

NOVEL OXY-NITRILES

FIELD OF THE INVENTION

The present invention relates generally to the field of fragrances. More particularly, the present invention relates to novel aromachemicals that provide perfumes and other articles with unique properties and advantages not shared by other aromachemicals. These derivatives find utility in any and all applications requiring certain aroma themes. The invention also relates to mixtures of these derivatives, methods for their preparation and their use as perfume materials for application to a variety of substrates.

BACKGROUND OF THE INVENTION

There are a large number and variety of known fragrances used as ingredients in perfumes and in a varied range of other products. For example, perfumes for application in laundry detergents, fabric softeners, rinse conditioners and other products intended for use on textile fibers primarily contain fragrances.

It should be mentioned that a large number of compounds belonging to the nitrile chemical family are known in the perfume industry. Nitriles have been known for use in augmenting or enhancing the aroma of perfume compositions, perfumed articles and colognes for a number of years. In the context of the present invention, one can cite the nitriles specified hereinafter, which are currently used in perfumery, in particular in functional perfumery.

Various aliphatic and aromatic nitriles were developed because of their good stability in aggressive media and their general odor similarity with the corresponding aldehydes, many of which were already used in perfumery before the development of the nitriles. Various examples are described in S. Arctander, Perfume and Flavor Chemicals (Montclair,

N.J., 1969). Certain ether-nitriles have been described in the art. They were prepared by addition of aliphatic alcohols to acrylonitrile, methacrylonitrile or crotonitrile. The ether-nitriles are reported to have odors reminiscent of the alcohols from which they were prepared. Thus, J. Kulesza et al, *Riechstoffe, Aromen, Körperpflegemittel*. Nr. 2/75, pages 34, 37 describe a series of addition products of alcohols to acrylonitrile. From the odor descriptions it is clear that the odors of most ether-nitriles are similar to those of the corresponding alcohols. Similarly, in DE-A-2601825 the addition products of various saturated and unsaturated aliphatic alcohols to acrylonitrile have been described as possibly of interest in perfumery and as polar solvents.

Although this reference gives very little information on the actual odors of the compounds, it does say that the odor is determined, at least in part, by the corresponding alcohol.

Geranyl nitrile (3,7-dimethyl-2,6-octadienenitrile) possesses a strong green, chemical odor resembling that of citral (Z-3,7-dimethyl-2,6-octadienal), the latter being itself a compound of widespread use in perfumery applications and of natural occurrence.

Citronellyl nitrile (3,7-dimethyl-6-octenenitrile) shows an olfactive note reminiscent of the odor of lemon, with an undertone characteristic of the nitriles. The citrus note is likewise quite pronounced in Ozonil.RTM. (mixture of 2-tridecenenitrile and 3-tridecenenitrile; origin: Haarmann & Reimer, Germany), but there are also present notes of the mandarine-fruity, peach type, which are associated with a floral undertone.

Finally, citronitrile (3-methyl-5-phenyl-2-pentenitrile) shows an odor of the same type as the compounds mentioned beforehand, namely of the fruity-citrus type.

The perfume uses of other nitrile-containing derivatives which contain phenyl moieties are well known in the prior art. Thus, such compounds are disclosed in U.S. Pat. No. 5,143,899 issued on Sep. 1, 1992 (title "Process For Preparing Phenyl Butyronitriles And Perfumery

Use Of 2,2-Dimethyl-4-Phenyl Valeronitrile"). Other perfume uses of nitrile-containing derivatives which also contain phenyl moieties which are shown in U.S. Pat. No. 4,837,351 issued on Jun. 6, 1989 wherein it is indicated that such compounds have a powerful, fresh, fruity, floral odor note accompanied by a citrus, green topnote. Furthermore, U.S. Pat. No. 3,325,369 discloses the use of cinnamonnitrile as a material useful in augmenting or enhancing the aroma of perfume compositions.

In addition, a mixture of such compounds is marketed as TABACENE® by Firmenich et cie, S.A. of Geneva, Switzerland (as referred to in the Fragrance Materials Association of The United States, Inc. "Trademark And Coined Names Catalogue" on page T1).

Detergents, deodorants or antiperspirants and soaps are examples of products which are aggressive media, in which citral, for example, which can be considered as the typical compound representing the citrus-type odor, with its powerful citrus-green note, is unstable, preventing it from being used in functional perfumery, and this in spite of its odor which is very prized by perfumers.

