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(54) **Titre : SYSTEMES PROTECTEURS NATURELS MULTIFONCTIONNELS AVEC DE L'HYDROXYACETOPHENONE**
 (54) **Title: MULTIFUNCTIONAL NATURAL PROTECTANT SYSTEMS WITH HYDROXYACETOPHENONE**

(57) **Abrégé/Abstract:**

The present invention relates to the use of multifunctional protectants comprising (i) hydroxyacetophenone with (ii) at least one of natural 1,3-propanediol and a mastic extract to protect a formulation from biodegradation. The present invention also relates to the use of a protectant comprising (i) hydroxyacetophenone with (ii) at least one of vitamin B5, vitamin C, and vitamin E to protect a formulation from biodegradation.

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(54) Title: MULTIFUNCTIONAL NATURAL PROTECTANT SYSTEMS WITH HYDROXYACETOPHENONE

(57) Abstract: The present invention relates to the use of multifunctional protectants comprising (i) hydroxyacetophenone with (ii) at least one of natural 1,3-propanediol and a mastic extract to protect a formulation from biodegradation. The present invention also relates to the use of a protectant comprising (i) hydroxyacetophenone with (ii) at least one of vitamin B5, vitamin C, and vitamin E to protect a formulation from biodegradation.



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Multifunctional Natural Protectant Systems with Hydroxyacetophenone

This application claims the benefit of U.S. Provisional Application No. 63/203,808, filed July 30, 2021, and U.S. Provisional Application No. 63/149,653, filed February 15, 2021, each of which is hereby incorporated by reference.

Field of the Invention

The present invention relates to the use of multifunctional protectants comprising (i) hydroxyacetophenone with (ii) at least one of natural 1,3-propanediol and a mastic extract to protect a formulation from biodegradation. The present invention also relates to the use of a protectant comprising (i) hydroxyacetophenone with (ii) at least one of vitamin B5, vitamin C, and vitamin E to protect a formulation from biodegradation.

Background

There are many drawbacks to currently available natural and naturally-derived antimicrobial formulations. They are expensive, and high concentrations of them (for instance, > 2%) are often required to prevent microbial growth and preserve a product. Many have undesirable colors and odors, have poor stability (for example, in aqueous systems), and are not effective against a broad spectrum of microorganisms. Additionally, some such natural or naturally-derived antimicrobial mixtures cause thinning of formulations. Many are oils or extracts which limits their usage in various formulations.

U.S. Patent No. 10,638,755 describes certain antimicrobial compositions comprising an acetophenone derivative and at least one second antimicrobial agent.

U.S. Patent No. 10,752,571 is directed to methods of purifying crude 4-hydroxyacetophenone.

U.S. Patent No. 8,226,931 is describes a mixture of compounds having the sensory properties of wintergreen.

International Publication No. WO 2015/144326 discloses a combination of one or more glycerol and/or oligoglycerol esters of branched chains and/or unbranched chains of alkane carboxylic acids and 4-hydroxyacetophenone.

There is a continuing need for low cost and safe natural preservative systems which are effective against a broad spectrum of microorganisms.

Summary of the Invention

The protectants (such as natural protectants) of the present invention are relatively cheap to make, easy to work with and incorporate into finished products, generally have no odor, and have reduced (compared to prior oil preservative systems) or no color. In one embodiment, the protectant comprises (i) hydroxyacetophenone with (ii) at least one of 1,3-propanediol and a mastic extract (e.g., in an amount to protect a formulation or product from biodegradation). One preferred embodiment is a protectant comprising hydroxyacetophenone and 1,3-propanediol. Another preferred embodiment is a protectant comprising hydroxyacetophenone and mastic oil. Yet another is a protectant comprising hydroxyacetophenone and mastic water. Preferably, the protectant includes a synergistic amount of its components. For example, in one embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone and 1,3-propanediol to inhibit microbial growth (e.g., fungi growth). In another embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone and mastic oil to inhibit microbial growth

(e.g., fungi growth). In yet another embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone and mastic water to inhibit microbial growth (e.g., fungi growth). Each of these embodiments may optionally include one or more additional natural or naturally derived compounds (e.g., natural or naturally derived antioxidants) and/or one or more other antimicrobials. In one embodiment, when the protectant includes 4-hydroxyacetophenone and 1,3-propanediol, the protectant does not contain 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin. In another embodiment, the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol is no more than 1:3 (e.g., the weight ratio can be 1:4 or 1:9). In yet another embodiment, the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol ranges from about 10:90 to about 30:70, such as about 20:80.

One embodiment is a product comprising an effective amount of a protectant described herein. Another embodiment is a product comprising an effective amount of (i) hydroxyacetophenone with (ii) at least one of 1,3-propanediol and a mastic extract to inhibit microbial growth (e.g., fungi growth) in the product. In one embodiment, the product is not intended for oral administration to an animal.

Another embodiment is a protectant comprising (a) 4-hydroxyacetophenone, (b) 1,3-propanediol, and (c) ethylhexylglycerin, wherein the protectant does not contain 3-phenylpropanol. In yet another embodiment, the protectant does not contain 1,2-hexanediol or 1,2-octanediol. Preferably, the protectant includes a synergistic amount of its components. For example, in one embodiment, the protectant comprises a synergistic amount of 4-hydroxyacetophenone, 1,3-propanediol, and ethylhexylglycerin to inhibit microbial growth (e.g., fungi growth). In another embodiment, the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol is no more than 1:3 (e.g., the weight ratio can be 1:4 or 1:9).

Yet another embodiment is a method of killing and/or inhibiting the growth of microorganisms (e.g., fungi) on a substrate by applying an effective amount of a protectant as described herein to the substrate. Yet another embodiment is a method of killing and/or inhibiting the growth of microorganisms (e.g., fungi) on a substrate by

applying an effective amount of (i) hydroxyacetophenone with (ii) at least one of 1,3-propanediol and a mastic extract to the substrate. In one embodiment, when the method includes applying 4-hydroxyacetophenone and 1,3-propanediol, the method does not include applying 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin to the substrate.

