

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

05 December 2019 (05.12.2019)



(10) International Publication Number

WO 2019/230974 A1

(51) International Patent Classification:

C07C 47/277 (2006.01) C11B 9/00 (2006.01)

(21) International Application Number:

PCT/JP2019/021862

(22) International Filing Date:

31 May 2019 (31.05.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/679,384 01 June 2018 (01.06.2018) US

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(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: FRAGRANCE MATERIAL

(57) Abstract: The present disclosure is related to the synthesis and application of novel compounds having unique and desired fragrance characteristics. The fragrance compounds of the present disclosure can be used alone or incorporated into fragrance compositions and/or consumer products to modify or enhance the odor of the fragrance compositions and/or consumer products.



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Description

Title of Invention: FRAGRANCE MATERIAL

Technical Field

[0001] The presently disclosed subject matter relates to compounds having uses in the fragrances as well as compositions containing such compounds.

Background Art

[0002] The fragrance industry is constantly reliant on the development of new chemicals with favorable organoleptic properties. Such new fragrance compounds can be used to create new fragrance compositions having unique odor characteristics or can modify or enhance the organoleptic properties of existing fragrance compositions. Fragrance compositions are used in a wide variety of consumer products, including fine fragrances, personal care products, home care products, air care products, and the like.

[0003] Differences in chemical structures can significantly impact odor, notes, and other organoleptic, chemical, and physical characteristics. Thus, there is a continuous need for new chemical structures that have favorable organoleptic properties. Once identified, these novel chemical compounds can provide perfumers and other persons with the ability to create new, unique fragrances.

[0004] The presently disclosed subject matter addresses these and other needs by providing a new fragrance compound with unique and desirable organoleptic properties, as discussed in detail below.

Summary of Invention

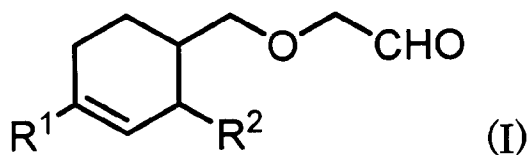
Technical Problem

[0005] The present disclosure provides fragrance compounds having natural green, floral, fruity odor notes with a fresh aquatic note. These compounds can be used alone or incorporated into a fragrance composition and/or consumer product.

Solution to Problem

[0006] In certain aspects, the present disclosure provides a fragrance composition comprising a fragrance compound of formula (I), or an isomer thereof.

[0007] [Chem.1]



[0008] Here, R¹ and R² are independently selected from hydrogen atom and methyl group.

[0009] In certain embodiments, the fragrance compound is selected from the group

consisting of 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde; 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde; isomers thereof; and combinations thereof.

- [0010] As embodied herein, the fragrance composition can further include an additional fragrance compound selected from a citrus compound, a floral compound, a fruity compound, a gourmand compound, a green compound, a musk compound, a spicy compound, a woody compound, an aldehydic compound, a balsamic compound, a marine compound, a mossy compound, an amber compound, an animalic compound, a herbaceous compound, a piney compound, a powdery compound, and combinations thereof. In certain embodiments, the fragrance composition can further include a solvent.
- [0011] In certain aspects, the present disclosure also provides methods of modifying the odor properties of a fragrance composition, including adding to the fragrance composition an olfactory effective quantity of a fragrance compound of formula (I). For example, the fragrance compound can be 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde or 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde.
- [0012] In certain other aspects, the present disclosure provides a consumer product comprising a consumer product base and a fragrance compound of formula (I) or an isomer thereof. The fragrance compound can be selected from the group consisting of 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde; 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde; isomers thereof; and combinations thereof. For example, the fragrance compound can be 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde or 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde.
- [0013] In certain embodiments, the consumer product is selected from a fine fragrance, a personal care product, a home care product, and an air care product. For example, the fine fragrance can be selected from parfum, extrait de parfum, eau de parfum, millesime, parfum de toilette, eau de toilette, eau de cologne, body splash, after shave, body mists, and baby colognes. The personal care product can be selected from lotions, creams, moisturizers, body washes, hand soaps, shampoos, conditioners, and soaps. The home care product can be selected from fabric conditioner, fabric softener, laundry detergent, laundry additive, rinse additive, bleach, dryer sheets, perfume beads, car care products, dishwashing detergent, and hard surface cleaners. The air care product can be selected from a candle, aerosol, air freshener, liquid electric air freshener, fragrance diffuser, gel air freshener, plug-in air freshener, plug-in oil, and wax melt.
- [0014] The present disclosure also provides methods of modifying the odor properties of a consumer product, including adding to a consumer product base an olfactory effective quantity of a fragrance compound of formula (I), or an isomer thereof.

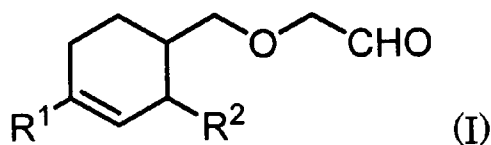
- [0015] In certain other aspects, the present disclosure provides methods of manufacturing a consumer product comprising admixing a fragrance compound of formula (I), or an isomer thereof, with a consumer product base. In certain embodiments, the fragrance compound is incorporated into a fragrance composition prior to admixing with the consumer product base.
- [0016] In additional aspects, the present disclosure provides novel compounds of the above formula (I), or an isomer thereof, wherein R¹ and R² are independently selected from hydrogen atom and methyl group. In additional aspects, the novel compounds are selected from the group consisting of 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde; 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde; and isomers thereof.
- [0017] The foregoing has outlined broadly the features and technical advantages of the present application in order that the detailed description that follows can be better understood. Additional features and advantages of the application will be described hereinafter which form the subject of the claims of the application. It should be appreciated by those skilled in the art that the conception and specific embodiment disclosed can be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present application. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the application as set forth in the appended claims. The novel features which are believed to be characteristic of the application, both as to its organization and method of operation, together with further objects and advantages will be better understood from the following description.

Advantageous Effects of Invention

- [0018] The present disclosure provides fragrance compounds having natural green, floral, fruity odor notes with a fresh aquatic note. These compounds can be used alone or incorporated into a fragrance composition and/or consumer product.

Description of Embodiments

- [0019] As noted above, to date, there remains a need in the art for fragrance compounds having improved organoleptic properties. Additionally, there remains a need for fragrance compositions and consumer products comprising such fragrance compounds.
- [0020] The present disclosure relates to compounds of formula (I), or an isomer thereof.
- [0021] [Chem.2]



- [0022] Here, R¹ and R² are independently selected from hydrogen atom and methyl group.

[0023] For example, the compounds of the present disclosure include, but are not limited to, 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde; 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde; and isomers thereof; and combinations thereof.

[0024] The presently disclosed compounds can have natural green, floral, fruity odor notes with a fresh aquatic note. These compounds can be used alone or incorporated into a fragrance composition to modify or enhance the odor of existing fragrance compositions, solvent, media, consumer products, and the like.

[0025] 1. Definitions

The terms used in this specification generally have their ordinary meanings in the art, within the context of this disclosed subject matter and in the specific context where each term is used. Certain terms are discussed below, or elsewhere in the specification, to provide additional guidance to the practitioner in describing the compositions and methods of the disclosed subject matter and how to make and use them.

[0026] As used herein, the use of the word “a” or “an” when used in conjunction with the term “comprising” in the claims and/or the specification can mean “one”, but it is also consistent with the meaning of “one or more”, “at least one”, and “one or more than one”. Still further, the terms “having”, “including”, “containing” and “comprising” are interchangeable and one of skill in the art is cognizant that these terms are open ended terms.

[0027] The term “about” or “approximately” means within an acceptable error range for the particular value as determined by one of ordinary skill in the art, which will depend in part on how the value is measured or determined, i.e., the limitations of the measurement system. For example, “about” can mean within 3 or more than 3 standard deviations, per the practice in the art. Alternatively, “about” can mean a range of up to 20%, preferably up to 10%, more preferably up to 5%, and more preferably still up to 1% of a given value. Alternatively, particularly with respect to biological systems or processes, the term can mean within an order of magnitude, preferably within 5-fold, and more preferably within 2-fold, of a value.