Now, in spite of showing promising olfactive properties, the known nitriles possess olfactive notes that are less characteristic of lemon, less fresh-citrus, and a fatty-metallic connotation is found in all these nitriles. For these reasons, the search for nitriles stable in aggressive media and possessing an odor close to the citrus-green note of the odor of citral continues to be a daunting task.

Novel fragrance and flavor aromachemicals are disclosed herein as well as methods of making the derivatives, uses of the aromachemicals and articles of manufacture including the aromachemicals. These novel derivatives find utility in any and all applications requiring certain aroma themes. The invention also relates to mixtures of these derivatives, methods for

their preparation and their use as perfume materials for application to a variety of substrates.

SUMMARY OF THE INVENTION

One embodiment of the invention is directed toward aromachemicals having the formula:



wherein: R is straight or branched chain alkyl, alkenyl having 1-16 carbon atoms, aryl, aralkyl, alkaryl, or substituted derivatives thereof.

A preferred compound is that according to the above formula wherein R is citronellyl having the formula:



A second embodiment of the invention concerns compositions, products, preparations or articles having improved aroma, fragrance or odor characteristics containing as active ingredient a compound described above or a mixture thereof.

Another embodiment of the invention relates to compositions, products, preparations or articles having improved flavor or taste characteristics containing as active ingredient a compound described above or a mixture thereof.

A further embodiment of the invention concerns methods to confer, improve, enhance or modify the taste or flavor property of a composition, product, preparation or article which comprises adding thereto a flavor effective amount of a compound described above or a mixture thereof.

A still further embodiment of the invention relates to a method to confer, improve, enhance or modify the aroma, fragrance or odor characteristics of compositions, products, preparations or articles which comprises adding thereto an aroma, fragrance or odor effective amount of a compound described above or a mixture thereof.

An additional embodiment of the invention concerns articles of manufacture comprising a compound described above or a mixture thereof.

The aromachemicals of the invention may be prepared according to the method set forth below which is directed to the synthesis of the above-noted preferred compound.

The aromachemicals of the invention possess the odor profile of the corresponding nitriles but with a greatly lessened unpleasant oily-metallic note typical of the nitriles.

Examples of suitable articles of manufacture in which the derivatives of the invention may be incorporated include perfumes and colognes, candles, air fresheners, detergent compositions and disinfectants.

DETAILED DESCRIPTION OF THE INVENTION

Examples of suitable articles of manufacture in which the derivatives of the invention may be incorporated include perfumes and colognes, candles, air fresheners, detergent compositions and disinfectants.

The compositions, products, preparations and articles in which the compounds and derivatives of the invention may be incorporated include candles, air fresheners, perfumes, fragrances, colognes, soaps, bath or shower gels, shampoos or other hair care products, cosmetic preparations, body odorants, deodorants or antiperspirants, liquid or solid fabric detergents or softeners, bleach products (hypochlorites), disinfectants, all-purpose household or industrial cleaners, foods, flavorings, beverages such as beer and soda, denture cleansers (tablets), flavored orally-delivered products such as lozenges, candies, chewing gums, matrices, pharmaceuticals and the like.

The compounds can be used as perfuming ingredients, as single compounds or as mixture thereof, preferably at a range of at least about 30% by weight of the perfume composition, more preferably at a range of at least about 60% by weight of the composition.

The compounds can even be used in their pure state or as mixtures, without added components. The olfactive characteristics of the individual compounds are also present in mixtures thereof, and mixtures of these compounds can be used as perfuming ingredients. This may be particularly advantageous where separation and/or purification steps can be avoided by using compound mixtures.

The derivatives of the invention can be included in virtually any article of manufacture that can include conventional aromachemicals, or for that matter, other fragrances, whether natural or artificial. Examples include bleach, detergents, flavorings and fragrances, beverages, including alcoholic beverages, and the like. The derivatives of the invention can be used in applications like soaps, shampoos, body deodorants and antiperspirants, solid or liquid detergents for treating textiles, fabric softeners, detergent compositions and/or all-purpose cleaners for cleaning dishes or various surfaces, for both household and industrial use. Of course, the use of the compounds is not limited to the above-mentioned products, as they be used in other current uses in perfumery, namely the perfuming of soaps and shower gels, hygiene or hair-care products, as well as of body deodorants, air fresheners and cosmetic preparations, and even in fine perfumery, namely in perfumes and colognes. The products of the invention also find utility in foods, flavorings, beverages such as beer and soda, denture cleansers (tablets), flavored orally-delivered products such as lozenges, candies, chewing gums, matrices, pharmaceuticals and the like. These uses are described in more detail below.

