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(54) Title: POWDERY, MUSKY ODORANT MACROCYCLES

(57) Abstract: The present invention concerns a composition of matter comprising i) from 35 to 55% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%; ii) from 27 to 40% of (R,E)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%; iii) from 3 to 20% of (S,E)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%; and iv) from 0 to 5% of (S,Z)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%; as well as the use as perfuming ingredient of said composition of matter.

POWDERY, MUSKY ODORANT MACROCYCLES

Technical field

The present invention relates to the field of perfumery. More particularly, it
5 concerns a composition of matter comprising

- i) from 35 to 55% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- ii) from 27 to 40% of (R,E)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- 10 iii) from 3 to 20% of (S,E)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%; and
- iv) from 0 to 5% of (S,Z)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%

Said composition of matter is a useful perfumery ingredient, and therefore the
15 present invention comprises the invention compound as part of a perfuming composition or of a perfuming consumer product.

Prior art

Muscenone[®] (Firmenich SA, Geneva, Switzerland) is well known ingredient used
20 in perfumery. Muscenone[®] is a racemic mixture of various isomers (mainly Z-3-methyl-cyclopentadec-5-en-1-one, E-3-methyl-cyclopentadec-5-en-1-one, E-3-methyl-cyclopentadec-4-en-1-one and Z-3-methyl-cyclopentadec-4-en-1-one) and is reported to possess very elegant nitromusk powdery type of odor reminiscent of Musk ketone (i.e. powdery/musky, nitromusk), with a "slight animal but natural undertone".

25 In EP 0584477, a remarkable difference between the odors of the 3-methyl-cyclopentadec-(4 or 5)-en-1-one position isomers is noticed. The 3-methyl-cyclopentadec-5-en-1-one exhibits a "very musky, slightly animal note, with a strong nitro-musk character" whereas the 3-methyl-cyclopentadec-4-en-1-one develops a very weak musky odor devoid of character.

30 The enantioselective synthesis of (3R,5Z)-methyl-cyclopentadecen-1-one and (3S,5Z)- 3-methyl-cyclopentadecen-1-one described in *Eur. J. Org. Chem.* **2004**, 1953 allowed to demonstrate the influence of the configuration of the methyl group. The R isomer distinguishes itself by an outstandingly low threshold value and a highly desirable

nitromusk character. A more detailed olfactory profile of the four isomers of 5-Muscenone® is given in *Biosci. Biotechnol. Biochem.* **2002**, 1389 presenting the (3R,5Z)-methyl-cyclopentadec-5-en-1-one as the only isomer having the powdery/musk note, but having also a strong warm, animal character which is overall detrimental when compared to the elegance of Muscenone®.

The powdery/musk note is very appreciated in perfumery and is the one which bring the value to Muscenone®.

Now in view of the importance of such note, there is a marked interest for new perfumery ingredients providing as strong as possible powdery/musk note which leads to the use of less material. We have now unexpectedly discovered a synergic effect between various isomers of 3-methyl-cyclopentadec-(4 or 5)-en-1-one which results in the present composition of matter possessing a stronger powdery character which maintains the roundness and elegance of the overall note, i.e. without an overdue animal character. The prior art does not anticipate that the present composition of matter provided such increase in performance.

Description of the invention

We have now surprisingly discovered that a composition of matter comprising from about:

- 35 to 55% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- 27 to 40% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- 3 and 20% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%; and
- 0 to 5% w/w of (S,Z)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%;

the percentage being relative to the total weight of the composition of matter; can be used as perfuming ingredient, for instance to impart odor notes of the powdery, musk type having also a sweet/vanilla aspect.

For the sake of clarity, the expression "ee" stands for "enantiomeric excess" which is defined as the excess of one enantiomer over the other, expressed as a percentage of the

whole and calculated as below wherein R and S are the respective fractions of enantiomers in a mixture:

$$ee = ((R-S)/(R+S)) \times 100$$

According to an embodiment of the invention, in the present composition of matter the various constituents mentioned above are present in the following amounts:

- 38 to 51% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one;
- 30 to 37% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one;
- 6 and 15% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one; and
- 0 to 2% w/w of (S,Z)-3-methyl-cyclopentadec-4-en-1-one.

According to an embodiment of the invention, in the present composition of matter the various constituents mentioned above are present in the following amounts:

- 40 to 50% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one;
- 32 to 36% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one;
- 8 and 14% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one; and
- 0 to 2% w/w of (S,Z)-3-methyl-cyclopentadec-4-en-1-one.

According to any one of the above embodiments of the invention, the present composition of matter may comprise from about 42 to 48% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one.

According to any one of the above embodiments of the invention, the present composition of matter may comprise from about 32 to 36% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one.

According to any one of the above embodiments of the invention, the present composition of matter may comprise from about 8 to 14% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one.