[0028] As used herein, the term “weight percent” or “wt-%” is meant to refer to the quantity by weight of a component in a material as a percentage of the total wet weight of the material (i.e., a fragrance formulation). Unless otherwise specified, all amounts expressed as a percentage herein represent the amount in weight percent.

[0029] The terms “fragrance composition”, “fragrance”, “fragrance formulation”, “perfume” and “perfume composition” mean the same to refer to a perfumed composition that is a mixture of fragrance compounds including for example, alcohols, aldehydes, ketones, esters, ethers, acetates, nitriles, terpene hydrocarbons, nitrogenous or sulphurous heterocyclic compounds and essential oils of natural or synthetic origin, which are admixed

so that the combined odors of the individual components produce a pleasant or desired fragrance. Many of these ingredients are listed in reference texts such as S. Arctander, *Perfume and Flavor Chemicals*, 1969, Montclair, New Jersey, USA (or any of its more recent versions), which is herein incorporated by reference in its entirety. As described herein, fragrance compositions can be a mixture of any number of fragrance compounds. For example, fragrance compositions include “simple accords”, e.g., having fewer than 10 fragrance compounds, and “complex fragrances”, e.g., having more than 30 fragrance compounds. In certain embodiments, the fragrance compositions of the present disclosure can be a combination of 2 or more accords.

[0030] As used herein, the term “improving” is understood to mean raising a fragrance composition to a more desirable character, the term “enhancing” is understood to mean making the fragrance composition greater in effectiveness, such as strength, and the term “modifying” is understood to mean providing the fragrance composition with a change in character.

[0031] As used herein, the term “isomers” refers to different compounds that have the same molecular formula but differ in arrangement and configuration of the atoms. Also as used herein, the term “stereoisomer” refers to any of the various stereo isomeric configurations which may exist for a given compound of the presently disclosed subject matter and includes geometric isomers. It is understood that a substituent may be attached at a chiral center of a carbon atom. Therefore, the presently disclosed subject matter includes enantiomers, diastereomers or racemates of the compound. Also as used herein, the terms “constitutional isomers” refers to different compounds which have the same numbers of, and types of, atoms but the atoms are connected differently.

[0032] As used herein, the term “diastereoisomers” refers to stereoisomers that have at least two asymmetric atoms, but which are not mirror-images of each other. The absolute stereochemistry is specified according to the Cahn-Ingold-Prelog R-S system. When a compound is a pure enantiomer the stereochemistry at each chiral carbon may be specified by either R or S. Resolved compounds whose absolute configuration is unknown can be designated (+) or (-) depending on the direction (dextro or levorotatory) which they rotate plane polarized light at the wavelength of the sodium D line. The compounds of the presently disclosed subject matter contain one or more asymmetric centers and may thus give rise to enantiomers, diastereomers, and other stereoisomeric forms that may be defined, in terms of absolute stereochemistry, as (R)- or (S)-. The presently disclosed subject matter is meant to include all such possible isomers, including racemic mixtures, optically pure forms and intermediate mixtures. Optically active (R)- and (S)-isomers may be prepared using chiral synthons or chiral reagents, or resolved using conventional techniques. If the compound contains a double bond, the substituent may be E or Z configuration. If the compound contains a

disubstituted cycloalkyl, the cycloalkyl substituent may have a cis- or trans-configuration. All tautomeric forms are also intended to be included.

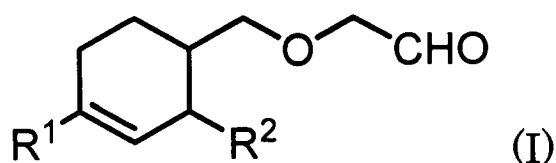
[0033] As used herein, the term “enantiomers” refers to a pair of stereoisomers that are non-superimposable mirror images of each other. A 1:1 mixture of a pair of enantiomers is a “racemic” mixture. The term is used to designate a racemic mixture where appropriate.

[0034] 2. Fragrance Compounds

The present disclosure provides fragrance compounds that are able to impart natural green, floral, fruity odor notes with a fresh aquatic note.

[0035] For example, and not limitation, the fragrance compounds can have the structure according to formula (I), or an isomer thereof, below.

[0036] [Chem.3]



[0037] Here, R¹ and R² are independently selected from hydrogen atom and methyl group.

[0038] The fragrance compounds of the present disclosure can impart a number of different odors, including for example and not limitation, one or more natural green, floral, fruity, aldehydic, aquatic, muguet, vegetable, marine, milky, lily, citrus, spicy, almond, balsamic, and/or styrax odors. The fragrance compounds of the present disclosure can impart multi-faceted odors having a combination of different odor notes.

[0039] In particular embodiments of a compound according to formula (I), R¹ is hydrogen atom; and R² is hydrogen atom. For example, such a fragrance compound can be 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde, or an isomer thereof. Such a fragrance compound can have natural green, floral, fruity, vegetable, aldehydic, milky, lily, citrus, aquatic, balsamic, and/or styrax odor, with unique freshness.

[0040] In other particular embodiments of a compound according to formula (I), R¹ is methyl group; and R² is methyl group. For example, such a fragrance compound can be 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde, or an isomer thereof. Such a fragrance compound can have a floral, green, aldehydic, muguet, and/or marine odor.

[0041] In addition to the fragrance compounds described generally and specifically herein, the present disclosure also includes isomers, such as stereoisomers, diastereoisomers, and enantiomers, thereof.

[0042] 3. Fragrance Compositions

The fragrance compounds of the presently disclosed subject matter can be formulated into different fragrance compositions. For example, a fragrance composition in ac-

cordance with the presently disclosed subject matter can include one or more, two or more, or three or more of the fragrance compounds described above.

[0043] Formulations of fragrance compounds into fragrance compositions span the range from “simple accords” (<10 fragrance compounds) to “complex fragrances” (>30 fragrance compounds). For example, full bodied fragrance compositions generally do not comprise less than about 30 fragrance compounds. Such fragrance compositions can also contain or consist of at least one fragrance base, solvent, or combination thereof. Said fragrance bases or solvents may be a liquid or a solid and typically do not significantly alter the olfactory properties of the fragrance compounds.

[0044] Some non-limiting examples of fragrance bases include an emulsifying system, encapsulating materials, natural or modified starches, polymers, gums, pectins, gelatinous or porous cellular materials, and waxes.

[0045] Some non-limiting examples of solvents include dipropylene glycol, propylene glycol, diethyl phthalate (DEP), diisononyl phthalate (DINP), benzyl benzoate, benzyl alcohol, isopropyl myristate (IPM), isopropyl palmitate (IPP/Deltyl Prime), butyl stearate, dioctyl adipate, triethyl citrate (TEC), methyl hydrogenated rosinat (CAS No. 8050-15-5), terpenes (e.g., Glidsol 100), paraffinic naphthenic solvent (e.g., LPA-170 Solvent), isoalkanes (e.g., Soltrol 170 Isoparaffin), isoparaffins, isoctadecanol (e.g., Tego Alkanol 66), phenoxyethanol, diethylene glycol monoethyl ether (Carbitol low gravity), glycol ether (Methyl Carbitol), Dipropylene Glycol Methyl Ether (e.g., Dowanol DPM), Dipropylene Glycol Methyl Ether Acetate (e.g., Dowanol DPMA), Propylene glycol methyl ether (e.g., Dowanol PM Glycol Ether), Tripropylene Glycol Methyl Ether, Diisoheptyl Phthalate (e.g., Jayflex (registered trademark) 77 available from Exxon), deionized or distilled water, specially denatured ethyl alcohol (e.g., SDA 40B), Dimethyl Adipate/Dimethyl Glutarate (e.g., DBE (registered trademark)-LVP Esters available from FLEXISOLV (registered trademark)), Racemic mixture (+/-)-2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (e.g., Augo Clean Multi Solvent), Alcohol 40B Anhydrous 200 Proof, alcohol SDA 40B 190 Proof, Triacetin, 3-Methoxy-3-methyl-1-butanol (Solfit), Benzyl Laurate, Tripropylene Glycol Methyl Ether (e.g., Dowanol TPM), Dipropylene glycol n-butyl ether (e.g., Dowanol DPNB), Dimethyl siloxane, trimethylsiloxo-terminated (e.g., Dowanol Corning 200 Fluid), Caprylic/Capric Triglycerides (e.g., Neobee M-5), propylene glycol and glyceryl oleate (e.g., Arlacel 186), Uniceth-IC20L (e.g., Arlasolve 200 L), 1,3-propanediol, Butyl Cellosolve, Hexylene glycol, Glycerine, Methyl Stearate, Isopropyl alcohol, 2-Methyl-1,3-propanediol (e.g., MP Diol Glycol), Diethyl Citrate, Triethyl Acetyl Citrate, 3-methyl-1,3-butandiol-acetate (IPD-AC), Dimethyl 2-methylpentanedioate (e.g., Rhodiasolv Iris), medium chain triglycerides (MCT), terpene hydrocarbons (e.g., Dipentene 5100), DL-limonene (e.g., Dipentene 122), 3,5,5-trimethylhexyl acetate,