In all cited applications, the derivatives of the invention can be used alone, in admixture with each other, or in admixture with other perfuming ingredients, solvents or adjuvants of current use in the art. The nature and the variety of these co-ingredients do not require a more detailed description here, which, moreover, would not be exhaustive, and the

person skilled in the art will be able to choose the latter through its general knowledge and as a function of the nature of the product to be perfumed and of the desired olfactive effect.

These perfuming ingredients typically belong to chemical classes as varied as alcohols, aldehydes, ketones, esters, ethers, acetates, nitrites, terpene hydrocarbons, sulfur- and nitrogen containing heterocyclic compounds, as well as essential oils of natural or synthetic origin. A large number of these ingredients described in reference textbooks such as the book of S. Arctander, *Perfume and Flavor Chemicals*, 1969, Montclair, N.J., USA, the contents of which are hereby incorporated by reference in its entirety, or its more recent versions, or in other works of similar nature.

The proportions in which the derivatives of the invention can be incorporated in the various products vary within a large range of values. These values depend on the nature of the article or product that one desires to perfume and the odor effect searched for, as well as on the nature of the co-ingredients in a given composition when the compounds are used in admixture with perfuming co-ingredients, solvents or adjuvants of current use in the art.

As an example, the derivatives of the invention are typically present at concentrations between about 0.1 and about 10%, or even more, by weight of these compounds relative to the weight of the perfuming composition in which they are incorporated. Far lower concentrations than those mentioned above can be used when the compounds are directly applied for perfuming the various consumer products cited beforehand.

The compounds may be used in detergents containing bleaching agents and activators such as, for example, tetraacetythylenediamine (TAED), hypohalites, in particular hypochlorite, peroxygenated bleaching agents such as, for example, perborates, etc. The compounds can also be used in body deodorants and antiperspirants, for example, those containing aluminum salts. These embodiments are described in more detail below.

In addition to the derivatives described herein, the compositions herein include a deterative surfactant and optionally, one or more additional detergent ingredients, including materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., perfumes, colorants, dyes, etc.). Non-limiting examples of synthetic deterative surfactants useful herein typically at levels from about 0.5% to about 90%, by weight, include the conventional C1-18 alkyl benzene sulfonates ("LAS") and primary, branch-chain and random C10-20 alkyl sulfates ("AS"), and the like.

Preferred compositions incorporating only synthetic detergents have a detergent level of from about 0.5% to 50%. Compositions containing soap preferably comprise from about 10% to about 90% soap.

The compositions herein can contain other ingredients such as enzymes, bleaches, fabric softening agents, dye transfer inhibitors, suds suppressors, and chelating agents, all well known within the art.

The derivatives described herein can be incorporated into beverages and impart various flavorings to the beverages. The beverage composition can be a cola beverage composition, and can also be coffee, tea, dairy beverage, fruit juice drink, orange drink, lemon-lime drink, beer, malt beverages, or other flavored beverage. The beverages can be in liquid or powdered form. The beverage compositions can also include one or more flavoring agents; artificial colorants; vitamin additives; preservatives; caffeine additives; water; acidulants; thickeners; buffering agents; emulsifiers; and or fruit juice concentrates.

Artificial colorants which may be used include caramel color, yellow 6 and yellow 5. Useful vitamin additives include vitamin B2, vitamin B6, vitamin B12, vitamin C (ascorbic acid), niacin, pantothenic acid, biotin and folic acid. Suitable preservatives include sodium or potassium benzoate. Salts which may be used include sodium, potassium and magnesium

chloride. Exemplary emulsifiers are gum arabic and purity gum, and a useful thickener is pectin. Suitable acidulants include citric, phosphoric and malic acid, and potential buffering agents include sodium and potassium citrate.