Yet another embodiment is a concentrate comprising (or consisting essentially of, or consisting of) (i) hydroxyacetophenone with (ii) at least one of 1,3-propanediol and a mastic extract for inhibiting microbial growth (e.g., fungi growth). In one embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone with (ii) at least one of 1,3-propanediol and a mastic extract and (iii) water. In another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) 1,3-propanediol, and (iii) optionally, water. In yet another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) mastic water, and (iii) optionally, water. In yet another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) mastic oil, and (iii) optionally, water. In a preferred embodiment, the concentrate consists of (i) hydroxyacetophenone, (ii) 1,3-propanediol, and (iii) optionally, water. The weight ratio of 4-hydroxyacetophenone and 1,3-propanediol in the concentrate may range from about 10:90 to about 30:70, such as about 20:80. In a preferred embodiment, the concentrate consists of (i) from about 10 to about 30% by weight of hydroxyacetophenone and (ii) from about 70 to about 90% by weight of 1,3-propanediol. In a more preferred embodiment, the concentrate consists of (i) about 20% by weight of hydroxyacetophenone and (ii) about 80% by weight of 1,3-propanediol. In one embodiment, when the concentrate includes 4-hydroxyacetophenone and 1,3-propanediol, the concentrate does not contain 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin.

In one embodiment, the concentrate comprises (or consists essentially of, or consists of) (a) 4-hydroxyacetophenone, (b) 1,3-propanediol, and (c) ethylhexylglycerin, wherein the concentrate does not contain 3-phenylpropanol. For example, the concentrate

may comprise from about 60 to about 80% by weight of 1,3-propanediol, from about 10 to about 25% by weight (such as from about 10 to about 20% by weight) of 4-hydroxyacetophenone, and from about 1 to about 15% by weight (such as from about 1 to about 10% by weight or from about 5 to about 15% by weight) of ethylhexylglycerin, based upon 100% total weight of concentrate. The concentrate may further comprise at least one of vitamin B5, vitamin C, and vitamin E, such as from about 1 to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E. In a preferred embodiment, the concentrate comprises about 69% by weight of 1,3-propanediol, about 20% by weight of 4-hydroxyacetophenone, about 10% by weight of ethylhexylglycerin, and about 1% by weight of vitamin B5 (or DL-panthenol), based upon 100% total weight of concentrate.

4-hydroxyacetophenone degrades upon exposure to light, oxygen, and elevated temperatures resulting in a darkened substance. This can result in products containing 4-hydroxyacetophenone changing color (darkening) over time, which is not desired for such products as personal care products (e.g., shampoos). The present inventors surprisingly discovered that the degradation of 4-hydroxyacetophenone can be prevented by the inclusion of at least one of vitamin B5, vitamin C, and vitamin E. 4-hydroxyacetophenone with the at least one of vitamin B5, vitamin C, and vitamin E can be incorporated into a product as a protectant (such as a natural protectant). The protectants (such as natural protectants) of the present invention are relatively cheap to make, easy to work with and incorporate into finished products, generally have no odor, and have reduced (compared to prior oil preservative systems) or no color.

One embodiment is a protectant comprising (i) 4-hydroxyacetophenone, and (ii) at least one of vitamin B5, vitamin C, and vitamin E (e.g., in an amount to protect a formulation or product from biodegradation). In one embodiment, the protectant includes a sufficient amount of the at least one of vitamin B5, vitamin C, and vitamin E to prevent degradation of the 4-hydroxyacetophenone.

Another embodiment is a protectant comprising (i) 4-hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) at least one of 1,3-

propanediol and a mastic extract (e.g., in an amount to protect a formulation or product from biodegradation). One preferred embodiment is a protectant comprising (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) 1,3-propanediol. Another preferred embodiment is a protectant comprising (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) mastic oil. Yet another is a protectant comprising (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) mastic water. Preferably, the protectant includes a synergistic amount of its components. For example, in one embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone, vitamin B5, and 1,3-propanediol to inhibit microbial growth (e.g., fungi growth). In another embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone, vitamin B5, and mastic oil to inhibit microbial growth (e.g., fungi growth). In yet another embodiment, the protectant comprises a synergistic amount of hydroxyacetophenone, vitamin B5 and mastic water to inhibit microbial growth (e.g., fungi growth). In one embodiment, the protectant includes a sufficient amount of the at least one of vitamin B5, vitamin C, and vitamin E to prevent degradation of the 4-hydroxyacetophenone.

Each of these embodiments may optionally include one or more additional natural or naturally derived compounds and/or one or more other antimicrobials. In one embodiment, when the protectant includes 4-hydroxyacetophenone and 1,3-propanediol, the protectant does not contain 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin. In another embodiment, the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol is no more than 1:3 (e.g., the weight ratio can be 1:4 or 1:9).

Another embodiment is a product comprising an effective amount of a protectant described herein. In one embodiment, the product comprises an effective amount of a protectant described herein. Another embodiment is a product comprising an effective amount of (i) hydroxyacetophenone with (ii) at least one of vitamin B5, vitamin C, and vitamin E to inhibit microbial growth (e.g., fungi growth) in the product. Another embodiment is a product comprising an effective amount of (i) hydroxyacetophenone, (ii)

at least one of vitamin B5, vitamin C, and vitamin E, and (iii) at least one of 1,3-propanediol and a mastic extract to inhibit microbial growth (e.g., fungi growth) in the product. In one embodiment, the product is not intended for oral administration to an animal.

Yet another embodiment is a method of killing and/or inhibiting the growth of microorganisms (e.g., fungi) on a substrate by applying an effective amount of a protectant as described herein to the substrate. Yet another embodiment is a method of killing and/or inhibiting the growth of microorganisms (e.g., fungi) on a substrate by applying an effective amount of (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) optionally, at least one of 1,3-propanediol and a mastic extract to the substrate. In one embodiment, when the method includes applying 4-hydroxyacetophenone and 1,3-propanediol, the method does not include applying 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin to the substrate.

Yet another embodiment is a concentrate comprising (or consisting essentially of, or consisting of) (i) hydroxyacetophenone, and (ii) at least one of vitamin B5, vitamin C, and vitamin E for inhibiting microbial growth (e.g., fungi growth). The concentrate may include a sufficient amount of the at least one of vitamin B5, vitamin C, and vitamin E to prevent degradation of the 4-hydroxyacetophenone.