Diethyl Malonate, Limonene (e.g., Unitene D), 4-tertiary-butylcyclohexyl acetate (e.g., Vertenex), Ethyl Acetate, Diethyl Succinate, and natural solvents including, but not limited to, vegetable oils, such as sunflower oil.

[0046] The amount of the fragrance compound of formula (I) present in a fragrance composition will depend on the formulation, but the compound of the present disclosure is typically present in an amount of from about 0.1% to about 30% by weight of the total fragrance composition. Typically a more preferred embodiment would contain between about 0.5% and about 20% by weight and a most preferred embodiment would contain between about 0.5% and about 10% by weight.

[0047] In certain embodiments, the one or more fragrance compounds of the present disclosure are formulated in a fragrance composition in amounts of from about 0.01% to about 99% by weight of the total fragrance composition, or from about 0.01% to about 90% by weight, or from about 0.5% to about 80% by weight, or from about 0.5% to about 70% by weight, or from about 0.5% to about 60% by weight, or from about 0.5% to about 50% by weight, or from about 0.5% to about 40% by weight, or from about 0.5% to about 30% by weight, or from about 0.5% to about 20% by weight, or from about 0.5% to about 10% by weight, or from about 0.5% to about 5% by weight, or from about 0.5% to about 2% by weight, or about 1% of the total fragrance composition. In certain embodiments, the fragrance compositions of the present disclosure contain at least about 0.1% by weight. For example, at a concentration of at least about 0.1% by weight of the fragrance composition, some odor notes of the fragrance compounds can be detected. In certain embodiments, the fragrance compositions of the present disclosure contain at least about 0.5% by weight. In more preferred embodiments, the fragrance compositions of the present disclosure contain at least about 1% by weight. For example, at a concentration of at least about 1% by weight of the fragrance composition, the full character of the fragrance compounds can be detected.

[0048] In certain embodiments, the fragrance compositions of the present disclosure contain at least about 98.5% by weight of a fragrance compound, e.g., a compound of formula (I). In one embodiment, the fragrance composition contains 100% by weight of a fragrance compound, e.g., a compound of formula (I).

[0049] In certain embodiments, the fragrance compound is 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde, 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde, or an isomer, stereoisomer, diastereomer, or enantiomer thereof, or a combination thereof.

[0050] A fragrance composition can further include one or more additional fragrance accords or compounds. In certain embodiments, the additional fragrance accords or compounds can be but are not limited to, one or more aldehydic compound(s), one or

more animalic compound(s), one or more balsamic compound(s), one or more citrus compound(s), one or more floral compound(s), one or more fruity compound(s), one or more gourmand compound(s), one or more green compound(s), one or more herbaceous compound(s), one or more marine compound(s), one or more mossy compound(s), one or more musk compound(s), one or more piney compound(s), one or more powdery compound(s), one or more spicy compound(s), and/or one or more woody compound(s), one or more amber compound(s), or combinations thereof.

- [0051] Non-limiting examples of suitable aldehydic compounds include acetaldehyde C-8, acetaldehyde C-9, acetaldehyde C-10, adoxal, aldehyde C-8, aldehyde C-9, aldehyde C-10, aldehyde C-11, aldehyde C-12, aldehyde C-12 lauric, aldehyde C-12 MNA, aldehyde supra, cyclomyral, trans-2-decenal, cis-4-decenal, trans-4-decenal, 9-decenal, trans-2-dodecenal, 1-methyl-4-(4-methylpentyl)cyclohex-3-ene-1-carbaldehyde (VERNALDEHYDE (registered trademark)), myrac aldehyde, precyclemone B, undecylenic aldehyde, and combinations thereof.
- [0052] Non-limiting examples of an animalic compound include civet, p-cresol, cresyl methyl ether, 5-cyclohexadecen-1-one (AMBRETONE (registered trademark)), indole, 2-methyl-5-(5,5,6-trimethylbicyclo[2.2.1]hept-2-yl)cyclohexanone (ALDRON (registered trademark)), 17-oxacycloheptadec-6-en-1-one (ambrettolide), skatole, 2,5,5-trimethyl-1,3,4,4a,6,7-hexahydronaphthalen-2-ol (ambrinol), and combinations thereof.
- [0053] Non-limiting examples of a balsamic compound include benzy salicylate, cyclohexyl salicylate, isopropoxy ethyl salicylate, phenethyl salicylate, styrax oil, and combinations thereof.
- [0054] Non-limiting examples of a citrus compound include delta-3-carene, citral, citronellal, DH-L-citronellol, L-citronellol, decanal, limonene, myrcenol, DH-myrcenol, nootkatone, sinensal, rhubafuran, bergamot oil, grapefruit oil, lemon oil, lime oil, orange oil, mandarin oil, tridecene-2-nitrile, and/or yuzu core base.
- [0055] Non-limiting examples of a floral compound include acetanisole, alpha amyl cinnamaldehyde, anisyl acetate, anisic aldehyde, benzyl acetate, bourgeonal, butyl acetate, L-citrol, cyclamen aldehyde, cyclohexyl lactone, delta-damascone, 9-decen-1-ol, dimethyl benzyl carbinol, farnesal, L-farnesal, L-dihydrofarnesal (BIOMUGUET (registered trademark)), ethyl linalool, farnesol, L-dihydrofarnesol (BIOCYCLAMOL (registered trademark)), 3-(3-isopropylphenyl)butanal (FLORHYDRAL (registered trademark)), 3-(4-ethylphenyl)-2,2-dimethylpropanal (floralozone), hexyl cinammic aldehyde, 4-methyl-2-(2-methylpropyl)oxan-4-ol (FLOROL (registered trademark)), geraniol, geranyl acetate, piperonal, methyl 3-oxo-2-pentylcyclopentaneacetate (Hedione (registered trademark)), 2-methyl-3-(3,4-methylenedioxyphenyl)propanal (Heliobouquet), hexyl cinnamaldehyde, hexyl salicylate, indole, alpha-ionone, beta-

ionone, isopropoxy ethyl salicylate, methyl-2-((1S*,2R*)-3-oxo-2-pentylcyclopentyl)acetate (JASMODIONE (registered trademark)), cis-jasmone, 4-(4-hydroxy-4-methylpentyl)cyclohex-3-ene-1-carbaldehyde (KOVANOL (registered trademark)), laural, linal, linalool, linalyl acetate, 2,4,6-trimethyl-4-phenyl-1,3-dioxane (LOREXAN (registered trademark)), 2,4-dimethyl-4,4a,5,9b-tetrahydroindeno[1,2-d][1,3]dioxine (Magnolan), (4-propan-2-ylcyclohexyl)methanol (Mayol (registered trademark)), methyl dihydrojasmonate, gamma-methyl ionone, methoxymelonal, methyl benzoate, 1-(4-propan-2-ylcyclohexyl)ethanol (Mugetanol), nerol, 1-(3-methyl-benzofuran-2-yl)-ethanone (Nerolione), neryl acetate, L-orantha, 2-pentyl cyclopentanone, 2-cyclohexylidene-2-phenylacetonitrile (PEONILE (registered trademark)), phenoxanol, phenoxy ethyl isobutyrate, phenylacetaldehyde, phenyl ethyl alcohol, prenyl salicylate, rose oxide, rosephenone, rosyran, 2-Methyl-3-[4-(2-methylpropyl)phenyl]propanal (SUZARAL (registered trademark)), terpeneol, undecavertol, 2,2,5-trimethyl-5-pentylcyclopentan-1-one (VELOUTONE (registered trademark)), yara yara, geranium oil, rose oil, lavender oil, ylang oil, and combinations thereof.