According to any one of the above embodiments of the invention, the various constituent may be present in specific molar ratio ranges. As non-limiting example, one may cite the following molar ratio (mr) ranges:

- (mr) of [(R,Z)-3-methyl-cyclopentadec-5-en-1-one / (R,E)-3-methyl-cyclopentadec-5-en-1-one] being comprised between 1.6 and 1.0, or between 1.5 and 1.1, or even between 1.4 and 1.2; and/or
- (mr) of [(R,Z)-3-methyl-cyclopentadec-5-en-1-one / (S,E)-3-methyl-cyclopentadec-4-en-1-one] being comprised between 6.0 and 2.5, or even between 4.5 and 3.0.

According to any one of the above embodiments of the invention, each compound specified in the present composition of matter (i.e. (R,Z)-3-methyl-cyclopentadec-5-en-1-one, (R,E)-3-methyl-cyclopentadec-5-en-1-one, (S,E)-3-methyl-cyclopentadec-4-en-1-one and (S,Z)-3-methyl-cyclopentadec-4-en-1-one) may have an ee of at least 85%, 90%
5 or even 95%.

According to a particular embodiment of the invention, the present composition of matter is one comprising from about:

- 42 to 48% w/w of (R,Z)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;
- 10 - 32 to 36% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;
- 8 to 14% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 90%; and
- 0 to 2% w/w of (S,Z)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least
15 90%.

As mentioned above, the composition of matter of the invention possesses a strong musk and tenaceous odor with a stronger than expected natural powdery note. The overall profile demonstrates to be of high interest for perfumer since it opens new perspectives to the perfumer's creativity when compared with the prior art racemic or enantiopure
20 analogues.

Indeed, when the odor of the invention's composition of matter is compared with that of the prior art racemic composition of matter (i.e. Muscenone®), then the invention's compositions of matter distinguish themselves by a clearly different odor profile characterized by a stronger powdery, and round note and by much weaker animal note, so
25 characteristic of the prior art compound. The invention's compositions of matter distinguish themselves also by showing a sweet/vanillic aspect. Overall, while the racemic composition of matter is more in the masculine direction due to its animal note, the present composition of matter is more on the feminine direction.

The pure enantiomer analogue (i.e. (3R,5Z)-methyl-cyclopentadec-5-en-1-one) is
30 described in the prior art as being the only isomer having the powdery/musk note, so any composition of matter wherein said isomer is diluted should have a weaker powdery note. However, this is not the case and when the odor of the invention's composition of matter is compared with that of the prior art pure enantiomer (i.e. (3R,5Z)-methyl-

cyclopentadec-5-en-1-one), then the invention's compositions of matter demonstrated to have an powdery/musk note as strong as the one of the pure enantiomer, but still the present compositions of matter distinguish themselves by a more equilibrated being clearly less animal, more feminine, sweet, round and elegant.

5 In other words, the present composition of matter combines the strength of powdery/musk notes of (3R,5Z)-methyl-cyclopentadecen-1-one with the elegance of Muscenone®, thus reaching an optimal perfumistic equilibrium which renders the invention composition of matter different from the prior art composition and/or compound.

10 Said differences lend the invention's compounds and the prior art compounds to be each suitable for different uses, i.e. to impart different organoleptic impressions.

As mentioned above, the present composition of matter can be used as perfuming ingredient. Therefore another object of the present invention concerns a method to confer, enhance, improve or modify the odor properties of a perfuming composition or of a
15 consumer product, which method comprises adding to said composition or consumer product an effective amount of the invention's composition of matter.

According to a particular embodiment, such method is aimed to boost the musk, powdery, sweet note and the feminine aspect of a perfuming composition or of a consumer product.

20 The present composition of matter can be advantageously employed as perfuming ingredients in a variety of compositions. Therefore, another object of the present invention is a perfuming composition comprising:

- i) as perfuming ingredient, the invention's composition of matter as defined above;
- ii) at least one ingredient selected from the group consisting of a perfumery carrier and a
25 perfumery base; and
- iii) optionally at least one perfumery adjuvant.

By "perfumery carrier" we mean here a material which is practically neutral from a perfumery point of view, i.e. that does not significantly alter the organoleptic properties of perfuming ingredients. Said carrier may be a liquid or a solid.

30 As liquid carrier one may cite, as non-limiting examples, an emulsifying system, i.e. a solvent and a surfactant system, or a solvent commonly used in perfumery. A detailed description of the nature and type of solvents commonly used in perfumery cannot be exhaustive. However, one can cite as non-limiting examples solvents such as

dipropyleneglycol, diethyl phthalate, isopropyl myristate, benzyl benzoate, 2-(2-ethoxyethoxy)-1-ethanol or ethyl citrate, which are the most commonly used. For the compositions which comprise both a perfumery carrier and a perfumery base, other suitable perfumery carriers than those previously specified, can be also ethanol, 5 water/ethanol mixtures, limonene or other terpenes, isoparaffins such as those known under the trademark Isopar® (origin: Exxon Chemical) or glycol ethers and glycol ether esters such as those known under the trademark Dowanol® (origin: Dow Chemical Company).