In one embodiment, the beverage is a carbonated cola beverage. The pH is generally about 2.8 and the following ingredients can be used to make the syrup for these compositions: Flavor Concentrate, including one or more of the derivatives described herein (22.22 ml), 80% Phosphoric Acid (5.55 g), Citric Acid (0.267 g), Caffeine (1.24 g), artificial sweetener, sugar or com syrup (to taste, depending on the actual sweetener) and Potassium Citrate (4.07 g). The beverage composition can be prepared, for example, by mixing the foregoing syrup with carbonated water in a proportion of 50 ml syrup to 250 ml of carbonated water.

Flavored food and pharmaceutical compositions including one or more of the derivatives described herein can also be prepared. The derivatives can be incorporated into conventional foodstuffs using techniques well known to those of skill in the art. Alternatively, the derivatives can be incorporated within polymeric particles, which can, in turn, be dispersed within and/or over a surface of an orally-deliverable matrix material, which is usually a solid or semi-solid substrate. When used in chewable compositions, the derivatives can be released into the orally-deliverable polymeric matrix material as the composition is chewed and held in the mouth, thus prolonging the flavor of the composition. In the case of dried powders and mixes, the flavor can be made available as the product is consumed or be released into the matrix material as the composition is further processed. When two flavors are combined with the polymeric particles, the relative amounts of the additives can be selected to provide simultaneous release and exhaustion of the compounds. In one embodiment, the flavored composition includes an orally-deliverable matrix material; a plurality of water insoluble polymeric particles dispersed in the orally-deliverable matrix

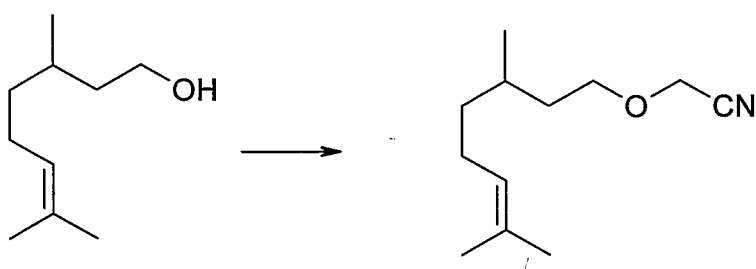
material, where the polymeric particles individually define networks of internal pores and are non-degradable in the digestive tract; and one or more derivatives as described herein entrapped within the internal pore networks. The derivatives are released as the matrix is chewed, dissolved in the mouth, or undergoes further processing selected from the group consisting of liquid addition, dry blending, stirring, mixing, heating, baking, and cooking. The orally-deliverable matrix material can be selected from the group consisting of gums, latex materials, crystallized sugars, amorphous sugars, fondants, nougats, jams, jellies, pastes, powders, dry blends, dehydrated food mixes, baked goods, batters, doughs, tablets, and lozenges.

A flavorless gum base can be combined with a derivative of the invention or other suitable derivative as described herein to a desired flavor concentration. Typically, a blade mixer is heated to about 110°F, the gum base is preheated so that it is softened, and the gum base is then added to the mixer and allowed to mix for approximately 30 seconds. The flavored derivative is then added to the mixer and mixed for a suitable amount of time. The gum can be then removed from the mixer and rolled to stick thickness on waxed paper while warm.

In one embodiment, the derivatives described herein are incorporated into a system which can release a fragrance in a controlled manner. These include substrates such as air fresheners, laundry detergents, fabric softeners, deodorants, lotions, and other household items. The fragrances are generally one or more derivatives of essential oils as described herein, each present in different quantities. U.S. Pat. No. 4,587,129, the contents of which are hereby incorporated by reference in their entirety, describes a method for preparing gel articles which contain up to 90% by weight of fragrance or perfume oils. The gels are prepared from a polymer having a hydroxy (lower alkoxy) 2-alkeneoate, a hydroxy (lower alkoxy) lower alkyl 2-alkeneoate, or a hydroxy poly (lower alkoxy)lower alkyl 2-alkeneoate