- [0056] Non-limiting examples of a fruity compound include aldehyde C-16, allyl caproate, allyl cyclohexyl propionate, allyl heptanoate, amyl acetate, benzaldehyde, L-citronellyl acetate, L-citronellyl nitrile, 3a,4,5,6,7,7a-hexahydro-4,7-methano-1H-inden-5(or 6)-yl acetate (CYCLACET (registered trademark)), 3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-1-yl propanoate (CYCLAPROP (registered trademark)), damascenone, beta-decalactone, gamma-decalactone, diethyl malonate, dimethyl benzyl carbinol acetate, dimethyl benzyl carbinyl butyrate, dimethyl phenyl ethyl carbinol, dimethyl sulfide, gamma-dodecalactone, ethyl acetate, ethyl butyrate, ethyl caproate, ethyl decadienotate, ethyl heptoate, ethyl-2-methylbutyrate, ethyl acetoacetate, ethyl methyl phenyl glycidate, ethyl propionate, 4-methyl-2-(2-methylpropyl)oxan-4-ol (FLOROL (registered trademark)), ethyl tricyclo [5.2.1.02.6] decan-2 carboxylate (FRUITATE (registered trademark)), hexyl acetate, hexyl isobutyrate, isoamyl acetate, 6-(pent-3-en-1-yl)tetrahydro-2H-pyran-2-one (Jasmolactone), ethyl 2-methylpentanoate (manzanate), 2,6-dimethylhept-5-enal (melonal), methyl anthranilate, methyl dioxolan, methyl heptyl ketone, gamma-nonolactone, 6-nonenol, gamma-octalactone, phenyl ethyl isobutyrate, prenyl acetate, raspberry ketone, (5S)-2-(2-mercaptopropan-2-yl)-5-methylcyclohexan-1-one (RINGONOL (registered trademark)), (1R, 6S)-ethyl 2,2,6-trimethylcloclohexanecarboxylate (THESARON (registered trademark)), tolyl aldehyde, gamma-undecalactone, 3,5,5-trimethylhexyl

acetate (vanoris), (2-tert-butylcyclohexyl) acetate (VERDOX (registered trademark)), and combinations thereof.

[0057] Non-limiting examples of a gourmand compound include angelica lactone-alpha, caprylic acid, coumarin, ethyl fraison, ethyl vanillin, ethyl maltol (e.g., VELTOL PLUS), filbertone, 4-hydroxy-2,5-dimethyl-3(2H)-furanone (FURANEOL (registered trademark)), guaiacol, maple furanone, 2-acetyl pyrazine, 2,5-dimethyl pyrazine, vanillin and combinations thereof.

[0058] Non-limiting examples of a green compound include allyl amyl glycolate, cyclo-galbanate, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-Penten-1-one (DYNASCONE (registered trademark)), galbanolene, galbanum, trans-2-hexenal, cis-3-hexenol, cis-3-hexenyl acetate, cis-3-hexenyl butyrate, cis-3-hexenyl formate, cis-3-hexenyl salicylate, liffarome, 2-methoxy-2-methylheptane, methyl octine carbonate, neofolione, 2,6-nonadienal, (2R,4S)-2-methyl-4-propyl-1,3-oxathiane (OXANE (registered trademark)), octahydro-5-methoxy-4,7-methano-1H-indene-2-carboxaldehyde (SCENTENAL (registered trademark)), N-(5-methylheptan-3-ylidene)hydroxylamine (STEMONE (registered trademark)), styrallyl acetate, 2,4-dimethylcyclohex-3-ene-1-carbaldehyde (TRIPLAL (registered trademark)), undecavertol, vionil, violet methyl carbonate (e.g., VIOLET T), violet leaf extract, and combinations thereof.

[0059] Non-limiting examples of an herbaceous compound include anethol, bamboo ketone, canthoxal, carvacrol, L-carvone, clary sage natural oil, p-cymene, 2,6-dimethylheptan-2-ol (DIMETOL (registered trademark)), menthol, methyl salicylate, thymol, natural basil oil, natural eucalyptus oil, eucalyptol, sweet natural fennel oil, natural cedar leaf oil, and combinations thereof.

[0060] Non-limiting examples of a marine compound include 8-methyl-1,5-benzodioxepin-3-one (Calone (registered trademark) 1951), 3-(4-ethylphenyl)-2,2-dimethylpropanal (floralozone), 4-tert-butylphenylacetonitrile (MARENIL (registered trademark)), 4-[(3E)-4,8-dimethylnona-3,7-dienyl]pyridine (MARITIMA (registered trademark)), myrac aldehyde, ULTRAZUR (registered trademark), and combinations thereof.

[0061] Non-limiting examples of a mossy compound include hinokitiol, isobutyl quinolone, isopropyl quinolone and/or methyl 2,4-dihydroxy-3,6-dimethylbenzoate (oakmoss#1), and combinations thereof.

[0062] Non-limiting examples of a musk compound include 17-oxacycloheptadec-6-en-1-one (ambrettolide), 5-cyclohexadecen-1-one (AMBRETONE (registered trademark)), (3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan (AMBROXAN (registered trademark)),

2,2,6-trimethyl- α -propylcyclohexanepropanol (DEXTRAMBER (trademark)),
 16-oxacyclohexadecan-1-one (EXALTOLIDE (registered trademark)),
 4,6,6,7,8,8-hexamethyl-1,3,4,6,7,8-hexahydro-cyclopenta[g]-isochromene
 (GALAXOLIDE (registered trademark)), (12E)-1-oxacyclohexadec-12-en-2-one
 (HABANOLIDE (registered trademark)),
 [2-[1-(3,3-dimethylcyclohexyl)ethoxy]-2-methylpropyl]propanoate (HELVETOLIDE
 (registered trademark)),
 (1'R)-3-methyl-5-(2,2,3-trimethylcyclopentan-1-yl)-2-pentanone,
 (5E)-3-methylcyclopentadec-5-en-1-one (MUSCENONE (registered trademark)),
 1,4-dioxacycloheptadecane-5,17-dione (Musk T (registered trademark)),
 3-methylcyclopentadecan-1-one (L-muscone),
 1-(3,5,5,6,8,8-hexamethyl-6,7-dihydronaphthalen-2-yl)ethenone (TONALID
 (registered trademark)), and combinations thereof.

[0063] Non-limiting examples of a piney compound include 1-borneol, 1-bornyl acetate, camphene, camphor gum powder, dihydroterpineol, beta-pinene, and combinations thereof.

[0064] Non-limiting examples of a spicy compound include acetyl isoeugenol, delta-caryophyllene, cinnamaldehyde, cuminaldehyde, eugenol, isoeugenol, perilla aldehyde, cardamom oil, clove oil, ginger extract, ginger oil, black pepper extract and combinations thereof.

