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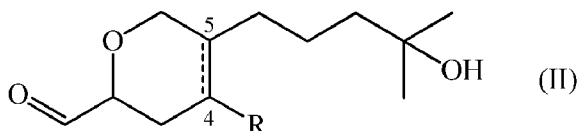
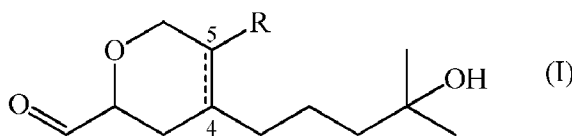
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(54) Title: PYRAN AS FLORAL ODORANT



(57) Abstract: The present invention relates to a composition of matter comprising 1) at least 70 % of at least a compound of formula (I) in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents - a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or - a CH₂ group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond; 2) at most 30% of at least a compound of formula (II) in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents - a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or - a CH₂ group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond; and wherein the percentages are w/w percentages relative to the total weight of the composition. Said compositions are useful perfuming ingredients of the floral, lily of the valley type.



WO 2014/124834 A1

PYRAN AS FLORAL ODORANT

Technical field

The present invention relates to the field of perfumery. More particularly, it concerns the use as perfuming ingredient of a composition of matter comprising derivatives of formula (I) and/or (II) as defined below, which are useful perfuming ingredients of the floral, lily of the valley type. Therefore, following what is mentioned herein, the present invention comprises the invention's compound as part of a perfuming composition or of a perfuming consumer product.

10

Prior art

To the best of our knowledge, the invention's compounds of formula (I) are novel.

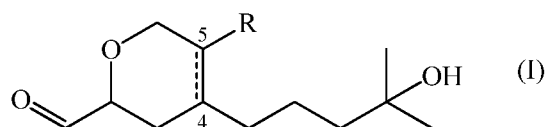
To the best of our knowledge, the closest analogue known in the perfumery is the chemical known as Lyr^{al}® (4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde plus as minor product, the isomer 3-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; origin: International Flavors & Fragrances, Inc., New York, USA) described in US 2947780. Moreover US 4007137 clearly indicates that the isomer 3-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde is an undesired component (see US 4007137 column 5, line 45).

20 These prior art documents do not report or suggest any organoleptic properties of the compounds of formula (I) or (II) and do not report or suggest any use of said compounds in the field of perfumery.

Description of the invention

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

1) at least 70% of at least a compound of formula

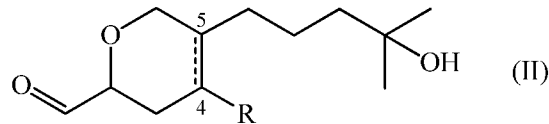


30 in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents

- a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or

- a CH₂ group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond;

2) at most 30% of at least a compound of formula



in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents

- a hydrogen atom and the dotted line represents a carbon-carbon single or double bond;
- a CH₂ group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond; and

wherein the percentages are w/w percentages relative to the total weight of the composition;

15 can be used as perfuming ingredient, for instance to impart odor notes of the floral, lily of the valley type.

For the sake of clarity, by the expression “any one of its stereoisomers”, or the similar, it is meant the normal meaning understood by a person skilled in the art, i.e. that the compound can be a pure enantiomer (if chiral) or diastereomer (if the dotted line represents a single bond).

For the sake of clarity, by the expression “wherein the dotted line represents a carbon-carbon single/double bond”, or the similar, it is meant the normal meaning understood by a person skilled in the art, i.e. that the whole bonding (solid and dotted line) between the carbon atoms connected by said dotted line, e.g. carbon 4 and 5, is a carbon-carbon single or double bond.

According to a particular embodiment of the invention, said dotted line and R have simultaneously the same meaning in formulae (I) and (II).

According to any one of the above embodiments of the invention, R represents a hydrogen atom and the dotted line represents a carbon-carbon single or double bond.

30 According to any one of the above embodiments of the invention, R represents a hydrogen atom and the dotted line represents a carbon-carbon double bond.

According to any one of the above embodiments of the invention, in said

composition of matter the compounds of formula (I) represent at least 75%, and the compounds of formula (II) at most 25%, of the total weight of the composition.

According to any one of the above embodiments of the invention, in said composition of matter the compounds of formula (I) represent at least 85%, and the
5 compounds of formula (II) at most 15%, of the total weight of the composition.

According to any one of the above embodiments of the invention, in said composition of matter, the compounds of formula (I) represent at least 95% of the total weight of the composition.

As specific examples of the invention's compounds, one may cite, as non-limiting
10 example, a composition comprising 88% of 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde (also mentioned as Composition 1 in the examples) which possesses a smooth, soft and balanced lily of the valley odor of an outstanding tenacity and exalt the white flower aspect of the composition to which it is added. The
15 organoleptic profile of this compound is very similar to the one of the well known perfumery ingredient Lyrall[®] (mentioned above in the prior art section), in particular in what concerns the odor, as well as the tenacity and the radiance.

Such similitude of odor properties is particularly surprising, since the replacement of a CH₂ group by an oxygen atom is known to dramatically change the physic-chemical
20 properties of a compound (such as log P or vapor pressure) and therefore its interaction with the olfactive receptors. For instance, the calculated values of the invention's compound compared to that of the prior art are for logP 1.57 vs 3.32, and for Vp 2.31 mPa vs 3.64 mPa, respectively.

For the sake of clarity the "logP" is the logarithm of the partition coefficient
25 between water and octanol, and the vapor pressure has the standard meaning in the art. Said logP and vapor pressure are calculated values and can be obtained according to the program EPI suite (4.0); EPA (US Environmental Protection Agency) and Syracuse Research Corporation (SRC), 2000.

