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QUATERNARY AMMONIUM ALKENYL SUCCINATES

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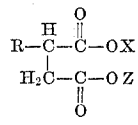
No Drawing. Continuation-in-part of application Ser. No. 365,796, May 7, 1964. This application Feb. 27, 1968, Ser. No. 708,520

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ABSTRACT OF THE DISCLOSURE

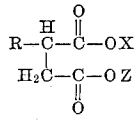
The products of this invention conform, in general, to the following structure:



wherein R is a straight or branched chain alkenyl radical containing from 6 to 18 carbon atoms; X or Z or both are cations of microbiocidal quaternary ammonium compounds; or either X or Z is such a quaternary ammonium cation and the other is hydrogen or an alkali metal cation such as sodium, potassium, etc., or an equivalent such as ammonium or triethanolammonium cation.

This is a continuation-in-part of application Ser. No. 365,796, filed May 7, 1964, now abandoned.

The object of the present invention is the preparation of microbiocidal compounds by reaction of certain quaternary ammonium hydroxides or their water-soluble salts with alkenyl succinic acids or their water-soluble salts. In this respect, when the reaction takes place in an aqueous medium, the water-soluble salts of the succinic acids are used. The products of this invention conform, in general, to the following structure:



wherein R is a straight or branched chain alkenyl radical containing from 6 to 18 carbon atoms; X or Z or both are cations of microbiocidal quaternary ammonium compounds; or either X or Z is such a quaternary ammonium cation and the other is hydrogen or an alkali metal cation such as sodium, potassium, etc., or an equivalent such as ammonium or triethanolammonium cation.

The alkenyl succinic acids used in this invention, containing from 10 to 22 carbon atoms in the molecule, are well known to the art and may be obtained commercially by synthetic methods such, for example, as by reaction of an olefin with maleic anhydride and subsequent hydrolysis as described in U.S. Pat. No. 2,741,597.

Typical examples of the quaternary ammonium compounds which may be used in this invention are the alkyl trimethyl ammonium chlorides, alkyl-benzyl trimethyl ammonium chlorides, alkyl dimethyl benzyl ammonium chlorides, alkyl dimethyl menaphthyl ammonium chlorides, alkyl dimethyl substituted-benzyl ammonium chlorides in which the benzyl radical is substituted with one or more side chains containing from 1 to 5 carbon atoms such, for example, as methyl, dimethyl, ethyl and the like and in which the carbon atoms may all be in the same or different side chains or in which the benzyl radical bears one, two or more halogen atoms such as chlorine

or bromine, alkyl pyridinium chlorides, alkyl isoquinolinium chlorides and bromides, alkyl lower-alkyl pyrrolidinium chlorides, alkyl lower-alkyl morpholinium chlorides in all of which the alkyl group may have from 8 to 22 carbon atoms and the lower-alkyl group may have from 1 to 4 carbon atoms, and alkyl phenoxy ethoxy ethyl dimethyl benzyl ammonium chloride in which the alkyl radical may be iso-octyl or nonyl and in which the phenyl radical may, if desired, be substituted by a methyl radical. Various other analogs of these quaternaries may also be employed such, for example, as cetyl dimethyl ethyl ammonium bromide or oleyl dimethyl ethyl ammonium bromide.

In general, the quaternary ammonium compounds used as starting materials to contribute the cation portion of the final product are the higher alkyl quaternary ammonium hydroxides, halides (chlorides or bromides), sulfates, methosulfates and the like possessing the following formula:



where R is an alkyl or alkaralkyl radical containing from 8 to 22 carbon atoms or an alkyl phenoxy ethoxy ethyl radical in which R is an alkyl radical containing from 8 to 9 carbon atoms and in which the phenyl radical may be substituted by a methyl group; R′ and R″ are methyl or ethyl radicals or members of a heterocyclic ring system such as pyridine, isoquinoline, pyrrolidine and morpholine; R‴ is a methyl radical or a benzyl group or a substituted-benzyl group such, for example, as a monochlorobenzyl radical or a dichlorobenzyl radical or mixture thereof or a methyl benzyl, dimethyl benzyl, ethyl benzyl, diethyl benzyl, isopropyl benzyl, tertiary butyl benzyl or another benzyl radical containing from 1 to 5 carbon atoms as side chains, either as a single side chain or a multiplicity of side chains including mixtures thereof or a menaphthyl group or hydrogenated menaphthyl group. When R′ and R″ are members of a morpholine or pyrrolidine ring, R‴ is a methyl, ethyl, propyl or butyl group. When R′ and R″ are members of an unsaturated heterocyclic ring such as pyridine or isoquinoline, R‴ is the same radical as R″. X in the above formula corresponds to a halide radical such as chloride, bromide or iodide or to any other water-soluble anion such as methosulfate.