As solid carrier one may cite, as non-limiting examples, absorbing gums or 10 polymers, or yet encapsulating materials. Examples of such materials may comprise wall-forming and plasticizing materials, such as mono, di- or trisaccharides, natural or modified starches, hydrocolloids, cellulose derivatives, polyvinyl acetates, polyvinylalcohols, proteins or pectins, or yet the materials cited in reference texts such as H. Scherz, Hydrokolloide: Stabilisatoren, Dickungs- und Geliermittel in Lebensmitteln, 15 Band 2 der Schriftenreihe Lebensmittelchemie, Lebensmittelqualität, Behr's Verlag GmbH & Co., Hamburg, 1996. The encapsulation is a well-known process to a person skilled in the art, and may be performed, for instance, using techniques such as spray-drying, agglomeration or yet extrusion; or consists of a coating encapsulation, including coacervation and complex coacervation technique.

20 By "perfumery base" we mean here a composition comprising at least one perfuming co-ingredient.

Said perfuming co-ingredient is not of formula (I). Moreover, by "perfuming co-ingredient" it is meant here a compound, which is used in a perfuming preparation or a composition to impart a hedonic effect. In other words such a co-ingredient, to be 25 considered as being a perfuming one, must be recognized by a person skilled in the art as being able to impart or modify in a positive or pleasant way the odor of a composition, and not just as having an odor.

The nature and type of the perfuming co-ingredients present in the base do not warrant a more detailed description here, which in any case would not be exhaustive, the 30 skilled person being able to select them on the basis of his general knowledge and according to intended use or application and the desired organoleptic effect. In general terms, these perfuming co-ingredients belong to chemical classes as varied as alcohols, lactones, aldehydes, ketones, esters, ethers, acetates, nitriles, terpenoids, nitrogenous or

sulphurous heterocyclic compounds and essential oils, and said perfuming co-ingredients can be of natural or synthetic origin. Many of these co-ingredients are in any case listed in reference texts such as the book by S. Arctander, Perfume and Flavor Chemicals, 1969, Montclair, New Jersey, USA, or its more recent versions, or in other works of a similar nature, as well as in the abundant patent literature in the field of perfumery. It is also understood that said co-ingredients may also be compounds known to release in a controlled manner various types of perfuming compounds.

By "perfumery adjuvant" we mean here an ingredient capable of imparting additional added benefit such as a color, a particular light resistance, chemical stability, etc. A detailed description of the nature and type of adjuvant commonly used in perfuming bases cannot be exhaustive, but it has to be mentioned that said ingredients are well known to a person skilled in the art.

An invention's composition consisting of invention's composition of matter and at least one perfumery carrier represents a particular embodiment of the invention as well as a perfuming composition comprising invention's composition of matter, at least one perfumery carrier, at least one perfumery base, and optionally at least one perfumery adjuvant.

For the sake of clarity, it is also understood that any mixture resulting directly from a chemical synthesis, e.g. a reaction medium without an adequate purification, in which the composition of matter of the invention would be involved as a starting, intermediate or end-product could not be considered as a perfuming composition according to the invention as far as said mixture does not provide the inventive compound in a suitable form for perfumery.

Furthermore, the invention's composition of matter can also be advantageously used in all the fields of modern perfumery, i.e. fine or functional perfumery, to positively impart or modify the odor of a consumer product into which said invention's composition of matter is added. Consequently, another object of the present invention is represented by a perfumery consumer product comprising, as perfuming ingredient, the invention's composition of matter, as defined above.

The invention's composition of matter can be added as such or as part of an invention's perfuming composition.

For the sake of clarity, it has to be mentioned that, by "perfumery consumer product" it is meant a consumer product which is expected to deliver at least a pleasant

perfuming effect to the surface to which it is applied (e.g. skin, hair, textile, or home surface). In other words, a perfumery consumer product according to the invention is a perfumed consumer product which comprises the functional formulation, as well as optionally additional benefit agents, corresponding to the desired consumer product, e.g. a detergent or an air freshener, and an olfactive effective amount of at least one invention's composition of matter. For the sake of clarity, said perfuming consumer product is a non-edible product.

The nature and type of the constituents of the perfumery consumer product do not warrant a more detailed description here, which in any case would not be exhaustive, the skilled person being able to select them on the basis of his general knowledge and according to the nature and the desired effect of said product.

Non-limiting examples of suitable perfumery consumer product can be a perfume, such as a fine perfume, a cologne or an after-shave lotion; a fabric care product, such as a liquid or solid detergent, a fabric softener, a fabric refresher, an ironing water, a paper, or a bleach; a body-care product, such as a hair care product (e.g. a shampoo, a coloring preparation or a hair spray), a cosmetic preparation (e.g. a vanishing cream or a deodorant or antiperspirant), or a skin-care product (e.g. a perfumed soap, shower or bath mousse, oil or gel, or a hygiene product); an air care product, such as an air freshener or a "ready to use" powdered air freshener; or a home care product, such as a wipe, a dish detergent or hard-surface detergent.

Some of the above-mentioned consumer products may represent an aggressive medium for the invention's composition of matter, so that it may be necessary to protect the latter from premature decomposition, for example by encapsulation or by chemically bounding it to another chemical which is suitable to release the invention's ingredient upon a suitable external stimulus, such as an enzyme, light, heat or a change of pH.