Yet another embodiment is a concentrate comprising (or consisting essentially of, or consisting of) (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, and (iii) at least one of 1,3-propanediol and a mastic extract for inhibiting microbial growth (e.g., fungi growth). The concentrate may include a sufficient amount of the at least one of vitamin B5, vitamin C, and vitamin E to prevent degradation of the 4-hydroxyacetophenone. In one embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E, (iii) at least one of 1,3-propanediol and a mastic extract and (iv) water. In another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5), (iii) 1,3-propanediol, and (iv) optionally, water. In yet

another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5), (iii) mastic water, and (iv) optionally, water. In yet another embodiment, the concentrate comprises (or consists essentially of, or consists of) (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5), (iii) mastic oil, and (iv) optionally, water. In a preferred embodiment, the concentrate consists of (i) hydroxyacetophenone, (ii) vitamin B5, (iii) 1,3-propanediol, and (iv) optionally, water. In a more preferred embodiment, the concentrate consists of (i) 20% by weight of hydroxyacetophenone, (ii) 1% by weight of vitamin B5, and (iii) 80% by weight of 1,3-propanediol. In one embodiment, when the concentrate includes 4-hydroxyacetophenone and 1,3-propanediol, the concentrate does not contain 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin.

In one embodiment, the concentrate comprises (or consists essentially of, or consists of) (a) from about 10 to about 20% by weight of 4-hydroxyacetophenone, (b) from about 60 to about 80% by weight of 1,3-propanediol, and (c) from about 1 to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5).

Detailed Description of the Invention

Definitions

As used herein, the term “about” represent an amount or condition near to the stated amount or condition that still performs a desired function or achieves a desired result. For example, the term “about” may refer to an amount or condition that deviates by no more than 10% (i.e., $\pm 10\%$), by no more than 5%, by no more than 1%, by no more than 0.1%, or by no more than 0.01% from a stated amount or condition.

The term “hydroxyacetophenone” unless indicated otherwise refers to 4-hydroxyacetophenone.

The term "microorganisms" includes, but is not limited to, bacteria, fungi, yeasts, algae, insects, and pests.

The term "personal care products" refers to products intended for application to the human body, such as to skin, hair, and nails, including, but not limited to, shampoos, conditioners, creams, lotions (such as body lotions), cosmetics, and soaps.

Mastic Extract

A mastic extract is derived from a mastic tree (*Pistacia lentiscus*). Suitable mastic extracts include, but are not limited to, mastic oil, mastic water, and any combination of any of the foregoing.

Mastic oil can be obtained from mastic by, for example, steam distillation.

Mastic water can be obtained as a byproduct during the steam distillation of mastic, such as from the steam distillation of mastic resin (the resin of *Pistacia lentiscus* var. *chia*).

In one embodiment, the product contains from about 0.001 to about 10% by weight of mastic extract, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.1 to about 2%, or from about 0.1 to about 1% by weight of mastic extract, based upon 100% total weight of product. For example, the product may contain from about 0.1 to about 10% by weight of mastic oil, such as from about 0.2 to about 8% or from about 0.3 to about 5% mastic oil. The product may contain from about 0.1 to about 10% by weight of mastic water, such as from about 0.5 to about 8% or from about 1 to about 7% mastic water (e.g., from about 1 to about 2% by weight of mastic water).

Additional Natural or Naturally Derived Compounds and Other Antimicrobials

The methods, products and concentrates may optionally include one or more additional natural or naturally derived compounds and/or one or more other antimicrobials.

Suitable natural or naturally derived compounds include, but are not limited to, quinic acid or a salt thereof, ethyl lauroyl arginate (ELA) or a salt thereof (including ethyl lauroyl arginate HCl), p-anisic acid or a salt thereof (e.g., sodium p-anisate), caprylhydroxamic acid or a salt thereof, 1,3-propanediol (only all natural type), glycereth-2 cocoate, benzyl alcohol (naturally derived from cassia), glycerin, organic solvents (e.g., ethylhexyl glycerin, phenoxyethanol, caprylyl glycols, pentylene glycol (natural), phenethyl alcohol (natural), and hexylene glycol), organic acids (e.g., sorbic acid, benzoic acid, and citric acid), and any combination of any of the foregoing.

Suitable other antimicrobials (for example, synthetic antimicrobials) include, but are not limited to, piroline olamine, and any combination of any of the foregoing.

Combinations

In one embodiment, the weight ratio of (i) hydroxyacetophenone and (ii) at least one of 1,3-propanediol and a mastic extract ranges from about 0.01:100 to about 100:0.01, preferably ranges from about 0.1:20 to about 20:0.1, such as from about 1:10 to about 10:1.

In one embodiment, the weight ratio of (i) hydroxyacetophenone and (ii) 1,3-propanediol ranges from about 1:1 to about 1:20, such as from about 1:1 to about 1:15 or from about 1:3 to 1:12 or from about 1:3 to about 1:4 (for example, 1:4 or 1:9). In another embodiment, the weight ratio of hydroxyacetophenone to 1,3-propanediol ranges from about 5:95 to about 30:50. In yet another embodiment, the weight ratio of hydroxyacetophenone to 1,3-propanediol ranges from about 5:95 to about 25:75.

In another embodiment, the weight ratio of (i) hydroxyacetophenone and (ii) mastic water ranges from about 1:1 to about 1:20, such as from about 1:5 to about 1:15 or from about 1:3 to 1:12 (for example, 1:4 or 1:9). In another embodiment, the weight ratio of hydroxyacetophenone to mastic water ranges from about 5:95 to about 30:50. In yet another embodiment, the weight ratio of hydroxyacetophenone to mastic water ranges from about 5:95 to about 25:75.

In yet another embodiment, the weight ratio of (i) hydroxyacetophenone and (ii) mastic oil ranges from about 1:1 to about 1:20, such as from about 1:5 to about 1:15 or from about 1:3 to 1:12 (for example, 1:4 or 1:9). In another embodiment, the weight ratio of hydroxyacetophenone to mastic oil from about 5:95 to about 30:50. In yet another embodiment, the weight ratio of hydroxyacetophenone to mastic oil ranges from about 5:95 to about 25:75.

In any embodiment described herein, the weight ratio of hydroxyacetophenone to the at least one of vitamin B5, vitamin C, and vitamin E can range from about 1:1 to about 50:1, such as from about 10:1 to about 30:1 (e.g., 20:1).

In yet another embodiment, the weight ratio of (i) hydroxyacetophenone to (ii) ethylhexylglycerin (if present) ranges from about 10:1 to about 3:1.

