with substantially equimolecular proportions of a mixture of primary monohydric aliphatic alcohols obtained by the hydrogenation of coconut oil, and then neutralizing the resulting product, said alcoholysis being carried out at a temperature varying from the melting point of said sulfonated ester up to a temperature at which

substantial decomposition of said alcoholysis-ester product is avoided.

JAMES O. HARRIS.

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