[0065] Non-limiting examples of a woody and/or amber compound include amber core, amber xtreme,
 4aR,5R,7aS,9R)-octahydro-2,2,5,8,8,9a-hexamethyl-4H-4a,9-methanoazuleno[5,6-d]-1,3-dioxole (AMBROCENIDE (registered trademark)),
 ((3aR,5aS,9aS,9bR)-3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan (AMBROXAN), 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol (BACDANOL (registered trademark)), ethoxymethoxycyclododecane (Boisambrene Forte (registered trademark)), 1,1,2,3,3-pentamethyl-2,5,6,7-tetrahydroinden-4-one (Cashmeran (registered trademark)),
 (2R,5S,7R,8R)-8-methoxy-2,6,6,8-tetramethyltricyclo[5.3.1.0^{1,5}]undecane (Cedramber), cedanol, cedarwood oil,
 (1S,2R,5S,7R,8R)-2,6,6,8-tetramethyltricyclo[5.3.1.0^{1,5}]undecan-8-ol (Cedrol),
 2,2,6-trimethyl- α -propylcyclohexanepropanol (DEXTRAMBER (trademark)),
 3-methyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol (EBANOL (registered trademark)), (R,E)-2-Methyl-4-(2,2,3-trimethylcyclopent-3-enyl) but-2-en-1-ol (HINDINOL (registered trademark)), hinokitiol, DH-ionone beta,
 [(1R,2S)-1-methyl-2-[[[(1R,3S,5S)-1,2,2-trimethyl-3-bicyclo[3.1.0]hexanyl]methyl]cyclopropyl]methanol (JAVANOL (registered trademark)),

5-butan-2-yl-2-(2,4-dimethyl-1-cyclohex-3-enyl)-5-methyl-1,3-dioxane (karanal), 2,4-dimethyl-2-(1,1,4,4-tetramethyltetralin-6-yl)-1,3-dioxolane (OKOUMAL (registered trademark)), 1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthyl)ethan-1-one (ORBITONE (registered trademark)), patchouli oil, polysantol, rhubofix, sandalwood, and combinations thereof.

[0066] In certain embodiments, the additional fragrance compounds are formulated in a composition in an amount of from about 0.001% to about 99% by weight, or from about 0.01% to about 90% by weight, or from about 0.1% to about 80% by weight, or from about 1% to about 70% by weight, or from about 2% to about 60% by weight, or from about 5% to about 50% by weight, or from about 10% to about 40% by weight, or from about 15% to about 30% by weight, or from about 20% to about 25% by weight.

[0067] In certain aspects, the present disclosure provides methods to modify, enhance, or improve the odor properties of a fragrance composition by adding an olfactory effective quantity of the compounds of the present disclosure, e.g., a compound of formula (I), to the fragrance composition. As used herein, the term “olfactory effective quantity” means the amount of said compound in a fragrance composition in which the individual component will contribute its characteristic olfactory properties, for example an olfactory property found to be more hedonically appealing. A person of ordinary skill in the art may optimize the olfactory effect of the fragrance composition based on the incorporation of a fragrance compound of the present disclosure. The olfactory effective quantity of the compounds of formula (I) in a fragrance composition will depend on the formulation, but the olfactory effective quantity of the compounds of the present disclosure is typically from about 0.1% to about 20% by weight of the fragrance composition. The fragrance compound may be used individually, or a part of mixture such that the sum of the effects of all fragrance ingredients present in the mixture yields a higher hedonistic rating. Therefore, the compound embodied in the present disclosure can be employed to modify the characteristics of existing fragrance composition via their own olfactory properties or through additively effecting the contributions of other ingredient(s) present within the said composition. The quantity will vary widely depending on the other ingredients present, their relative amounts, the desired effect and the nature of the product.

[0068] 4. Consumer Products

In certain embodiments, the fragrance compounds and compositions of the present disclosure can be formulated as part of a consumer product. For example and not limitation, the fragrance compounds and/or compositions can be used in perfumes, colognes, shampoos, rinses, skin cares, body shampoos, body rinses, body powders, air

fresheners, deodorants, baths, foods, snacks, beverages, and the like, if necessary in combination with auxiliary materials.

[0069] As embodied herein, a compound of formula (I) can be employed alone or incorporated into fragrance compositions, which can advantageously be used in a wide variety of consumer products. For example, the consumer products can be those intended to perfume a suitable substrate. As used herein, the term “substrate” means any surface to which the consumer product can be applied without causing any undue adverse effect. The substrate can be a wide range of materials including human or animal skin or hair, paper (e.g., fragranced paper), air in a room, fabric, furnishings, dishes, hard surfaces, and related materials. Thus, substrates can include body surfaces such as, for example, hair and skin.

[0070] For example, the present disclosure provides a consumer product comprising: (a) at least one compound of formula (I); and (b) a consumer product base. As used herein, “consumer product base” means a composition for use as a consumer product to fulfill the specific purpose of the consumer product, such as cleaning, softening, and caring or the like. The present disclosure also provides a method for improving, enhancing, or modifying the odor properties of a consumer product base by adding thereto an olfactory effective amount of at least one compound of formula (I).

[0071] The compound described herein may be employed in a consumer product base simply by directly mixing at least one compound of formula (I), or a fragrance composition comprising at least one compound of formula (I), with the consumer product base, or the compound described herein can, in an earlier step, be entrapped with an entrapment material, for example, polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, or it can be chemically bonded to substrates, which are adapted to release the fragrance molecule upon application of an external stimulus such as light, enzymes, or the like, and then mixed with the consumer product base. Thus, the present disclosure additionally provides a method of manufacturing a perfumed consumer product, comprising incorporating a compound of formula (I), as a fragrance ingredient, either by directly admixing the compound to the consumer product base, or by admixing a fragrance composition comprising a compound of formula (I) with a consumer product base (i.e. incorporating the compound into the fragrance composition prior to admixing with the consumer product base). Admixing can be performed using conventional techniques and methods. Through the addition of an olfactory effective amount of at least one compound of the present disclosure, the odor notes of a consumer product base can be improved, enhanced, or modified. For example, the consumer product base can be modified to improve or enhance natural green, floral odor notes with a fresh aquatic note

[0072] In certain embodiments, the consumer products of the present disclosure can be, but are not limited to, air care products (e.g., candles, aerosols, air fresheners, liquid electric air fresheners, fragrance diffusers, gel air fresheners, plug-in air fresheners and oils, wax melts, etc.); baby care products (e.g., consumer products relating to disposable absorbent and/or non-absorbent articles, including adult incontinence garments, bibs, diapers, training pants, infant and toddler care wipes; and personal care products including hand soaps, shampoos, lotions, shower gels, and clothing); fabric and home care products (e.g., consumer products for fabric conditioning (including softening), laundry detergency, laundry and rinse additive and/or care, bleach, dryer sheets, perfume beads, air care, car care, dishwashing, hard surface cleaning and/or treatment, and other cleaning for consumer and or institutional use, etc.); personal care products (e.g., lotions, creams, moisturizers, body washes, hand soaps, shampoos, conditioners, soaps, etc.); family care products (e.g., wet or dry bath tissue, facial tissue, disposable handkerchiefs, disposable towels, and/or wipes, towels, toilet paper, tissue paper, wet towels, etc.); feminine care products (e.g., catamenial pads, incontinence pads, interlabial pads, panty liners, pessaries, sanitary napkins, tampons and tampon applicators, and/or wipes, etc.); sexual health care products (e.g., products relating to sexual aids or sexual health, including lubricants and condoms, etc.); pet care products (e.g., pet malodor cat litter, pet deodorizers, pet health and nutrition including pet foods, treats, other orally deliverable products, grooming aids, products for treating pet hair/fur including shampooing, styling, conditioning; deodorants and antiperspirants; products for cleansing or treating pet skin, including soaps, creams, lotions, and other topically applied products; training aids, toys and diagnostics techniques); fine fragrance (including hydro alcoholic solutions of perfume oil, such as parfum, extrait de parfum, eau de parfum, millesime, parfum de toilette, eau de toilette, eau de cologne, body splash, after shave, body mists, including baby colognes); auto care products (e.g., cleaners, air fresheners, wipes, soaps, etc.); cosmetics (e.g., skin cream, cleansing cream, night cream, hand cream, lotion, after-shave lotion, body lotion, foundation, lip stick, lip cream, nail polish, nail polish remover, talcum powder, anti-wrinkle and/or anti-aging cosmetics, sun protection products, massage oil, etc.); beauty care (e.g., products for treating human hair including shampooing, styling, conditioning; deodorants and antiperspirants; products for personal cleansing; products for treating human skin, including application of creams, lotions, and other topically applied products; products for shaving, rinse, rinse in shampoo; hair styling agents such as pomade, hair tonic, hair gel, hair cream and hair mousse; hair growing agents; hair coloring agents, etc.); and bath agents (e.g., powder bath additives, solid foaming bath additives, bath oils, bubble bath aroma generators, bath salts, etc.); hair removal products (e.g., products for hair removal including depilatory creams, sugar pastes or