In yet another embodiment, the product contains (i) from about 0.001 to about 10% by weight of hydroxyacetophenone, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.1 to about 2%, or from about 0.1 to about 1% by weight of hydroxyacetophenone, based upon 100% total weight of product, and (ii) from about 0.001 to about 10% by weight of 1,3-propanediol and/or a mastic extract, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.1 to about 2%, or from about 0.1 to about 1% by weight of 1,3-propanediol and/or a mastic extract, based upon 100% total weight of product.

In yet another embodiment, the product contains an effective amount of (i) hydroxyacetophenone and (ii) one or more 1,3-propanediol and/or a mastic extract to inhibit microbial growth in the product.

In one embodiment, the product contains hydroxyacetophenone and 1,3-propanediol. The product may contain (i) from about 0.001 to about 10% by weight of hydroxyacetophenone, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.01 to about 1%, or from about 0.05 to about 0.5% by weight of hydroxyacetophenone, based upon 100% total weight of product, and (ii) from about 0.001 to about 10% by weight of 1,3-propanediol, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.01 to about 1%, from about 0.01 to about 0.1%, or from about 0.02 to about 0.08% by weight of 1,3-propanediol, based upon 100% total weight of product.

In another embodiment, the product contains hydroxyacetophenone and mastic water. The product may contain (i) from about 0.001 to about 10% by weight of hydroxyacetophenone, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.01 to about 1%, or from about 0.05 to about 0.5% by weight of hydroxyacetophenone, based upon 100% total weight of product, and (ii) from about 0.001 to about 10% by weight of mastic water, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.01 to about 1%, from about 0.01 to about 0.1%, or from about 0.02 to about 0.08% by weight of mastic water, based upon 100% total weight of product.

In yet another embodiment, the product contains hydroxyacetophenone and mastic water. The product may contain (i) from about 0.001 to about 10% by weight of hydroxyacetophenone, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.01 to about 1%, or from about 0.05 to about 0.5% by weight of hydroxyacetophenone, based upon 100% total weight of product, and (ii) from about 0.001 to about 10% by weight of mastic oil, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.01 to about 1%,

from about 0.01 to about 0.1%, or from about 0.02 to about 0.08% by weight of mastic oil, based upon 100% total weight of product.

In yet another embodiment, the product contains hydroxyacetophenone, 1,3-propanediol, and ethylhexylglycerin. The product may contain (i) from about 0.001 to about 5% by weight of hydroxyacetophenone, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.01 to about 1%, or from about 0.05 to about 0.5% by weight of hydroxyacetophenone, (ii) from about 0.001 to about 10% by weight of 1,3-propanediol, such as from about 0.1 to about 8%, from about 0.2 to about 6%, from about 0.2 to about 5%, from about 0.2 to about 0.4%, or from about 0.2 to about 3% by weight of 1,3-propanediol, and (iii) from about 0.001 to about 5% by weight of ethylhexylglycerin, such as from about 0.001 to about 4%, from about 0.01 to about 2%, from about 0.05 to about 2%, from about 0.01 to about 1%, or from about 0.05 to about 0.5% by weight of ethylhexylglycerin, based upon 100% total weight of product.

In one of any of the aforementioned embodiments, the product comprises from about 0.001 to about 2% by weight of the at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of the product. In one embodiment, the product does not contain (a) a glycerol ester of an alkane carboxylic acid or (b) an oligoglycerol ester of an alkane carboxylic acids.

The product or concentrate also preferably comprises a synergistic protective amount of (i) hydroxyacetophenone and (ii) at least one of 1,3-propanediol and mastic extract (e.g., a synergistic protective amount against fungi or bacteria). In another preferred embodiment, the product or concentrate comprises a synergistic protective amount of (i) hydroxyacetophenone, (ii) at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5), and (iii) at least one of 1,3-propanediol and mastic extract (e.g., a synergistic protective amount against fungi or bacteria). In yet another preferred embodiment, the product or concentrate comprises a synergistic protective amount of (i) hydroxyacetophenone, (ii) ethylhexylglycerin, (iii) 1,3-propanediol, and

optionally (iv) at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5) (e.g., a synergistic protective amount against fungi or bacteria).

Products

The products described above may be a solid or liquid. In a preferred embodiment, the products described herein (as well as the concentrates described herein) are substantially free or completely free of parabens (such as methylparaben, ethylparaben, and propylparaben), formaldehyde donors, and/or isothiazolinones. According to one embodiment, the product (or concentrate) contains less than about 2, 1.5, 1, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, or 0.01% by weight of parabens, formaldehyde donors, and/or isothiazolinones, based upon 100% total weight of product (or concentrate). According to one embodiment, the product (or concentrate) does not contain a preservative effective amount of a preservative. According to yet another embodiment, the product (or concentrate) is all natural. According to yet another embodiment, the product contains less than a smelling or coloring effective amount of the mastic extract.

In another embodiment, the product is substantially free or completely free of artificial (or synthetic) preservatives. According to one embodiment, the product contains less than about 2, 1.5, 1, 0.5, 0.4, 0.3, 0.25, 0.2, 0.15, 0.1, 0.09, 0.08, 0.07, 0.06, 0.05, 0.04, 0.03, 0.02, or 0.01% by weight of synthetic preservatives, based upon 100% total weight of product.

In one embodiment, the product (for example, a shampoo) has a pH below about 8. In another embodiment, the product has a pH from about 3 to about 9.

In one embodiment, the product is not intended for oral administration to an animal (e.g., a human subject). In another embodiment, the product is other than a foodstuff, pharmaceutical, cosmetic, or nutritional supplement. For example, the product can be a household (e.g., personal care), industrial, or institutional product. In one

preferred embodiment, the product is a personal care product, such as a shampoo, body lotion, conditioner, or soap.

The protectant, such as hydroxyacetophenone in combination with (b)(i) at least one of 1,3-propanediol and mastic extract and/or (b)(ii) at least one of vitamin B5, vitamin C, and vitamin E, may be incorporated into substrates susceptible to microbial growth as a protectant to inhibit microbial growth. Suitable substrates include, but are not limited to, a personal care product, such as a shampoo, conditioner, cream, lotion (such as body lotion), cosmetic, or soap; a household product, such as a fabric softener, laundry detergent, or hard surface cleaner; or an industrial product, such as paint, coatings, wood, textile, adhesive, sealant, leather, rope, paper, pulp, paper board, sheet rock, ceiling tiles, plastic, fuel, petroleum, oil, rubber working fluid, metal working fluid, starches (such as pet food starch), or mineral slurry, such as a slurry of clay, calcium carbonate, or titanium oxide (TiO₂).