The proportions in which the invention's composition of matters according to the invention can be incorporated into the various aforementioned articles or compositions vary within a wide range of values. These values are dependent on the nature of the article to be perfumed and on the desired organoleptic effect as well as the nature of the co-ingredients in a given base when the compounds according to the invention are mixed with perfuming co-ingredients, solvents or additives commonly used in the art.

For example, in the case of perfuming compositions, typical concentrations are in the order of 0.1 % to 10 % by weight, or even more, of the composition of matter of the

invention based on the weight of the composition into which they are incorporated. Concentrations lower than these, such as in the order of 0.01% to 5% by weight, can be used when these compositions of matter are incorporated into perfumed articles, percentage being relative to the weight of the article.

5 The invention's composition of matter can be prepared from a treatment with strong acid of the enantioenriched hydroxy ketone (3R)-5-hydroxy-3-methylcyclopentadecan-1-one or the corresponding enantioenriched enolether (14R)-14-methyl-16-oxabicyclo[10.3.1]hexadec-12-ene according to EP 0584477. In any case the composition of matter can be obtained from 3-methylcyclopentadecane-1,5-dione. In one
10 case, the enantioenriched enolether can be synthesized according to different methods. One example is described in *Eur. J. Org. Chem.* **2004** 1953 wherein the key steps is a intramolecular aldol condensation of the readily available 3-methylcyclopentadecane-1,5-dione (*Helv. Chim. Acta.* **1967**, 50, 705) following by the kinetic resolution using Corey's oxazaborolidine and an Eschenmoser fragmentation. The aldol condensation and kinetic
15 resolution could be substituted by an enantioselective intramolecular aldol condensation as reported in *Angew. Chem. Int. Ed.* **2007**, 1307. An alternative to synthesis the enantioenriched enolether is an enantioselective mono reduction of 3-methylcyclopentadecane-1,5-dione. As not limiting examples, one can cite transition metal mediated desymmetrization using Noyori's asymmetric transfer hydrogenation
20 catalyst (*Tetrahedron: Asymmetry* **2003**, 1407) or Noyori's hydrogenation catalyst (*Angew. Chem. Int. Ed.* **2001**, 40). Iridium-Catalyzed Transfer Hydrogenation of Ketones is a possible alternative (*Helv. Chim. Acta* **1991**, **74**, 232). Oxazaborolidine-catalyst is also well known to perform this kind of reduction (*Angew. Chem. Int. Ed.* **1998**, 1986). The enantioselective borohydride reduction of carbonyl compounds could be also performed
25 in the presence of a catalytic amount of an optically active cobalt (II) complex (*Synthesis* **2008**, 1628). Modified metal hydride reagent with optically active ligand could lead to the desired chiral hydroxyketone (*J. Am. Chem. Soc.* **1979**, 3129). In second case, enzymatic method could also be considered for the enantioselective mono reduction of 3-methylcyclopentadecane-1,5-dione. The skilled person in the art will be able to select the
30 suitable enzyme by standard screening method of library of known enzymes as baker' yeast, alcohol dehydrogenase or ketoreductase.

In any case, the chiral reaction mixture accessible via the methodologies mentioned above contains various proportions of (14R)-14-methyl-16-

oxabicyclo[10.3.1]hexadec-12-ene and (3R)-5-hydroxy-3-methylcyclopentadecan-1-one. The reaction is preferably performed to lead to partial conversion, in order to avoid subsequent diol formation. Therefore the reaction mixture could contain also some remaining 3-methylcyclopentadecane-1,5-dione. This mixture can be separated into the individual ingredients, or submitted as such to the acid treatment below, yielding the composition of matter.

A preferred way of proceeding consists in a thermal and/or acid treatment followed by purification of the resulting reaction mixture in order to convert (3R)-5-hydroxy-3-methylcyclopentadecan-1-one into the corresponding enolether. The subsequent distillation allows the recovery of possibly present higher boiling 3-methylcyclopentadecane-1,5-dione, in order to recycle it into the process.

Examples

The invention will now be described in further detail by way of the following examples, wherein the abbreviations have the usual meaning in the art, the temperatures are indicated in degrees centigrade (°C); the NMR spectral data were recorded in CDCl₃ (if not stated otherwise) with a 360 or 400 MHz machine for ¹H and ¹³C, the chemical shifts δ are indicated in ppm with respect to TMS as standard, the coupling constants J are expressed in Hz.