In general, we prefer to use such quaternary ammonium compounds which have a phenol coefficient of at least 100 with respect to both *Staphylococcus aureus* and *Salmonella typhosa* at 20° C., when determined by the standard method given in the "Official Methods of Analysis Of The Association Of Official Agricultural Chemists," Ninth Edition (1960), page 63 et seq.

The compounds of this invention may be prepared by mixing aqueous solutions of the quaternary ammonium salts or hydroxides with an aqueous solution of the water-soluble salts of the acid in question.

After thorough mixing, the organic product layer is separated from the aqueous layer (as with a separatory funnel) since two distinct phases are formed. Separation may be facilitated by the addition of an organic solvent immiscible with water. The product layer may be washed with water to remove any residual by-product or unreacted materials. The solvent, if any, may be evaporated and the product air or vacuum dried to a paste, wax, oil or solid.

It is not necessary to use an aqueous medium. Any solvent or solvent mixture in which the starting materials are soluble will be satisfactory. Non-aqueous solvents facilitate the separation of by-product inorganic salt and reduce the need for vacuum drying to get an anhy-

drous product. When a non-aqueous medium is employed, it is usually necessary to add a small amount of water to facilitate ionic reaction.

The product may be used, if desired, without drying since any entrapped water is irrelevant to the microbiological activity of the compounds. In other applications, removal of water may be essential for reasons not related to biological activity.

An alternative method for the preparation of compounds especially applicable to the treatment of fabric, ropes, net, woven and non-woven fabric and reticulated or convoluted materials involves a two-step process. In the first step, the material is passed through a bath containing the anionic moiety. Excess solution is removed by methods well known to those skilled in the art. The treated material is then passed through a second bath wherein the concentration of quaternary ammonium compound is such that the material pickup will result in an equivalent amount of quaternary ammonium compound reacting with the anionic moiety, depositing the product in the most intimate way on the surface and in the interstices, convolutions and reticulations of the material.

The method of adjustment of solution concentration to achieve the required pickup is well known to those skilled in the art. The order of treatment may be reversed without affecting the biological activity or durability of the product on the material. The products of this invention may be formulated as dispersions by dissolving them in a water miscible organic solvent such as acetone or methanol and diluting with water or by dissolving them in emulsifiable oils such, for example, as sulfonated castor oil or pine oil and diluting with water. In preparing aqueous dispersions, emulsifying agents such, for example, as ethylene oxide condensates of alkyl phenols may be used with or without organic solvents.

It is surprising that the compounds of this invention exhibit high microbiocidal activity despite their substantial insolubility in water. Because of their unusual combination of physical and microbiocidal properties, they can be used to impart laundry-resistant anti-microbial characteristics to textiles. They can also be used as the active agent in antimildew finishes for textiles which are resistant to leaching with water.

Although the compounds are substantially insoluble in water, they are compatible with various organic solvents, plasticizers and high molecular weight compounds. Consequently, they may be incorporated as anti-microbial agents in synthetic resins and plastics. The compounds are compatible with natural and synthetic rubber latices. Therefore, they may be used to prepare bacteriostatic films and molded objects deposited from such latices.

The compounds can be incorporated into cutting and grinding fluids without precipitation. Also, they blend well with non-ionic and anionic surface active agents. In such compositions they retain their microbiocidal activity.

It will be understood that the properties of the products described herein will vary depending upon the nature of the cationic quaternary ammonium compound used in their preparation as well as the anionic compound reacted therewith.

The chemical, physical and biological properties of the products of our invention make them especially appropriate for the following applications when suitably incorporated in active amounts in an appropriate vehicle, binder, medium or substrate:

(1) Mildewproofing fabric, canvas, ropes, textiles, awnings, sails, tenting and other woven and non-woven reticulated materials.

(2) Paint mildewstats.

(3) Jet plane fuel additive to control growth of microorganisms.