Generally, the protectant, such as hydroxyacetophenone in combination with (b)(i) at least one of 1,3-propanediol and mastic extract and/or (b)(ii) at least one of vitamin B5, vitamin C, and vitamin E, acts quickly (e.g., reduces the microorganism (e.g., bacteria and/or fungi) count by 95, 99, 99.9, or 99.99% typically within an hour) and maintains efficacy (e.g., maintains less than 1,000 or 100 cfu/g) over long periods of time (e.g., for at least 7, 10, 14, or 28 days).

The protectant, such as that containing the hydroxyacetophenone in combination with (b)(i) at least one of 1,3-propanediol and mastic extract and/or (b)(ii) at least one of vitamin B5, vitamin C, and vitamin E, may include a solvent, such as water and water miscible solvents, including, but not limited to, alcohols (e.g., methanol, ethanol, propanol, iso-propanol, and butanol), glycols (e.g. glycerin, diglycerin, butylene glycol, butoxydiglycol, propylene glycol, and dipropylene glycol), esters, ethers, polyethers, and any combination of any of the foregoing. For example, the solvent may comprise water and one or more glycol and/or one or more alcohol, such as glycerin, phenoxyethanol, benzyl alcohol, or ethanol. A specific solvent system comprises water and a glycol, such

as glycerin. A second specific solvent system comprises water and an alcohol, such as ethanol.

The protectant may be incorporated into an aqueous or oil-based system or an emulsion. A suitable solvent for an oil-based system is phenoxyethanol and/or benzyl alcohol.

In one embodiment, the protectant is comprised of all-natural products. The protectant can be a liquid or a solid (e.g., a powder).

To prepare a formulation containing the product of the present invention, a concentrate of the protectant may be first prepared. The concentrate may be prepared by mixing the individual components. The concentrate may include from about 0.01 to about 100% by weight of the protectant such as from about 5 to about 80% by weight of the protectant, based upon 100% total weight of concentrate. For a two-component protectant, the concentrate may contain from about 0.01 to about 99.99% by weight of the hydroxyacetophenone and from about 99.99% to about 0.01% by weight of at least one of 1,3-propanediol and mastic extract, based upon 100% total weight of concentrate. Alternatively, the two-component protectant may contain from about 0.01 to about 99.99% by weight of the hydroxyacetophenone and from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate, with any remainder being a solvent (such as water). For a three-component protectant, the concentrate broadly contains (i) from about 0.01 to about 99.99% by weight of the hydroxyacetophenone, (ii) from about 99.99% to about 0.01% by weight of at least one of 1,3-propanediol and mastic extract, and (iii) from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate.

One embodiment is a concentrate comprising from about 5 to about 50% by weight of hydroxyacetophenone and from about 50% to about 95% by weight of 1,3-propanediol, based upon 100% total weight of the concentrate. In one preferred embodiment, the concentrate comprises from about 5 to about 30% by weight of

hydroxyacetophenone and from about 70% to about 95% by weight of 1,3-propanediol. In another preferred embodiment, the concentrate comprises from about 5 to about 20% by weight of hydroxyacetophenone and from about 80% to about 95% by weight of 1,3-propanediol. In a preferred embodiment, the concentrate comprises, consists of, or consists essentially of (i) from about 10 to about 30% by weight of hydroxyacetophenone and (ii) from about 70 to about 90% by weight of 1,3-propanediol. A more preferred embodiment is a concentrate comprising about 10% hydroxyacetophenone thereof and about 90% 1,3-propanediol. Another more preferred embodiment is a concentrate comprising about 20% hydroxyacetophenone thereof and about 80% 1,3-propanediol. In any of the aforementioned embodiments, the concentrate may include from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate. In one preferred embodiment, the concentrate comprises about 20% hydroxyacetophenone thereof, about 1% of at least one of vitamin B5, vitamin C, and vitamin E, and about 79% 1,3-propanediol. In a more preferred embodiment, the concentrate comprises about 20% hydroxyacetophenone thereof, about 1% vitamin B5, and about 79% 1,3-propanediol.

Another embodiment is a concentrate comprising from about 5 to about 50% by weight of hydroxyacetophenone and from about 50% to about 95% by weight of mastic water, based upon 100% total weight of the concentrate. In one preferred embodiment, the concentrate comprises from about 5 to about 30% by weight of hydroxyacetophenone and from about 70% to about 95% by weight of mastic water. In another preferred embodiment, the concentrate comprises from about 5 to about 20% by weight of hydroxyacetophenone and from about 80% to about 95% by weight of mastic water. A more preferred embodiment is a concentrate comprising about 10% hydroxyacetophenone thereof and about 90% mastic water. In any of the aforementioned embodiments, the concentrate may include from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate.

Yet another embodiment is a concentrate comprising from about 5 to about 50% by weight of hydroxyacetophenone and from about 50% to about 95% by weight of mastic oil, based upon 100% total weight of the concentrate. In one preferred embodiment, the concentrate comprises from about 5 to about 30% by weight of hydroxyacetophenone and from about 70% to about 95% by weight of mastic oil. In another preferred embodiment, the concentrate comprises from about 5 to about 20 or 30% by weight of hydroxyacetophenone and from about 80% to about 95% by weight of mastic oil. A more preferred embodiment is a concentrate comprising about 10% hydroxyacetophenone thereof and about 90% mastic oil. In any of the aforementioned embodiments, the concentrate may include from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate.

Yet another embodiment is a concentrate comprising hydroxyacetophenone, mastic water, and 1,3-propanediol. The concentrate may contain from about 5 to about 30% by weight of hydroxyacetophenone, from about 5% to about 95% by weight of mastic water, and from about 5 to about 95% by weight of 1,3-propanediol. In another embodiment, the concentrate comprises from about 5 to about 20% by weight of hydroxyacetophenone, from about 30% to about 85% by weight of mastic water, and from about 10 to about 40% by weight of 1,3-propanediol. In any of the aforementioned embodiments, the concentrate may include from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate. For example, the concentrate may comprise from about 5 to about 20 or 30% by weight of hydroxyacetophenone, from about 0.2 to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, from about 30% to about 85% by weight of mastic water, and from about 10 to about 40% by weight of 1,3-propanediol.