Example 1

Synthesis of composition of matter

Distilled (14R)-14-methyl-16-oxabicyclo[10.3.1]hexadec-12-ene (88% pure; 46.5 g; 0.173 mol) containing 3% residual 3-methylcyclopentadecane-1,5-dione was dissolved in toluene (60 g). Phosphoric acid (85% aq; 35.0 g; 0.304 mol) was added and the heterogeneous mixture heated to 100°C under vigorous stirring. The reaction progress was monitored by GC. In order to reliably dose thermally labile (3R)-5-hydroxy-3-methylcyclopentadecan-1-one, samples were derivatized (excess MSTFA, 80°C, 30 min; conversion of (3R)-5-hydroxy-3-methylcyclopentadecan-1-one to the corresponding TMS ether) prior to GC injection. After 4 hours, the mixture was cooled to 50°C and the lower phase decanted (34.4 g, recovered aq. H₃PO₄). This aqueous phase was extracted with MTBE (2 x 50 ml). The pooled organic phases were washed with 5% aq. NaHCO₃ (40 g)

and a saturated solution of NaCl (50 g), dried (Na_2SO_4) and concentrated under vacuum to give the crude compound (42.2 g).

Bulb-to-bulb distillation (115-120°C oven temperature, 0.1 mbar) afforded a colorless oil (39.6 g, 75.4% yield). Vacuum distillation (Widmer column) gave the target mixture (bp 5 90°C/ 0.05 mbar) having the following isomer composition: 44% (R,Z)-3-methyl-cyclopentadec-5-en-1-one, 34% (R,E)-3-methyl-cyclopentadec-5-en-1-one, 12% (S,E)-3-methyl-cyclopentadec-4-en-1-one, and 1% (S,Z)-3-methyl-cyclopentadec-4-en-1-one. $[\alpha]_{\text{D}_{20}}(\text{CH}_3\text{OH}, c=2.84) +2.32$. This corresponds to an enantiomer excess (ee) of 90%.

The ee was measured employing the following procedure: a sample of above mixture was 10 converted into muscone (5% Pd/C / H_2 , ethyl acetate, 25°C). Analysis by GC using a ChirasilDex CB (Chrompack) chiral column (chemically bonded beta cyclodextrin permethylether, 25m, 0.25 μm) had allowed determination of the ee. The order of elution from this column is: (R)-(-)-muscone, (S)-(+)-muscone.

15 Example 2

Preparation of a perfuming composition

A perfuming composition for fine fragrance, of the powdery/floral type, was prepared by 20 admixing the following ingredients:

	<u>Parts by weight</u>	<u>Ingredient</u>
	50	Benzyl Acetate
	30	10%*Cis-3-Hexenol Acetate
25	20	Citronellyl Acetate
	10	Geranyl Acetate Extra
	30	Hexyl Acetate
	40	Isoeugenyl Acetate
	100	Hexylcinnamic Aldehyde
30	40	10%* Allyl Amyl Glycolate
	300	Bergamote Abergapt
	50	10%* Cascalone ^{TM 1)}
	80	Cashmeran ²⁾
	200	Cedarwood Oil
35	70	Cetalox ^{® 3)}

	50	10% * Cis-3-Hexenol
	50	Citronellol
	800	Coranol ⁴⁾
	10	Cyclogalbanate ⁵⁾
5	20	Cyclosal
	80	10% * Damascenone
	150	Dihydromyrcenol ⁶⁾
	80	Ethylvanilline
	200	Exaltolide ^{® 7)}
10	50	2-methyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-1-ol
	300	Floral ^{® 8)}
	80	3-(4-methoxyphenyl)-2-methylpropanal
	100	Gamma Decalactone
15	100	Gamma Undecalactone
	150	Geraniol 60
	1750	Hedione ^{® 9)}
	300	Heliopropanal ¹⁰⁾
	200	Helvetolide ^{® 11)}
20	300	Hydroxycitronellal
	20	10% * 1-Phenylvinyl acetate
	250	Ionone Beta
	1000	Iso E Super ¹²⁾
	50	10% * Jasminlactone
25	300	Lilial ^{® 13)}
	200	Linalol
	70	Mandarine
	30	10% * 2,6-dimethyl-5-heptanal
	40	Methyl Pamplermousse ¹⁴⁾
30	300	Methylionone Alpha Iso
	100	Muscone
	10	Myrrhone ^{® 15)}
	20	10% * Neobutenone ^{® Alpha 16)}

	50	10%* (Z)-1-[(E)-2-butenyloxy]-3-hexene
	20	Patchouli oil
	200	Phenylhexanol
	50	Polysantol® ¹⁷⁾
5	200	Orange Essential Oil
	300	Benzyle Ethyl Salicylate
	250	Cis-3-Hexenol Salicylate
	200	Sclareolate® ¹⁸⁾
	<u>150</u>	Cis-3-Hexenyl Cis-3-Hexenoate
10	9600	