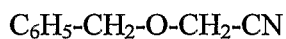
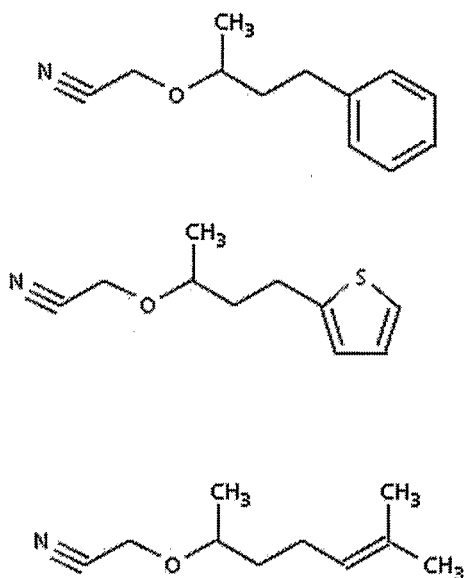
and a polyethylenically unsaturated crosslinking agent. These materials have continuous slow release properties, i.e., they release the fragrance component continuously over a long period of time. Advantageously, all or a portion of those derivatives that include an aldehyde group can be modified to include an acetal group, which can cause the formulations to release fragrance over a period of time as the acetal hydrolyzes to form the aldehyde compound.

EXAMPLE 1



To a suspension of sodium hydride (0.60g) in THF (20mL) was added B-citronellol and the solution stirred for one hour at reflux. The solution was cooled to room temperature and chloroacetonitrile (0.90mL) was added. The reaction was stirred at room temperature for two days then worked up under normal aqueous conditions. Chromatography gave the alkylated product as a colorless oil.

Other preferred aromachemical compounds coming within the scope of the present invention include those having the structural formulae:



Having hereby disclosed the subject matter of the present invention, it should be apparent that many modifications, substitutions, and variations of the present invention are possible in light thereof. It is to be understood that the present invention can be practiced other than as specifically described. Such modifications, substitutions and variations are intended to be within the scope of the present application.

I CLAIM:

1. A compound or a mixture of compounds comprising an aromachemical compound of the formula:

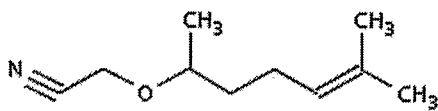


wherein: R is straight or branched chain alkyl, alkenyl having 1-16 carbon atoms, aryl, aralkyl, alkaryl, thiophenyl or substituted derivatives thereof.

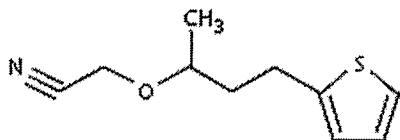
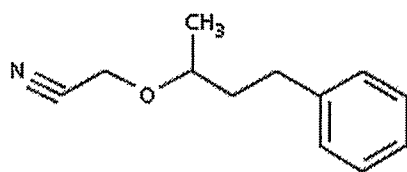
2. An aromachemical compound of claim 1 having the formula:



3. An aromachemical compound of claim 1 having the formula:



4. An aromachemical compound of claim 1 having one of the formulae:



5. A composition, product, preparation or article having improved aroma, fragrance or odor characteristics containing as active ingredient a compound or mixture of compounds of claim 1.

6. The composition, product, preparation or article of claim 5, wherein the compound or mixture of compounds is present in an amount of at least 30 percent by weight.

7. The composition, product, preparation or article of claim 5, wherein the compound or mixture of compounds is present in an amount of at least 60 percent by weight.

8. A composition, product, preparation or article of claim 5 in the form of a perfume, fragrance or cologne, a soap, a bath or shower gel, a shampoo or other hair care product, a cosmetic preparation, a body odorant, deodorant or antiperspirant, an air freshener, a liquid or solid fabric detergent or softener, bleach product, disinfectant or an all-purpose household or industrial cleaner.

9. A perfuming composition, product, preparation or article of claim 8, wherein the compound or mixture of compounds is present in admixture with other perfuming ingredients, solvents, or adjuvants of current use in the art.

10. A perfumed article according to claim 8, in the form of a perfume or cologne, a soap, a bath or shower gel, a shampoo or other hair care product, a cosmetic preparation, a body deodorant or antiperspirant, an air freshener, a fabric detergent or softener or an all-purpose household cleaner.

11. A composition, product, preparation or article of claim 10 in the form of a perfume wherein the compound or mixture of compounds is in admixture with other perfuming ingredients, solvents or adjuvants.