(4) Odor preservative agents for clothes and shoes.

(5) Mildew retardant and odor suppressant for shoes and other leather products.

(6) Topical antiseptics.

(7) Antidandruff agents.

(8) Disinfection agents for hair and gut of man and beast.

(9) Bacteriostatic furniture dressing.

(10) Surface finishes for stone, plaster, title, cement, brick and other inorganic building materials to retard growth of microorganisms, fungi, mold and algae.

(11) Wool preservative.

(12) Plant and tree spray to combat fungi.

(13) Antimycotic agents for soap wrappers.

(14) Self-sanitizing brushes.

(15) Mildewproofing agent in and on plastic and film.

(16) Mildewproofing of cellulosics, cardboard, fibreboard, paper and cordage.

(17) Contact biostat for application to film, waxes and cloth to preserve cheese, meats and vegetables and other food products.

(18) Algal inhibition, especially on surfaces and in solution where low foaming is desirable.

(19) Paper pulp slime control.

(20) Sanitizing agent for rug, carpet, curtains.

(21) Egg preservation.

(22) Adhesive preservation.

(23) Preservation of latex paints.

(24) Preservation of metal-working compounds.

(25) Additives for soap and for both anionic and non-ionic detergents in liquid, bar, powder, bead, solution and other forms to impart bacteriostatic and fungistatic properties thereto.

(26) Bacteriostatic agents for household laundry softeners.

(27) Algastat and bacteriostat in recirculated water for cooling towers, air conditioners and humidifiers.

(28) Bacteriostat and algastat for flood waters and brines used in secondary oil recovery.

(29) Fungistat for seed and soil treatment against damping-off.

The microbiological activity of our compounds has been evaluated for microbiological stasis by the Standard Tube Dilution Test, the technique for which is common knowledge to those skilled in the art. A Difco Bacto CSMA Broth #0826 was used in the study. This test is used to determine the lowest concentration of microbiologically active compounds which will inhibit the growth of the organism in question. For a wide range of applications, the inhibition of growth rather than outright kill is satisfactory.

Briefly put, the Tube Dilution Test consists in placing 9 cc. of the CSMA Broth in a test tube which is then sterilized in an autoclave. One cc. solution of the microbiologically active compound at an appropriate concentration is added to the test tube which is then inoculated with 0.1 cc. of a twenty-four hour old culture of the organism under study. The test tube is then incubated at 37° C., for forty-eight hours and observed for bacterial growth.

The same procedure is followed for fungi. In such tests, however, the tubes are incubated for fourteen days at a temperature suitable for optimum fungal growth, usually 25° C.

The invention is illustrated by, but not restricted to, the following examples:

EXAMPLE I

An aqueous stock solution of disodium dodecenyl succinic acid was prepared by saponifying the corresponding anhydride with the required amount of sodium hydroxide solution. An aliquot of this solution containing 0.284 chemical equivalents of the compound was agitated vigorously while adding a chemically equivalent amount of a solution of a commercial grade of alkyl dimethyl ethyl-benzyl ammonium chloride (Onyx Chemical Corporation's "BTC–471" in which the alkyl distribution is 50% C_{12}, 30% C_{14}, 17% C_{16}, 3% C_{18}). The mixture was transferred to a separatory funnel,

wherein it separated into two phases. The organic product layer was removed and vacuum dried to yield a light yellow paste of di(alkyl dimethyl ethyl-benzyl ammonium) dodecenyl succinate in 93% of the theoretical yield.

Using the Standard Tube Dilution Test described above, the following bacteriostatic levels were determined:

Staphylococcus aureus	$1:10^6$
Salmonella typhosa	$1:10^5$
Aspergillus niger	$1:10^5$

EXAMPLE II

A 250 ml. aliquot of the stock solution of disodium dodecenyl succinate of Example I was reacted with one liter of an aqueous-alcohol solution containing a chemically equivalent amount of a commercial grade of dodecyl dimethyl menaphthyl ammonium chloride (Onyx Chemical Corporation's "BTC–1100" containing 98% C_{12} and 2% C_{14}) in the manner described above. After removing the alcohol by evaporation and separating and drying the organic product layer, a light yellow paste of di(dodecyl dimethyl menaphthyl ammonium) dodecenyl succinate was obtained in the theoretical yield.