* in dipropyleneglycol

- I) 7-isopropyl-2H,4H-1,5-benzodioxepin-3-one; origin: Firmenich SA, Geneva, Switzerland
- 15 2) 1,2,3,5,6,7-hexahydro-1,1,2,3,3-pentamethyl-4-indenone; origin: International Flavors & Fragrances, USA
- 3) dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1-b]furan; origin: Firmenich SA, Geneva, Switzerland
- 4) 4-cyclohexyl-2-methyl-2-butanol; origin: Firmenich SA, Geneva, Switzerland
- 20 5) allyle (cyclohexyloxy)-acetate; origin: Symrise, Holzminden, Allemagne
- 6) 2,6-dimethyl-7-octen-2-ol; origin: International Flavors & Fragrances, USA
- 7) pentadecanolide; origin: Firmenich SA, Geneva, Switzerland
- 8) tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin: Firmenich SA, Geneva, Switzerland
- 25 9) methyl dihydrojasmonate; origin: Firmenich SA, Geneva, Switzerland
- 10) 3-(1,3-benzodioxol-5-yl)-2-methylpropanal; origin: Firmenich SA, Geneva, Switzerland
- II) (1S,rR)-2-[1-(3',3'-dimethyl-l'-cyclohexyl)ethoxy]-2-methylpropyl propanoate; origin: Firmenich SA, Geneva, Switzerland
- 30 12) 1-(octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-1-ethanone; origin: International Flavors & Fragrances, USA
- 13) 3-(4-tert-butylphenyl)-2-methylpropanal; origin: Givaudan SA, Vernier, Switzerland

- 14) 6,6-dimethoxy-2,5,5-trimethyl-2-hexene; origin: Givaudan SA, Vernier, Switzerland
- 15) 4-(2,2,c-3,t-6-tetramethyl-R-1-cyclohexyl)-3-buten-2-one; origin: Firmenich SA, Geneva, Switzerland
- 5 16) 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one; origin: Firmenich SA, Geneva, Switzerland
- 17) 3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol; origin: Firmenich SA, Geneva, Switzerland
- 18) propyl (S)-2-(1,1-dimethylpropoxy)propanoate; origin: Firmenich SA, Geneva, Switzerland
- 10

The addition of 400 parts by weight of the composition of matter described in Example 1 to the above-described feminine fragrance composition imparted to the latter a musky character with a strong powdery character as well as and rising and elegant note.

- 15 The addition of the same amount of the racemic Muscenone® imparted a similar effect but much less powdery and more animal, less rising.

The addition of the same amount of (3R,5Z)-3-methyl-cyclopentadecen-1-one provided a totally different results with a musk / powdery character of similar amplitude but more masculine, and clearly animal.

20

Example 3

Preparation of a perfuming composition

- 25 A perfuming composition for fine fragrance, of musky/fruity type, was prepared by admixing the following ingredients:

	<u>Parts by weight</u>	<u>Ingredient</u>
	160	Benzyl Acetate
30	80	Benzyl dimethyl carbinol
	40	1%* Cis-3-Hexenol Acetate
	500	Hexylcinnamic Aldehyde
	40	Ambrox® DL ¹⁾
	160	10%* Cascalone ^{TM 2)}
35	80	Cassis Base ³⁾

	160	Raspberry ketone
	100	Citronellol
	280	Coranol ⁴⁾
	20	Allyl Cyclohexylpropionate
5	80	10% * Damascenone
	160	(1'R,E)-2-ethyl-4-(2\2\3'-trimethyl-3'-cyclopenten-1'-yl)-2-buten-1-ol
	40	Decal
	360	Dihydromyrcenol ⁵⁾
10	160	10% * Ethylpraline
	40	10% * Gamma Damascone
	20	Gamma Nonalactone
	20	Gamma Undecalactone
	80	Granny Smith ³⁾
15	60	Heliopropanal ⁶⁾
	100	Helvetolide ^{® 7)}
	60	Allyle Heptanoate
	40	Hivernal [®] Neo ⁸⁾
	20	Methyl Jasmonate
20	260	Lilial ^{® 9)}
	800	Linalol
	300	Magnolan ¹⁰⁾
	100	Mandarine
	20	10% * 2,6-dimethyl-5-heptanal
25	100	10% * Crystal moss
	2600	Hedione ^{® ")}
	80	10% * (Z)-1-[(E)-2-butenyloxy]-3-hexene
	20	10% * Rose Oxide
	160	10% * Cis-3-Hexenol Dist
30	60	Orange Essential Oil
	60	Benzyl Propionate
	600	Romandolide ^{® 12)}
	200	Cis-3-Hexenol Salicylate

	240	3-methyl- 5-(2,2,3-trimethyl-3 -cyclopenten- 1-yl)-2-pentanol
	60	Undecavertol ® ¹³⁾
	280	Verdox ® ¹⁴⁾
5	100	Ionone Beta
	<u>100</u>	10% * 2,4-Dimethyl-3-cyclohexene-1-carbaldehyde
	9000	