gels, waxes); writing products (e.g., pens, crayons, paints, pencils, paper, origami, seals, etc.); products for play (e.g., balls, beanbags, cards, tops, dolls, building blocks, etc.); flavored products (e.g., confections, beverages, snacks, prepared meals, over-the-counter medications, gum, etc.); pharmaceuticals (e.g., plasters, ointments, suppositories, tablets, liquid medicines, capsules, granules, pharmacologically active molecular and/or biological entities; their use in the treatment and/or prevention of diseases and/or alleviation of symptoms in humans and/or animals, and formulations, regimens, kits and/or routes of delivering such entities to subjects in need of treatment and/or prevention and/or alleviation, etc.); health care products (e.g., oral health care products, including any composition for use with any soft and/or hard tissue of the oral cavity or conditions associated therewith (e.g., anti-cavities compositions, anti-plaque chewing gum compositions, breath compositions, dentrifices, denture compositions, lozenges, rinses, and tooth whitening compositions), cleaning devices, floss and flossing devices and toothbrushes; over-the-counter health care including cough and cold remedies and treatments for other respiratory conditions, pain relievers whether topical, oral, or otherwise, gastrointestinal remedies including any composition suitable for the alleviation of gastrointestinal conditions such as heartburn, upset stomach, diarrhea, and irritable bowel syndrome, and nutrient supplementation such as calcium or fiber supplementation, etc.); and foods and drinks or beverage (e.g., confectioneries consisting of gum, candy, snack such as potato crisps, baked sweets such as cookie and biscuit; drinks including refreshing drinks such as flavored tea, herb tea, juice, soda and powdered drink, fancy drinks such as tea and coffee, and milk drinks; frozen desserts such as ice cream, sherbet, mousse and frozen yogurt; desserts such as custard pudding, jelly, bavarois, yogurt and cream; cooked foods such as soup, curry and stew; seasonings such as condensed soup for noodles, dressing and mayonnaise; bakery products such as bread and donuts; daily products such as butter cream and margarine; fish paste products; etc.). In certain embodiments, the disclosed subject matter provides for use of the fragrance compounds and compositions described herein in a consumer product as described herein.

[0073] A broad range of concentrations and/or amounts of the fragrance composition can be employed in a consumer product. In certain embodiments of the present disclosure, the fragrance composition is admixed with a consumer product wherein the composition is present in an amount from about 0.0001 to about 90% weight/weight (w/w), or from about 0.001 to about 75% w/w, or from about 1 to about 50% w/w, or from about 5 to about 25% w/w, or from about 10 to about 15% w/w, and values in between.

[0074] In certain embodiments, the fragrance composition admixed with the consumer product comprises 2-(cyclohex-3-en-1-yl)methoxyacetaldehyde, 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde, or an isomer,

stereoisomer, diastereomer, or enantiomer thereof, or a combination thereof.

[0075] In certain embodiments, the consumer product base additionally includes one or more bases, solvents, and combinations thereof.

[0076] For example and not limitation, bases can include, but are not limited to, essential oils, lactones, aldehydes, alcohols, ketones, nitriles, esters, amides, oximes, and other fragrant compounds and perfuming co-ingredients.

[0077] For further example and not limitation, the solvents can include, but are not limited to, dipropylene glycol, propylene glycol, diethyl phthalate (DEP), diisononyl phthalate (DINP), benzyl benzoate, benzyl alcohol, isopropyl myristate (IPM), isopropyl palmitate (IPP/Deltyl Prime), butyl stearate, dioctyl adipate, triethyl citrate (TEC), methyl hydrogenated rosinat (CAS No. 8050-15-5), terpenes (e.g., Glidsol 100), paraffinic naphthenic solvent (e.g., LPA-170 Solvent), isoalkanes (e.g., Soltrol 170 Isoparaffin), isoparaffins, isooctadecanol, (e.g., Tego Alkanol 66), phenoxyethanol, diethylene glycol monoethyl ether (Carbitol low gravity), glycol ether (Methyl Carbitol), Dipropylene Glycol Methyl Ether (e.g., Dowanol DPM), Dipropylene Glycol Methyl Ether Acetate (e.g., Dowanol DPMA), Propylene glycol methyl ether (e.g., Dowanol PM Glycol Ether), Tripropylene Glycol Methyl Ether, Diisoheptyl Phthalate (e.g., Jayflex (registered trademark) 77 available from Exxon), deionized or distilled water, specially denatured ethyl alcohol (e.g., SDA 40B), Dimethyl Adipate/Dimethyl Glutarate (e.g., DBE (registered trademark)-LVP Esters available from FLEXISOLV (registered trademark)), Racemic mixture (+/-)-2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane (e.g., Augo Clean Multi Solvent), Alcohol 40B Anhydrous 200 Proof, alcohol SDA 40B 190 Proof, Triacetin, 3-Methoxy-3-methyl-1-butanol (Solfit), Benzyl Laurate, Tripropylene Glycol Methyl Ether (e.g., Dowanol TPM), Dipropylene glycol n-butyl ether (e.g., Dowanol DPNB), Dimethyl siloxane, trimethylsiloxo-terminated (e.g., Dowanol Corning 200 Fluid), Caprylic/Capric Triglycerides (e.g., Neobee M-5), propylene glycol and glyceryl oleate (e.g., Arlacel 186), Uniceth-IC20L (e.g., Arlasolve 200 L), 1,3-propanediol, Butyl Cellosolve, Hexylene glycol, Glycerine, Methyl Stearate, Isopropyl alcohol, 2-Methyl-1,3-propanediol (e.g., MP Diol Glycol), Diethyl Citrate, Triethyl Acetyl Citrate, 3-methyl-1,3-butandiol-acetate (IPD-AC), Dimethyl 2-methylpentanedioate (e.g., Rhodiasolv Iris), medium chain triglycerides (MTC), terpene hydrocarbons (e.g., Dipentene 5100), DL-limonene (e.g., Dipentene 122), 3,5,5-trimethylhexyl acetate, Diethyl Malonate, Limonene (e.g., Unitene D), 4-tertiary-butylcyclohexyl acetate (e.g., Vertenex), Ethyl Acetate, Diethyl Succinate, and combinations thereof.

[0078] Examples

The presently disclosed subject matter will be better understood by reference to the following Examples, which are provided as exemplary of the disclosed subject matter,

and not by way of limitation.

Example 1

[0079] Synthesis of 4-((2,2-diethoxyethoxy)methyl)cyclohex-1-ene

To a suspension of sodium hydride (60% dispersion in paraffin liquid, 53.5 g, 1.34 mol) in toluene (300 mL) was added 3-cyclohexene-1-methanol (100 g, 892 mmol) dropwise with stirring at 0 °C under nitrogen. The reaction mixture was stirred for 30 minutes, then 2-bromo-1,1-diethoxyethane (264 g, 1.34 mol) was added dropwise. The reaction mixture was then heated to 100 °C and stirred for 10 hours. The reaction was cooled to room temperature and was quenched with water (100 mL). The resultant mixture was extracted with toluene (100 mL×3). The combined organic layers were washed with brine (100 mL×2) and water (100 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (59.6 - 66.7 °C /20 Pa) to yield 4-((2,2-diethoxyethoxy)methyl)cyclohex-1-ene as a colorless oil (176 g, Yield: 87%). The odor was earthy, green and mushroom.