EXAMPLE III

By substituting for the alkyl dimethyl ethyl-benzyl ammonium chloride of Example I, respectively, alkyl dimethyl dimethyl-benzyl ammonium chloride (Onyx Chemical Corporation's "BTC–927") or alkyl isoquinolinium bromide (Onyx Chemical Corporation's "Isothan Q–75" in each of which the alkyl distribution is 50% C_{12}, 30% C_{14}, 17% C_{16}, 3% C_{18}) or alkyl dimethyl benzyl ammonium chloride (Onyx Chemical Corporation's "BTC–824" in which the alkyl distribution is 60%, C_{14}, 30% C_{16}, 5% C_{12}, 5% C_{18}), in each case the corresponding dibasic quaternary ammonium salt of dodecenyl succinic acid was obtained.

EXAMPLE IV

A stock solution was prepared of disodium octadecenyl succinate and reacted in chemically equivalent amount with the alkyl dimethyl ethyl-benzyl ammonium chloride of Example I, and in the same manner, to yield the di(alkyl dimethyl ethyl-benzyl ammonium) octadecenyl succinate.

EXAMPLE V

The stock solution of disodium octadecenyl succinate of Example IV was reacted in the same way with the dodecyl dimethyl menaphthyl ammonium chloride of Example II to obtain the di(dodecyl dimethyl menaphthyl ammonium) octadecenyl succinate.

EXAMPLE VI

Aliquots of the stock solution of disodium octadecenyl succinate of Example IV were reacted, respectively, with the solutions of alkyl dimethyl dimethyl-benzyl ammonium chloride; the alkyl isoquinolinium bromide; and the alkyl dimethyl benzyl ammonium chloride of Example III to produce the corresponding di(quaternary ammonium) salts of octadecenyl succinic acid.

EXAMPLE VII

A stock solution of disodium hexenyl succinate was prepared and reacted in the same manner with a chemically equivalent amount of the alkyl dimethyl ethyl-benzyl ammonium chloride of Example I to produce the di(alkyl dimethyl ethyl-benzyl ammonium) hexenyl succinate.

EXAMPLE VIII

A solution of disodium decenyl succinate was prepared in aqueous solution and reacted with a chemically equivalent amount of a solution of the alkyl isoquinolinium bromide of Example III to yield the di(alkyl isoquinolinium) decenyl succinate.

EXAMPLE IX

53.2 grams of dodecenyl succinic anhydride or 0.20 mole was saponified by boiling it in water with 8.0 grams or 0.20 mole of sodium hydroxide. The resulting monosodium dodecenyl succinate solution was diluted to make a 10% solution.

An aliquot of this solution containing 0.025 molecular weights of the compound was reacted under vigorous agitation with 0.025 molecular weights of a 10% solution of a commercial grade of alkyl dimethyl benzyl ammonium chloride (Onyx Chemical Corporation's "BTC–824" in which the alkyl distribution is 60% C_{14}, 30% C_{16}, 5% C_{12}, 5% C_{18}), to produce a solution of mono-(alkyl dimethyl benzyl ammonium) dodecenyl succinate.

EXAMPLE X

In a similar manner, the corresponding mono-(quaternary ammonium) dodecenyl succinates were prepared by substituting for alkyl dimethyl benzyl ammonium chloride, the alkyl dimethyl ethyl-benzyl ammonium chloride of Example I; the dodecyl menaphthyl ammonium chloride of Example II; the alkyl isoquinolinium bromide of Example III; and the alkyl dimethyl dimethyl-benzyl ammonium chloride of Example III respectively, in stoichiometric proportions.

EXAMPLE XI

An aliquot of the mono-(alkyl dimethyl benzyl ammonium) hydrogen dodecenyl succinate of Example IX was neutralized with a stoichiometric amount of a solution of ammonia to form the mixed salt of mono-ammonium-mono-(alkyl dimethyl benzyl ammonium) dodecenyl succinate.

Other aliquots were neutralized with stoichiometric amounts of sodium hydroxide, potassium hydroxide and triethanolamine solutions to form the corresponding double salts with the mono-(alkyl dimethyl benzyl ammonium) dodecenyl succinate.

EXAMPLE XII

Monosodium hydrogen hexenyl succinate solution was prepared by saponifying 36.4 grams of the anhydride or 0.20 mole with 8.0 grams or 0.20 mole of sodium hydroxide, as in Example IX, and diluting to 10% concentration.