* in dipropyleneglycol

- 10 1) (-)-(8R)-8,12-epoxy-13, 14,15,16-tetranorlabdane; origin: Firmenich SA, Geneva, Switzerland
- 2) 7-isopropyl-2H,4H-1,5-benzodioxepin-3-one; origin: Firmenich SA, Geneva, Switzerland
- 3) compounded perfumery basis; origin: Firmenich SA, Geneva, Switzerland
- 15 4) 4-cyclohexyl-2-methyl-2-butanol; origin: Firmenich SA, Geneva, Switzerland
- 5) 2,6-dimethyl-7-octen-2-ol; origin: International Flavors & Fragrances, USA
- 6) 3-(1,3-benzodioxol-5-yl)-2-methylpropanal; origin: Firmenich SA, Geneva, Switzerland
- 7) (1S, 1'R)-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxycarbonyl]methyl propanoate; origin: Firmenich SA, Geneva, Switzerland
- 20 8) 3-(3,3/1,1-dimethyl-5-indanyl)propanal; origin: Firmenich SA, Geneva, Switzerland
- 9) 3-(4-tert-butylphenyl)-2-methylpropanal; origin: Givaudan SA, Vernier, Switzerland
- 25 10) 2,4-dimethyl-4,4a,5,9b-tetrahydroindeno[1,2-d][1,3]dioxine; origin: Symrise, Holzminden, Allemagne
- 11) methyl dihydrojasmonate; origin: Firmenich SA, Geneva, Switzerland
- 12) (1S ,rR)-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxycarbonyl]methyl propanoate origin: Firmenich SA, Geneva, Switzerland
- 30 13) 4-methyl-3-decen-5-ol; origin: Givaudan SA, Vernier, Switzerland
- 14) 2-tert-butyl-1-cyclohexyl acetate; origin: International Flavors & Fragrances, USA

The addition of 100 parts by weight of the composition of matter described in Example 1 to the above-described floral/fruity composition imparted to the latter a reinforced sweet, vanilla connotation with an exaltation of the musk and powdery aspect.

The addition of the same amount of the racemic Muscenone[®] imparted a totally different
5 result which was less sweet more animal and with a classical musk note.

The addition of the same amount of the (3R,5Z)-3-methyl-cyclopentadecen-1-one, overwritten the whole fragrance by its strong animal note.

Example 4

10

Preparation of a perfuming composition

A perfuming composition for liquid detergent, was prepared by admixing the following ingredients:

15

	<u>Parts by weight</u>	<u>Ingredient</u>
	20	Amyl Acetate
	40	Hexyl Acetate
	100	Phenylethyl Acetate
20	100	StyrallyleAcetate
	50	Aldehyde C 10
	400	Aldehyde Hexylcinnamic
	50	Aldehyde Supra
	40	Allyl Amyl Glycolate
25	80	Ethyl 2-methyl-pentanoate
	200	Benzylacetone
	300	Bergamote oil
	20	Cascalone ^{™ 1)}
	50	Cetalox ^{®2)}
30	10	Raspberry ketone
	50	Cetyver
	250	Citron
	150	Citronellol
	500	Coranol ³⁾
35	100	Cis-2-pentyl- 1-cyclopentanol

	50	Damascenone
	200	Damascone Alpha
	500	Dihydromyrcenol
	10	Ethylvanilline
5	400	Exaltolide® Total ⁴⁾
	300	Florol® ⁵⁾
	50	Galbex® ⁶⁾
	30	Gamma Undecalactone
	100	Geraniol
10	400	Habanolide® ⁷⁾
	200	Heliopropanal ⁸⁾
	100	Heliotropine ⁹⁾
	100	Helvetolide® ¹⁰⁾
	100	Hivernal® ¹¹⁾
15	100	10%* Methyl Jasmonate
	50	Lemonile® ¹²⁾
	50	Lime oil
	400	Linalol
	10	2,6-dimethyl-5-heptanal
20	50	2-Ethyl Methylbutyrate
	50	10%* Trans-2-Hexenal
	1500	Hedione® ¹³⁾
	10	Isojasmone
	20	(Z)- 1-[(E)-2-butenyloxy]-3-hexene
25	40	Cis-3-Hexenol Dist
	300	Orange Essential Oil
	200	Verdyl Propionate
	300	Romandolide® ¹⁴⁾
	100	Cis-3-Hexenol Salicylate
30	300	Salicynile
	300	Sclareolate® ¹⁵⁾
	50	Tamarine Base ⁶⁾
	200	Terpineol

	100	3-(4,4-dimethyl-1-cyclohexen-1-yl)propanal
	20	Vanilline Perf
	300	Verdox [®] 16)
5	250	(+)-(1S,2S,3S)-2,6,6-trimethyl-
		bicyclo[3.1.1]heptane-3-spiro-2'-cyclohexen-4'-one
	<u>50</u>	2,4-Dimethyl-3-cyclohexene-1-carbaldehyde
	9800	