Example 2

[0080] Synthesis of 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde

A solution of 4-((2,2-diethoxyethoxy)methyl)cyclohex-1-ene (176 g, 769 mmol) in water (176 mL) and acetic acid (324 g, 5.40 mol) was stirred at 70 °C under nitrogen for 6 hours. The solution was cooled to room temperature, concentrated under reduced pressure, and diluted with water (176 mL). The resulting mixture was extracted with toluene (176 mL×3). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (59.2 - 59.6 °C /230 Pa) to yield 2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde as a colorless oil (93.3 g, Yield: 79%). The odor was natural green, floral, fruity, vegetable, aldehydic, milky, lily, citrus, aquatic, balsamic, and styrax.

[0081] GC/MS(EI): m/z(%) 154 (2), 136 (3), 107 (3), 94 (72), 79 (100), 67 (41), 55 (15).

[0082] ¹H NMR (400 MHz, CDCl₃) δ: 9.73 (t, 1H), 5.62-5.70 (m, 1H), 5.61-5.69 (m, 1H), 4.06 (d, 2H), 3.37-3.45 (m, 2H), 1.70-2.17 (m, 2H), 2.01-2.10 (m, 2H), 1.89-2.00 (m, 1H), 1.22-1.86 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ: 201.2, 127.1, 125.7, 76.9, 76.5, 33.8, 28.3, 25.4, 24.5.

Example 3

[0083] Synthesis of (2,4-dimethylcyclohex-3-en-1-yl)methanol

To a stirred solution of 2,4-dimethylcyclohex-3-ene-1-carbaldehyde (150 g, 1.09 mol) in tetrahydrofuran (450 mL) at 0 °C was added sodium borohydride (20.7 g, 546

mmol) in portions and the mixture was stirred at room temperature for 2 hours. Then, 5 mol/L hydrochloric acid (115 mL) was added dropwise to quench the reaction. The reaction mixture was concentrated under reduced pressure and the residue was diluted with toluene (300 mL). The organic phase was separated, washed with brine and water, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residual oil was purified by distillation under reduced pressure (72.3 °C /390 Pa) to afford (2,4-dimethylcyclohex-3-en-1-yl)methanol as a colorless oil (125 g, Yield: 82%). The odor was green, floral, and spicy.

[0084] GC/MS(EI): m/z(%) 140 (7), 138 (1), 122 (36), 107 (100), 93 (17), 91 (14), 82 (22), 79 (16), 67 (58), 55 (10).

Example 4

[0085] Synthesis of 4-((2,2-diethoxyethoxy)methyl)-1,3-dimethylcyclohex-1-ene

To a suspension of sodium hydroxide (22.3 g, 558 mmol) in toluene (102 mL) was added 3-cyclohexene-1-methanol (50.7 g, 362 mmol) dropwise with stirring at 0 °C under nitrogen. Then 2-Bromo-1,1-diethoxyethane (110 g, 558 mmol) was added dropwise followed by a solution of tetrabutylammonium iodide (6.85 g, 18.5 mmol, 5.1 mol%) in toluene (25 mL). The reaction mixture was heated to 120 °C and stirred for 24 hours. The reaction was cooled to room temperature and extracted with toluene (101 mL×3). The combined organic layers were washed with brine (101 mL×2) and water (101 mL), dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (88.9 - 90.4 °C /89 Pa) to yield 4-((2,2-diethoxyethoxy)methyl)-1,3-dimethylcyclohex-1-ene as a colorless oil (59.6 g, Yield: 64%). The odor was vegetable, earthy, and green.

Example 5

[0086] Synthesis of 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde

A solution of 4-((2,2-diethoxyethoxy)methyl)-1,3-dimethylcyclohex-1-ene (109 g, 425 mmol) in water (162 mL) and tetrahydrofuran (378 mL) was stirred at 65 °C under nitrogen. Then, 5 mol/L hydrochloric acid (21.1 mL, 105 mmol) was added dropwise and stirred for 2 hours. The solution was cooled to room temperature, concentrated under reduced pressure, and diluted with water (54.5 mL). The resulting mixture was extracted with toluene (109 mL×3). The combined organic layers were washed with saturated aqueous sodium hydrogen carbonate and brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure (51.2 - 53.7 °C /30 Pa) to yield 2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde as a colorless oil (68.6 g, Yield: 88%). The odor was floral, green, aldehydic, muguet, and marine.

Example 6

[0087] Fragrance compositions and shampoo formulations with
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde

A perfume composition with a floral fruity aquatic note was prepared from the compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde) to demonstrate its use in a shampoo. The formulation, with and without
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde, is provided in Table 1, below.

[0088] [Table 1]

Table 1

Component	Formulation without Example 2 (wt-%)	Formulation with Example 2 (wt-%)
Floral compound(s)	43.30	43.30
Fruity compound(s)	24.60	24.60
Musk compound(s)	8.00	8.00
Herbal compound(s)	6.00	6.00
Green compound(s)	5.70	5.70
Gourmand compound(s)	4.70	4.70
Citrus compound(s)	4.20	4.20
Woody compound(s)	2.50	2.50
Compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde)	-	1.00
Solvent (Dipropylene Glycol)	1.00	-
Total	100	100

[0089] The fragrance was used at 0.8% in a shampoo and a panel of five experts evaluated the samples.

[0090] The composition of this Example, using the compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde) was found to have added floral aquatic notes and total volume of notes, compared to the composition of this example without the compound of Example 2. The compound of Example 2 also gives cleanliness to the fragrance composition. It's excellent connotation for shampoo application.

Example 7

[0091] Fragrance compositions and fabric softener formulations with
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde

A perfume composition with a white floral note was prepared from the compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde) to demonstrate its use in a fabric softener. The formulation, with and without

2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde, is provided in Table 2, below.

[0092] [Table 2]

Table 2

Component	Formulation without Example 2 (wt-%)	Formulation with Example 2 (wt-%)
Floral compound(s)	34.20	34.20
Musk compound(s)	26.50	26.50
Woody compound(s)	13.00	13.00
Balsamic compound(s)	11.00	11.00
Citrus compound(s)	5.00	5.00
Fruity compound(s)	3.90	3.90
Herbal compound(s)	3.10	3.10
Gourmand compound(s)	2.00	2.00
Green compound(s)	0.30	0.30
Compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde)	-	1.00
Solvent (Dipropylene Glycol)	1.00	-
Total	100	100

[0093] The fragrance was used at 1.0% in a fabric softener and a panel of five experts evaluated the samples.

[0094] The composition of this Example, using the compound of Example 2 (2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde) was found to add a more natural and fresher character to the fragrance composition. In particular, the compound of Example 2 gives watery white floral facet which is a key character of this fragrance.

[0095] Although the presently disclosed subject matter and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the disclosed subject matter as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the disclosure of the presently disclosed subject matter, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein can be utilized according to the presently disclosed subject matter. Accordingly, the appended

claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

[0096] Patents, patent applications publications product descriptions, and protocols are cited throughout this application the disclosures of which are incorporated herein by reference in their entireties for all purpose.

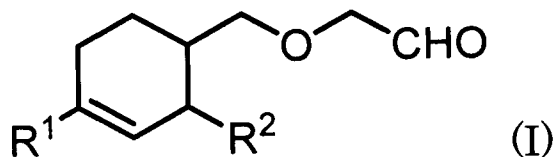
[0097] While the present invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof. This application is based on US provisional Application No. 62/679,384 filed on June 1, 2018, the entire subject matter of which is incorporated herein by reference.

Industrial Applicability

[0098] The present disclosure provides fragrance compounds having natural green, floral, fruity odor notes with a fresh aquatic note. These compounds can be used alone or incorporated into a fragrance composition and/or consumer product.