An aliquot of this solution containing 0.025 molecular weights was reacted with 0.025 molecular weights of a 10% solution of the alkyl dimethyl ethyl-benzyl ammonium chloride of Example I to yield the mono-(alkyl dimethyl ethyl-benzyl ammonium) hexenyl succinate.

EXAMPLE XIII

Similarly, the mono-(alkyl dimethyl benzyl ammonium) hexenyl succinate, the mono-(alkyl isoquinolinium) hexenyl succinate, the mono-(alkyl dimethyl dimethyl-benzyl ammonium) hexenyl succinate, and the mono-(dodecyl menaphthyl ammonium) hexenyl succinate were prepared by substituting for the alkyl dimethyl ethyl-benzyl ammonium chloride of Example XII of the corresponding quaternary ammonium compounds of Examples IX, III and II.

EXAMPLE XIV

Aliquots of the solutions of the mono-quaternary ammonium hexenyl succinates disclosed in Examples XII and XIII were neutralized in stoichiometric proportion with, respectively, solutions of ammonia, sodium hydroxide, potassium hydroxide and triethanolamine to produce the corresponding double salts with the mono-quaternary ammonium hexenyl succinate.

EXAMPLE XV

An aliquot of the solution of disodium hexenyl succinate

of Example XII containing 0.10 molecular weights of the compound was reacted with 0.20 average molecular weights of a solution of a commercially available mixture of two quaternary ammonium salts (Onyx Chemical Corporation's "BTC–2125" which is a mixture of "BTC–471" and "BTC–824"), to form the double salt of mono-(alkyl dimethyl ethyl-benzyl ammonium) mono-(alkyl dimethyl benzyl ammonium) hexenyl succinate.

The invention claimed is:

1. A quaternary ammonium compound selected from the group consisting of mono and di-quaternary ammonium salts of alkenyl succinates, the alkenyl having 6 to 18 carbon atoms, the quaternary ammonium cation being selected from the group consisting of alkyl dimethyl menapthyl ammonium, alkyl dimethyl benzyl ammonium, alkyl dimethyl ethyl-benzyl ammonium, alkyl dimethyl dimethyl-benzyl ammonium and alkyl isoquinolium, wherein alkyl has 8 to 22 carbon atoms.

2. The compound of claim **1** wherein the cationic portion is di(alkyl dimethyl ethyl-benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is dodecenyl succinate.

3. The compound of claim **1** wherein the cationic portion is di(dodecyl dimethyl menaphthyl ammonium) and the anionic portion is dodecenyl succinate.

4. The compound of claim **1** wherein the cationic portion is di(alkyl dimethyl ethyl-benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is octadecenyl succinate.

5. The compound of claim **1** wherein the cationic portion is di(dodecyl dimethyl menaphthyl ammonium) and the anionic portion is octadecenyl succinate.

6. The compound of claim **1** wherein the cationic portion is di(alkyl dimethyl ethyl-benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is hexenyl succinate.

7. The compound of claim **1** wherein the cationic portion is di(alkyl isoquinolinium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is decenyl succinate.

8. The compound of claim **1** wherein the cationic portion is di(alkyl isoquinolinium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is octadecenyl succinate.

9. The compound of claim **1** wherein the cationic portion is di(alkyl dimethyl benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is dodecenyl succinate.

10. The compound of claim **1** wherein the cationic portion is mono-(alkyl dimethyl benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is dodecenyl succinate.

11. The compound of claim **1** wherein the cationic portion is mono-(alkyl dimethyl benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is dodecenyl succinate.

12. The compound of claim **1** wherein the cationic portion is mono-(alkyl dimethyl dimethyl-benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is dodecenyl succinate.

13. The compound of claim **1** wherein the cationic portion is mono-(alkyl dimethyl ethyl-benzyl ammonium) wherein the alkyl has 8 to 22 carbon atoms, and the anionic portion is hexenyl succinate.

14. The compound of claim **1** wherein the cationic portion consists of mono-(alkyl dimethyl ethyl-benzyl ammonium) and mono-(alkyl dimethyl benzyl ammonium) each alkyl having 8 to 22 carbon atoms, and the anionic portion is hexenyl succinate.

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DONALD G. DAUS, Primary Examiner

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