* in dipropyleneglycol

- | | | | |
|----|-----|---|---|
| 10 | 1) | 7-isopropyl-2H,4H-1,5-benzodioxepin-3-one; | origin: Firmenich SA, Geneva, Switzerland |
| | 2) | dodecahydro-3a,6,6,9a-tetramethyl-naphtho[2,1-b]furan; | origin: Firmenich SA, Geneva, Switzerland |
| | 3) | 4-cyclohexyl-2-methyl-2-butanol; | origin: Firmenich SA, Geneva, Switzerland |
| 15 | 4) | pentadecanolide; | origin: Firmenich SA, Geneva, Switzerland |
| | 5) | tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; | origin: Firmenich SA, Geneva, Switzerland |
| | 6) | compounded perfumery basis; | origin: Firmenich SA, Geneva, Switzerland |
| | 7) | pentadecenolide; | origin: Firmenich SA, Geneva, Switzerland |
| 20 | 8) | 3-(1,3-benzodioxol-5-yl)-2-methylpropanal; | origin: Firmenich SA, Geneva, Switzerland |
| | 9) | 1,3-benzodioxole-5-carbaldehyde; | origin: Firmenich SA, Geneva, Switzerland |
| | 10) | (1S,rR)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate; | origin: Firmenich SA, Geneva, Switzerland |
| 25 | 11) | 3-(3,3/1,1-dimethyl-5-indanyl)propanal; | origin: Firmenich SA, Geneva, Switzerland |
| | 12) | 3,7-dimethyl-2/3,6-nonadienenitrile; | origin: Givaudan SA, Vernier, Switzerland |
| | 13) | methyl dihydrojasmonate; | origin: Firmenich SA, Geneva, Switzerland |
| | 14) | (1S,1'R)-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxycarbonyl] methyl propanoate | origin: Firmenich SA, Geneva, Switzerland |
| 30 | 15) | propyl (S)-2-(1,1-dimethylpropoxy)propanoate; | origin: Firmenich SA, Geneva, Switzerland |
| | 16) | 2-tert-butyl-1-cyclohexyl acetate; | origin: International Flavors & Fragrances, USA |

The addition of 200 parts by weight of the composition of matter described in Example 1 to the above-described composition imparted to the latter a reinforced round, fresh and "feminine" connotation, reinforcing the aldehydic aspect of the original composition.

- 5 The addition of the same amount of the racemic Muscenone[®] imparted a less sophisticated effect.

Claims

1. A composition of matter comprising:

- 35 to 55% w/w of (**R,Z**)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- 27 to 40% w/w of (**R,E**)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 80%;
- 3 and 20% w/w of (**S,E**)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%; and
- 0 to 5% w/w of (**S,Z**)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 80%;

the percentage being relative to the total weight of the composition of matter;

and wherein the various constituent are present in specific molar ratio ranges:

of [(**R,Z**)-3-methyl-cyclopentadec-5-en-1-one / (**R,E**)-3-methyl-cyclopentadec-5-en-1-one] being comprised between 1.6 and 1.0, or between 1.5 and 1.1, or even between 1.4 and 1.2; and/or

of [(**R,Z**)-3-methyl-cyclopentadec-5-en-1-one / (**S,E**)-3-methyl-cyclopentadec-4-en-1-one] being comprised between 6.0 and 2.5, or even between 4.5 and 3.0.

2. A composition of matter according to claim 1, characterized in that said composition comprises:

- 38 to 51% w/w of (**R,Z**)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;
- 30 to 37% w/w of (**R,E**)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;
- 6 and 15% w/w of (**S,E**)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 90%; and
- 0 to 2% w/w of (**S,Z**)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 90%.

3. A composition of matter according to claim 1, characterized in that said composition comprises:

- 42 to 48% w/w of (**R,Z**)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;

- 32 to 36% w/w of (R,E)-3-methyl-cyclopentadec-5-en-1-one, having an ee of at least 90%;
- 8 to 14% w/w of (S,E)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 90%; and
- 5 - 0 to 2% w/w of (S,Z)-3-methyl-cyclopentadec-4-en-1-one, having an ee of at least 90%.

4. A method to confer, enhance, improve or modify the odor properties of a perfuming composition or of a perfumed article, which method comprises adding to said
10 composition or consumer product an effective amount of a composition of matter according to any one of claims 1 to 3.

5. Method according to claim 4, characterized in that it boosts the musk, powdery, sweet note and the feminine aspect.

15

6. A perfuming composition comprising

- i) the composition of matter, as defined in any one of claims 1 to 3;
- ii) at least one ingredient selected from the group consisting of a perfumery carrier and a perfumery base; and
- 20 iii) optionally at least one perfumery adjuvant.

7. A perfumery consumer product comprising the composition of matter, as defined in any one of claims 1 to 3.

25 8. A perfumery consumer product according to claim 7, characterized in that the perfumery consumer product is a perfume, a fabric care product, a body-care product, an air care product or a home care product.

9. A perfumery consumer product according to claim 7, characterized in that
30 the perfumery consumer product is a fine perfume, a cologne, an after-shave lotion, a liquid or solid detergent, a fabric softener, a fabric refresher, an ironing water, a paper, a bleach, a shampoo, a coloring preparation, a hair spray, a vanishing cream, a deodorant or antiperspirant, a perfumed soap, shower or bath mousse, oil or gel, a hygiene product, an air freshener, a "ready to use" powdered air freshener, a wipe, a dish detergent or hard-
35 surface detergent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/050393

A. CLASSIFICATION OF SUBJECT MATTER
INV. C11B9/00 A61Q13/00 C11D3/50
ADD.

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)

C11B A61Q C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal , WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 584 477 A1 (FIR MENICH & CIE) 2 March 1994 (1994-03-02) cited in the application claims -----	1-9
A	US 5 354 735 A (DEMOLE EDOUARD ET AL) 11 October 1994 (1994-10-11) claims ; examples -----	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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