Yet another embodiment is a concentrate comprising hydroxyacetophenone, 1,3-propanediol, and ethylhexylglycerin. In one embodiment, the concentrate does not contain 3-phenylpropanol. In another embodiment, the concentrate does not contain 1,2-

hexanediol or 1,2-octanediol. In yet another embodiment, the concentrate comprises from about 60 to about 80% by weight of 1,3-propanediol, from about 10 to about 25% by weight (such as from about 10 to about 20% by weight) of 4-hydroxyacetophenone, and from about 1 to about 15% by weight (such as from about 1 to about 10% by weight or from about 5 to about 15% by weight) of ethylhexylglycerin, based upon 100% total weight of concentrate. In any of the aforementioned embodiments, the concentrate may include from about 1% to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate. In any of the aforementioned embodiments, the concentrate may include from about 0.01% (e.g., 0.1 or 0.2%) to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of concentrate. For example, the concentrate may comprise about 69% by weight of 1,3-propanediol, about 20% by weight of 4-hydroxyacetophenone, about 10% by weight of ethylhexylglycerin, and about 1% by weight of vitamin B5 (or DL-panthenol), based upon 100% total weight of concentrate.

In one embodiment, the concentrate comprises (or consists essentially of, or consists of) (a) from about 10 to about 20% by weight of 4-hydroxyacetophenone, (b) from about 60 to about 80% by weight of 1,3-propanediol, and (c) from about 0.1% or 1% to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E (such as vitamin B5).

Before use, the concentrate may be diluted, such as with the same solvent as was used in the concentrate, and/or incorporated into a product. Use dilutions of the composition typically include an effective amount of protectant to inhibit microbial growth (e.g., fungi growth).

Generally, use dilutions contain from about 0.0001% or 0.01% to about 2% by weight of the concentrate. According to one preferred embodiment, use dilutions contain from about 0.1 to about 1% by weight of the concentrate. In more preferred embodiments, the use dilution contains 0.2, 0.25 or 0.30% by weight of the concentrate.

According to another embodiment, the protectant is incorporated into a product at a concentration of about 0.1 to about 1 or 2% by weight, based upon 100% total weight of product.

Method of Inhibiting Microbial Growth

Another embodiment of the present invention is a method for killing and/or inhibiting the growth of microorganisms, such as bacteria (e.g., *S. aureus* (ATCC #6538), *P. aeruginosa* (ATCC #9027), and *E. coli* (ATCC #8739)) and/or fungi (including plant and tree fungi) (e.g., *Candida albicans*, *Aspergillus niger* and *Phytophthora ramrum*), on a substrate by applying an effective amount of the protectant to the substrate or incorporating an effective amount of the protectant into the substrate. The protectant may be applied to or incorporated into the substrate by any method known in the art including, but not limited to, brushing, dipping, soaking, vacuum impregnation, and pressure treatment.

The protectant may be prepared by mixing the components and optionally, one or more solvents, and/or adjuvants. The mixture may be heated and/or stirred to expedite mixing.

Example 1

The CTFA Preservative Challenge Test was performed on a shampoo containing the samples below against a mixture of fungi (*C. albicans* (ATCC# 10231) and *A. brasiliensis* (ATCC# 16404)) having an initial count of 7.9×10^5 cfu/mL or a mixture of bacteria having an initial count of 4×10^6 cfu/mL. The shampoos inoculated with bacteria were allowed to stand for 14 days and the shampoos inoculated with fungi were allowed to stand for 7 days. The samples were evaluated for surviving organisms on day 7 for fungi-innoculated shampoos and days 7 and 14 for bacteria-innoculated shampoos.

The results are shown in the table below.

Sample	Day 7 Count	
	Mixed Bacteria (cfu/mL)	Mixed Fungi (cfu/mL)
5% 1,3-propanediol	5.2×10^2	9.2×10^2
0.35% hydroxyacetophenone	3.2×10^2	1.5×10^2
1.8% 1,3-propanediol and 0.2% hydroxyacetophenone	< 10	< 10

From the table, synergism for the combinations above against mixed bacteria in shampoo was calculated by the method described in C. E. Kull *et al.*, "Mixtures of Quaternary Ammonium Compounds and Long-chain Fatty Acids as Antifungal Agents", Applied Microbiology, 9:538-541 (1961). The synergism value ($Q_A/Q_a + Q_B/Q_b$) was determined. Q_A and Q_B are concentrations of the first and second components, respectively, (in percent by weight) in the mixture, which yielded 100% retardation of the bacteria and fungi, i.e., resulted in a plate count of <10 cfu/g after 7 days. Q_a is the concentration of the first component alone (in percent by weight) required to yield 100% retardation of the bacteria or fungi. Q_b is the concentration of the second component alone (in percent by weight) required to yield 100% retardation of the bacteria or fungi. When the value of ($Q_A/Q_a + Q_B/Q_b$) is less than one, the mixture is synergistic. Values for ($Q_A/Q_a + Q_B/Q_b$) of 1 and greater represent an additive effect and an antagonistic effect, respectively. Here, ($Q_A/Q_a + Q_B/Q_b$) is $((1.8\% / >5\%) + (0.2\% / >0.35\%))$ or <0.93. Accordingly, the mixture of 1.8% 1,3-propanediol and 0.2% hydroxyacetophenone is synergistic.

Example 2

Aqueous solutions containing 2% of one of the protectants below were prepared by mixing and stored in sealed containers at 50° C for 4 weeks.

Protectant A: 20% 4-hydroxyacetophenone and 80% 1,3-propanediol

Protectant B: 20% 4-hydroxyacetophenone, 1% vitamin B5, and 79% 1,3-propanediol

After the 4 weeks of storage, the solution containing vitamin B5 (Protectant B) was clear and colorless, while the other solution (Protectant A) was dark (medium amber) due to degradation of the 4-hydroxyacetophenone.

All references, patent applications, and patents cited herein are hereby incorporated by reference.