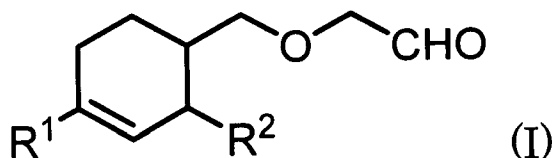
Claims

[Claim 1] A compound of formula (I), or an isomer thereof:
[Chem.1]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

[Claim 2] A fragrance composition comprising a fragrance compound of formula (I), or an isomer thereof:
[Chem.2]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

[Claim 3] The compound of claim 1, which is selected from the group consisting of:

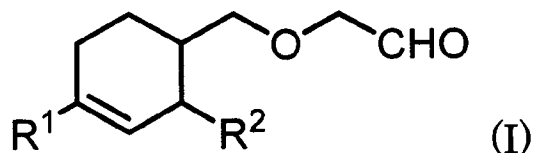
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde;
2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde;
and isomers thereof.

[Claim 4] The fragrance composition of claim 2, wherein the fragrance compound is selected from the group consisting of:

2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde;
2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde;
and combinations thereof.

[Claim 5] The fragrance composition of claim 2, further comprising an additional fragrance compound selected from an aldehydic compound, an amber compound, an animalic compound, a balsamic compound, a citrus compound, a floral compound, a fruity compound, a gourmand compound, a green compound, a herbaceous compound, a marine compound, a mossy compound, a musk compound, a piney compound, a powdery compound, a spicy compound, a woody compound, and combinations thereof.

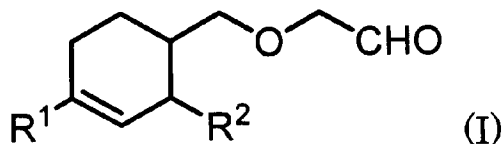
- [Claim 6] The fragrance composition of claim 2, further comprising a solvent.
- [Claim 7] A method of modifying the odor properties of a fragrance composition, comprising adding to the fragrance composition an olfactory effective quantity of a fragrance compound of formula (I), or an isomer thereof:
[Chem.3]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

- [Claim 8] The method of claim 7, wherein the fragrance compound is selected from the group consisting of:
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde;
2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde; and
combinations thereof.

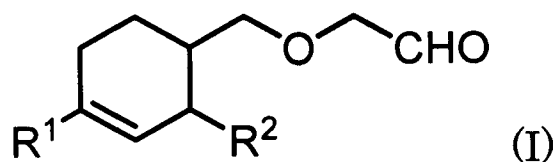
- [Claim 9] A consumer product, comprising a consumer product base and a fragrance compound of formula (I), or an isomer thereof:
[Chem.4]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

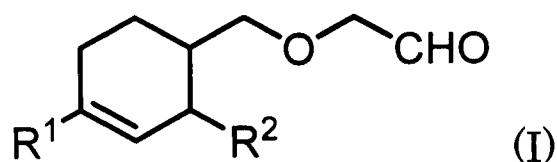
- [Claim 10] The consumer product of claim 9, wherein the fragrance compound is selected from the group consisting of:
2-(cyclohex-3-en-1-ylmethoxy)acetaldehyde;
2-((2,4-dimethylcyclohex-3-en-1-yl)methoxy)acetaldehyde;
and combinations thereof.
- [Claim 11] The consumer product of claim 9, wherein the consumer product is selected from a fine fragrance, a personal care product, a home care product, and an air care product.
- [Claim 12] The consumer product of claim 11, wherein the fine fragrance is selected from parfum, extrait de parfum, eau de parfum, millesime, parfum de toilette, eau de toilette, eau de cologne, body splash, after shave, body mists, and baby colognes.

- [Claim 13] The consumer product of claim 11, wherein the personal care product is selected from lotions, creams, moisturizers, body washes, hand soaps, shampoos, conditioners, and soaps.
- [Claim 14] The consumer product of claim 11, wherein the home care product is selected from fabric conditioner, fabric softener, laundry detergent, laundry additive, rinse additive, bleach, dryer sheets, perfume beads, car care products, dishwashing detergent, and hard surface cleaners.
- [Claim 15] The consumer product of claim 11, wherein the air care product is selected from a candle, aerosol, air freshener, liquid electric air freshener, fragrance diffuser, gel air freshener, plug-in air freshener, plug-in oil, and wax melt.
- [Claim 16] A method of modifying the odor properties of a consumer product, comprising adding to a consumer product base an olfactory effective quantity of a fragrance compound of formula (I), or an isomer thereof:
[Chem.5]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

- [Claim 17] A method of manufacturing a consumer product, comprising:
admixing, with a consumer product base, a fragrance compound of formula (I), or an isomer thereof:
[Chem.6]



wherein R¹ and R² are independently selected from hydrogen atom and methyl group.

- [Claim 18] The method of claim 17, wherein the fragrance compound is incorporated into a fragrance composition prior to admixing with the consumer product base.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2019/021862

A. CLASSIFICATION OF SUBJECT MATTER		
Int.Cl. C07C47/277 (2006.01) i, C11B9/00 (2006.01) i		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Int.Cl. C07C47/277, C11B9/00		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2019 Registered utility model specifications of Japan 1996-2019 Published registered utility model applications of Japan 1994-2019		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
CAplus (STN), REGISTRY (STN)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-256470 A (TAKASAGO INTERNATIONAL CORPORATION) 2013.12.26, Claims, Examples (No Family)	1-18
A	JP 2014-148614 A (TAKASAGO INTERNATIONAL CORPORATION) 2014.08.21, Claims, Examples (No Family)	1-18
A	WO 2017/046071 A1 (FIRMENICH SA) 2017.03.23, Claims, Examples & JP 2018-530646 A & US 2018/0282660 A1 & EP 3349862 A1 & CN 108025194 A & MX 2018002222 A	1-18
A	JP 61-268643 A (KAO CORPORAION) 1986.11.28, Claims, Examples (No Family)	1-18
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
03.09.2019		17.09.2019
Name and mailing address of the ISA/JP		Authorized officer
Japan Patent Office		MIZUSHIMA, Eiichiro
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2019/021862

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 61-115041 A (KAO CORPORATION) 1986.06.02, Claims, Examples (No Family)	1-18
A	JP 2010-506861 A (GIVAUDAN SA) 2010.03.04, Claims, Examples & US 2010/0105782 A1, Claims, Examples & WO 2008/046239 A1 & EP 2074080 A1 & CN 101528655 A & MX 2009003459 A	1-18
A	KUGATOVA-SHEMYAKINA, G. P. et al., Condensation of vinyl ethers with aldehydes of 3- and 6-cyclohexene and cyclohexane series, Zhurnal Obshchei Khimii, 1966, 2(3), 442-446, ISSN 0044-460X	1-18
A	JP 10-84989 A (T. HASEGAWA CO., LTD.) 1998.04.07, [0064] (No Family)	1-18
A	DATABASE REGISTRY [Online], 2010.10.28, RN 1247821-26-6, CN Acetaldehyde, 2-[(6-methyl-3-cyclohexene-1-yl)methoxy]- (CA INDEX NAME)	1-18
A	WO 2017/214455 A1 (TAKASAGO INTERNATIONAL CORPORATION (USA)) 2017.12.14, EXAMPLE 12-16 & US 2019/0153354 A1 & EP 3468526 A1 & CN 109310601 A	1-18

The term "isomers" is defined as "different compounds that have the same molecular formula but differ in arrangement and configuration of the atoms" in the paragraph [0031] of the description. Under this definition, the "isomers" in the present invention of claims 1-3, 5-7, 9, 11-18 can include many compounds other than compounds of formula (I). However, the compounds disclosed in the description are only the compounds that fall within formula (I) and none of the "isomer" compounds are disclosed in the description.

Therefore, only the compounds of formula (I) are disclosed in the meaning of PCT Article 5, and the "isomers" of the formula (I) compound of claims 1-3, 5-7, 9, 11-18 lack support within the meaning of PCT Article 6.