12. A body deodorant or antiperspirant composition, product, preparation or article, of claim 10.

13. A body deodorant or antiperspirant composition, product, preparation or article, of claim 12, wherein the compound or mixture of compounds is present in admixture with other perfuming ingredients, solvents, or adjuvants of current use in the art.

14. A detergent composition, product, preparation or article of claim 10.

15. A detergent composition, product, preparation or article of claim 14 wherein the compound or mixture of compounds is in admixture with other detergent ingredients, solvents or adjuvants.

16. A bleach composition, product, preparation or article of claim 10.

17. A bleach composition, product, preparation or article of claim 16 wherein the compound or mixture of compounds is in admixture with other bleach ingredients, solvents or adjuvants.

18. A composition, product, preparation or article of claim 10 in the form of a disinfectant.

19. The disinfectant composition, product, preparation or article of claim 18 wherein the compound or mixture of compounds is in admixture with other disinfectant ingredients, solvents or adjuvants.

20. A composition, product, preparation or article having improved flavor or taste characteristics containing as active ingredient a compound or mixture of compounds of claim 1.

21. A composition, product, preparation or article of claim 20 in the form of a beverage.

22. A beverage composition, product, preparation or article of claim 21 wherein the compound or mixture of compounds is in admixture with other beverage ingredients, solvents or adjuvants.

23. A composition, product, preparation or article of claim 20 in the form of a flavoring.

24. A flavoring composition, product, preparation or article of claim 23 wherein the compound or mixture of compounds is in admixture with other flavoring ingredients, solvents or adjuvants.

25. A composition, product, preparation or article of claim 20 in the form of a food.

26. A food composition, product, preparation or article of claim 25 wherein the compound or mixture of compounds is in admixture with other food ingredients, solvents or adjuvants.

27. A composition, product, preparation or article of claim 20 in the form of a chewing gum.

28. A chewing gum composition, product, preparation or article of claim 27 wherein the compound or mixture of compounds is in admixture with other chewing gum ingredients, solvents or adjuvants.

29. A composition, product, preparation or article of claim 20 in the form of a pharmaceutical.

30. A pharmaceutical composition, product, preparation or article of claim 29 wherein the compound or mixture of compounds is in admixture with other pharmaceutical ingredients, solvents or adjuvants.

31. A composition, product, preparation or article of claim 20 in the form of an orally-deliverable matrix material.

32. A composition, product, preparation or article of claim 31 wherein the compound or mixture of compounds is in admixture with other matrix material ingredients, solvents or adjuvants.

33. A method to confer, improve, enhance or modify the taste or flavor property of a composition, product, preparation or article which comprises adding thereto a flavor effective amount of a compound or mixture of compounds of claim 1.

34. The method of claim 33 wherein said composition, product, preparation or article is in the form of a beverage.

35. The method of claim 33 wherein said composition, product, preparation or article is in the form of a flavoring.

36. The method of claim 33 wherein said composition, product, preparation or article is in the form of a food.

37. The method of claim 33 wherein said composition, product, preparation or article is in the form of a chewing gum.

38. The method of claim 33 wherein said composition, product, preparation or article is in the form of a pharmaceutical.

39. The method of claim 33 wherein said composition, product, preparation or article is in the form of an orally deliverable matrix.

40. A method to confer, improve, enhance or modify the aroma, fragrance or odor characteristics of a composition, product, preparation or article which comprises adding thereto an aroma, fragrance or odor effective amount of a compound or mixture of compounds of claim 1.

41. The method of claim 40 wherein said composition, product, preparation or article is in the form of a perfume.

42. The method of claim 40 wherein said composition, product, preparation or article is in the form of a body odorant, deodorant or antiperspirant.

43. The method of claim 40 wherein said composition, product, preparation or article is in the form of a detergent.

44. The method of claim 40 wherein said composition, product, preparation or article is in the form of a bleach product.

45. The method of claim 40 wherein said composition, product, preparation or article is in the form of a disinfectant.

46. An article of manufacture comprising packaging material and an aroma, odor, fragrance, taste or flavor enhancing agent contained within said packaging material, wherein said agent is effective for the enhancement of the aroma, odor, fragrance, taste or flavor of a composition, preparation, product or article to which it is added, and wherein said packaging material comprises a label which indicates that said agent can be used for enhancing aroma, odor, fragrance, taste or flavor, and wherein said agent is a compound or mixture of compounds of claim 1.