Claims:

1. A product comprising an effective amount of (a) 4-hydroxyacetophenone and (b) at least one of a mastic extract and 1,3-propanediol to inhibit microbial growth in the product, wherein, when the product includes 4-hydroxyacetophenone and 1,3-propanediol, the product does not contain 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin.
2. The product of claim 1, wherein the product is not intended for oral administration to an animal.
3. The product of claim 1 or 2, wherein the product comprises mastic extract, and the mastic extract is selected from mastic oil, mastic water, and any combination of any of the foregoing.
4. The product of claim 3, wherein the mastic extract is mastic water.
5. The product of claim 3, wherein the mastic extract is mastic oil.
6. The product of any one of the preceding claims, wherein the mastic extract is soluble in water.
7. The product of any one of the preceding claims, wherein the mastic extract is naturally derived.
8. The product of any one of the preceding claims, wherein the product comprises 1,3-propanediol.
9. The product of claim 8, wherein the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol is no more than 1:3.
10. The product of any one of the preceding claims, wherein (i) the product is substantially free or free of artificial preservatives, (ii) the product is substantially free or free of parabens, or (iii) any combination of any of the foregoing.

11. The product of any one of the preceding claims, wherein the product is substantially free of parabens, formaldehyde donors, and isothiazolinones.

12. The product of any one of the preceding claims, wherein the product is free of parabens.

13. The product of any one of the preceding claims, wherein the product comprises from about 0.001 to about 10% by weight of 4-hydroxyacetophenone, based upon 100% total weight of the product.

14. The product of any one of the preceding claims, wherein the product comprises from about 0.001 to about 10% by weight of the mastic extract, based upon 100% total weight of the product.

15. The product of any one of the preceding claims, wherein the product comprises from about 0.001 to about 10% by weight of the 1,3-propanediol, based upon 100% total weight of the product.

16. The product of any one of claims 1-12, wherein the product comprises hydroxyacetophenone and mastic water.

17. The product of claim 16, wherein the weight ratio of 4-hydroxyacetophenone to mastic water ranges from about 5:95 to about 30:50.

18. The product of claim 16, wherein the weight ratio of 4-hydroxyacetophenone to mastic water ranges from about 5:95 to about 25:75.

19. The product of any one of claims 1-12, wherein the product comprises 4-hydroxyacetophenone and mastic oil.

20. The product of claim 19, wherein the weight ratio of 4-hydroxyacetophenone to mastic oil ranges from about 5:95 to about 30:50.

21. The product of any one of claims 1-12, wherein the product comprises 4-hydroxyacetophenone and 1,3-propanediol.

22. The product of claim 21, wherein the weight ratio of 4-hydroxyacetophenone to 1,3-propanediol ranges from about 5:95 to about 30:50.

23. The product of claim 21, wherein the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol ranges from about 10:90 to about 30:70.

24. The product of any one of claims 1-12, wherein the product comprises 4-hydroxyacetophenone, mastic water, and 1,3-propanediol.

25. The product of claim 24, wherein the product comprises from about 5 to about 20% by weight of hydroxyacetophenone. from about 30% to about 85% by weight of mastic water, and from about 10 to about 40% by weight of 1,3-propanediol.

26. The product of any one of the preceding claims, wherein the product further comprises at least one of vitamin B5, vitamin C, and vitamin E.

27. The product of claim 26, wherein the product comprises an effective amount of at least one of vitamin B5, vitamin C, and vitamin E to suppress degradation of 4-hydroxyacetophenone.

28. A product comprising an effective amount of (a) 4-hydroxyacetophenone, (b) at least one of vitamin B5, vitamin C, and vitamin E.

29. The product of claim 28, wherein the product comprises an effective amount of at least one of vitamin B5, vitamin C, and vitamin E to suppress degradation of 4-hydroxyacetophenone.

30. The product of any one of claims 26-29, wherein the weight ratio of (a) 4-hydroxyacetophenone and (b) the at least one of vitamin B5, vitamin C, and vitamin E is from about 1:1 to about 50:1.

31. The product of claim 30, wherein the weight ratio of (a) 4-hydroxyacetophenone and (b) the at least one of vitamin B5, vitamin C, and vitamin E is from about 10:1 to about 30:1.

32. The product of claim 31, wherein the weight ratio of (a) 4-hydroxyacetophenone and (b) the at least one of vitamin B5, vitamin C, and vitamin E is about 20:1.

33. The product of any one of claims 26-32, wherein the product comprises from about 0.001 to about 2% by weight of the at least one of vitamin B5, vitamin C, and vitamin E, based upon 100% total weight of the product.

34. The product of any one of claims 26-33, wherein the product does not contain (a) a glycerol ester of an alkane carboxylic acid or (b) an oligoglycerol ester of an alkane carboxylic acids.

35. The product of any one of the preceding claims, wherein the product is other than a foodstuff, pharmaceutical, cosmetic, or nutritional supplement.

36. The product of any one of the preceding claims, wherein the product is a household, industrial, or institutional product.

37. The product of any one of the preceding claims, wherein the product is a personal care product.

38. The product of claim 37, wherein the personal care product is a shampoo, body lotion, conditioner, or soap.

39. A concentrate comprising (a) 4-hydroxyacetophenone and (b) at least one of a mastic extract and 1,3-propanediol.

40. The concentrate of claim 39, wherein the concentrate comprises from about 5 to about 20% by weight of hydroxyacetophenone, from about 30% to about 85% by weight of mastic water, and from about 10 to about 40% by weight of 1,3-propanediol.

41. The concentrate of claim 39 or 40, further comprising at least one of vitamin B5, vitamin C, and vitamin E.

42. The concentrate of claim 41, wherein the concentrate comprises from about 0.2 to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E.

43. The concentrate of claim 41, wherein the concentrate comprises about 20% by weight of hydroxyacetophenone and 1% by weight of vitamin B5.

44. The concentrate of claim 41, wherein the concentrate comprises from about 5 to about 30% by weight of hydroxyacetophenone, from about 0.2 to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E, from about 30% to about 85% by weight of mastic water, and from about 10 to about 40% by weight of 1,3-propanediol.

45. The concentrate of claim 41, wherein the concentrate comprises (a) from about 10 to about 20% by weight of 4-hydroxyacetophenone, (b) from about 60 to about 80% by weight of 1,3-propanediol, and (c) from about 1 to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E.

46. A concentrate consisting of (a) 20% by weight of 4-hydroxyacetophenone, (b) 1% by weight of vitamin B5, and (b) 79% by weight of 1,3-propanediol.

47. A concentrate comprising (a) 4-hydroxyacetophenone and (b) at least one of vitamin B5, vitamin C, and vitamin E.

48. The concentrate of claim 47, wherein the weight ratio of (a) 4-hydroxyacetophenone and (b) the at least one of vitamin B5, vitamin C, and vitamin E is from about 1:1 to about 50:1.

49. The concentrate of claim 47 or 48, wherein the concentrate comprises from about 5 to about 40% by weight of hydroxyacetophenone and from about 0.2 to about 4% by weight of at least one of vitamin B5, vitamin C, and vitamin E.

50. The concentrate of claim 49, wherein the concentrate comprises about 20% by weight of hydroxyacetophenone and 1% by weight of vitamin B5.

51. A concentrate consisting of (a) from about 10% to about 30% by weight of 4-hydroxyacetophenone and (b) from about 70% to about 90% by weight of 1,3-propanediol.

52. The concentrate of claim 51, wherein the concentrate consists of (a) about 20% by weight of 4-hydroxyacetophenone and (b) about 80% by weight of 1,3-propanediol.

53. A product comprising an effective amount of (a) 4-hydroxyacetophenone, (b) 1,3-propanediol, and (c) ethylhexylglycerin to inhibit microbial growth in the product, wherein the product does not contain 3-phenylpropanol.

54. The product of claim 53, wherein the product does not contain 1,2-hexanediol or 1,2-octanediol.

55. The product of claim 53 or 54, wherein the weight ratio of 4-hydroxyacetophenone and 1,3-propanediol is no more than 1:3.

56. The product of any one of claims 53-55, wherein (i) the product is substantially free or free of artificial preservatives, (ii) the product is substantially free or free of parabens, or (iii) any combination of any of the foregoing.

57. The product of any one of claims 53-56, wherein the product is substantially free of parabens, formaldehyde donors, and isothiazolinones.

58. The product of any one of claims 53-57, wherein the product is free of parabens.

59. The product of any one of claims 53-58, wherein the product comprises from about 0.001 to about 10% by weight of 4-hydroxyacetophenone, based upon 100% total weight of the product.

60. The product of any one of claims 53-59, wherein the product comprises from about 0.001 to about 10% by weight of the 1,3-propanediol, based upon 100% total weight of the product.

61. The product of any one of claims 53-60, wherein the weight ratio of 4-hydroxyacetophenone to 1,3-propanediol ranges from about 5:95 to about 30:50.

62. The product of any one of claims 53-61, wherein the weight ratio of 4-hydroxyacetophenone to 1,3-propanediol ranges from about 1:3 to about 1:4.

63. The product of any one of claims 53-62, wherein the weight ratio of 4-hydroxyacetophenone to ethylhexylglycerin ranges from about 10:1 to about 3:1.

64. The product of any one of the preceding claims, wherein the product further comprises at least one of vitamin B5, vitamin C, and vitamin E.

65. The product of claim 64, wherein the product comprises an effective amount of at least one of vitamin B5, vitamin C, and vitamin E to suppress degradation of 4-hydroxyacetophenone.

66. A concentrate comprising (a) 4-hydroxyacetophenone, (b) 1,3-propanediol, and (c) ethylhexylglycerin, wherein the concentrate does not contain 3-phenylpropanol.

67. The concentrate of claim 66, wherein the concentrate comprises from about 60 to about 80% by weight of 1,3-propanediol, from about 10 to about 25% by weight of 4-hydroxyacetophenone, and from about 5 to about 15% by weight of ethylhexylglycerin, based upon 100% total weight of concentrate.

68. The concentrate of claim 66, wherein the concentrate comprises from about 60 to about 80% by weight of 1,3-propanediol, from about 10 to about 20% by weight of 4-hydroxyacetophenone, and from about 1 to about 10% by weight of ethylhexylglycerin, based upon 100% total weight of concentrate.

69. The concentrate of any one of claims 66-68, further comprising at least one of vitamin B5, vitamin C, and vitamin E.

70. The concentrate of claim 69, wherein the concentrate comprises from about 1 to about 5% by weight of at least one of vitamin B5, vitamin C, and vitamin E.

71. The concentrate of claim 69, wherein the concentrate comprises about 69% by weight of 1,3-propanediol, about 20% by weight of 4-hydroxyacetophenone, about 10% by weight of ethylhexylglycerin, and about 1% by weight of vitamin B5, based upon 100% total weight of concentrate.

72. A method of killing and/or inhibiting the growth of microorganisms on a substrate comprising applying an effective amount of a product of any one of claims 1-38 and 53-65.

73. A method of killing and/or inhibiting the growth of microorganisms on a substrate comprising applying an effective amount of (a) 4-hydroxyacetophenone and (b) at least one of a mastic extract and 1,3-propanediol to the substrate, wherein when the method includes applying 4-hydroxyacetophenone and 1,3-propanediol, the method does not include applying 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin to the substrate.

74. The method of claim 73, wherein the mastic extract is mastic water.

75. The method of claim 73, wherein the mastic extract is mastic oil.

76. A method of killing and/or inhibiting the growth of microorganisms on a substrate comprising applying an effective amount of (a) 4-hydroxyacetophenone, (b) at least one of vitamin B5, vitamin C, and vitamin E, and (c) optionally, at least one of a mastic extract and 1,3-propanediol to the substrate.

77. The method of claim 76, wherein when the method includes applying 4-hydroxyacetophenone and 1,3-propanediol, the method does not include applying 3-phenylpropanol, 1,2-hexanediol, 1,2-octanediol, or ethylhexylglycerin to the substrate.

78. A method of killing and/or inhibiting the growth of microorganisms on a substrate comprising applying an effective amount of (a) 4-hydroxyacetophenone, (b) 1,3-propanediol, and (c) ethylhexylglycerin to the substrate, wherein the method does not include applying 3-phenylpropanol, 1,2-hexanediol, or 1,2-octanediol to the substrate.

79. The method of any one of claims 72-78, wherein the microorganisms are selected from *S. aureus*, *P. aeruginosa*, *E. coli*, *Candida albicans*, *Aspergillus niger* and *Phytophthora ramrum*.