Furthermore, such similitude of odor properties is also surprising since the prior
30 art composition comprises as main, and only desirable isomer, the compound wherein the carbaldehyde group and the chain group are para, while the present composition comprises as main, and most preferred isomer, the compound wherein the carbaldehyde group and the chain group are meta.

As other example, one may cite a composition comprising 88% of 4-(4-hydroxy-4-methylpentyl)tetrahydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)tetrahydro-2H-pyran-2-carbaldehyde, which possesses an odor similar to the one mentioned above but distinguishes itself by having also a lactonic, mandarin note.

5 According to a particular embodiment of the invention, the invention's composition is a composition comprising 88% of 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde.

As mentioned above, the invention concerns the use of the invention's composition of matter as perfuming ingredient. In other words, it concerns 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 composition or article an effective amount of the invention's composition of matter. By "use of the invention's composition of matter" it has to be understood here also the use of any composition
10 containing the invention's composition of matter and which can be advantageously employed in perfumery industry.

Said compositions, which in fact can be advantageously employed as perfuming ingredients, are also an object of the present invention.

Therefore, another object of the present invention is a perfuming composition
20 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 perfumery base; and
- iii) optionally at least one perfumery adjuvant.

25 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.

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
30 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, 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 carriers one may cite, as non-limiting examples, absorbing gums or 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*, 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.

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

Said perfuming co-ingredient is not of formula (I) or formula (II). 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 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 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 at least the 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 at least the 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 invention’s composition of matter 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 composition of matter in a suitable form for perfumery. Thus, unpurified reaction mixtures are generally excluded from the present invention unless otherwise specified.

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 perfuming 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 “perfuming 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 perfuming 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 the 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 base 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 base 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 product bases 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 composition of matter upon a suitable external stimulus, such as an enzyme, light, heat or a change of pH.

The proportions in which the composition of matter 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 composition of matter 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 0.5 % to 25 % by weight, or even more, of the invention's composition of

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

10

Synthesis of compounds of formula (I)

- A composition of matter comprising 88% of 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde (also referred to as Composition 1)

15

a) *ethyl 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carboxylate (as main compound) and 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carboxylate (as minor compound)*

20

A mixture of ethyl glyoxylate (50% solution in toluene) (38.6 mL, 194 mmol) and myrcenol (20 g, 130 mmol) was heated to reflux for 29h. Excess ethyl glyoxylate and toluene were evaporated, and the residue was purified by flash column chromatography on silica gel using gradient mixtures of heptane and ethyl acetate (85:15 to 60:40) to afford pure ester (80% yield) as a colorless oil and a 88:12 mixture of regioisomers.

25

Major isomer:

¹H NMR: 5.44 (m, 1H), 4.36 (m, 1H), 4.18-4.28 (m, 4H), 2.21-2.37 (m, 2H), 2.01-2.05 (m, 2H), 1.42-1.53 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 6H)

¹³C NMR: 171.6 (s), 134.4 (s), 119.3 (d), 72.4 (d), 70.8 (s), 65.5 (t), 61.1 (t), 43.3 (t), 37.2 (t), 30.7 (t), 29.3 (q, 2C), 21.8 (t), 14.2 (q).

30

b) *4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde (as main compound) and 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde (as minor compound)*

To a solution of ethyl 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carboxylate (5.00 g, 19.5 mmol) in dichloromethane at -78°C was added DIBAL (1 M in dichloromethane, 48.8 mL, 48.8 mmol) over a 45 minutes period and the reaction was stirred at -78°C for an additional hour. It was quenched with 50 mL of methanol, followed by 100 mL of water and 100 mL of a 5% HCl aqueous solution. The aqueous layer was extracted three times with diethyl ether, the combined organic extracts were dried over sodium sulfate and the solvent was evaporated. The residue was purified by bulb-to-bulb distillation (155-160°C, 10⁻³ mbar) to afford desired product (51% yield) as a colorless oil and in the form of a 88:12 mixture of regioisomers.

4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde:

¹H NMR: 9.74 (s, 1H), 5.46 (m, 1H), 4.19-4.37 (m, 2H), 4.05 (dd, *J* = 9.0, 4.9 Hz, 1H), 2.02-2.25 (m, 4H), 1.42-1.55 (m, 4H), 1.22 (s, 6H)

¹³C NMR: 201.8 (d), 134.1 (s), 119.6 (d), 77.7 (d), 70.9 (s), 65.4 (t), 43.3 (t), 37.2 (t), 29.3 (q, 2C), 28.0 (t), 21.8 (t).

- A composition of matter comprising 88% of 4-(4-hydroxy-4-methylpentyl)tetrahydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)tetrahydro-2H-pyran-2-carbaldehyde

In a 70-mL autoclave were placed 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde (1.75 g, 8.24 mmol) and 5% Pd/C (114 mg) in 20 mL ethyl acetate. The autoclave was sealed, purged with argon and reacted at room temperature under 45 bar pressure of H₂. After one hour, the autoclave was purged with argon, opened, the catalyst was filtered and the solvent was evaporated. The residue was purified by flash column chromatography on silica gel (Heptane/AcOEt 4:6) and bulb-to-bulb distillation (10⁻³ mbar, 130°C) to afford desired product (95% yield) as a colorless oil and in the form of a 73:15:12 mixture of isomers.

Major isomer:

¹H NMR: 9.61 (s, 1H), 4.13 (m, 1H), 3.79 (dd, *J* = 12.0, 2.5 Hz, 1H), 3.49 (dt, *J* = 12.0, 2.1 Hz, 1H), 1.93 (m, 1H), 1.25-1.67 (m, 10H), 1.22 (s, 6H).

¹³C NMR: 201.5 (d), 81.6 (d), 70.9 (s), 68.0 (t), 43.9 (t), 37.3 (t), 34.8 (d), 32.8 (t), 32.3 (t), 29.3 (q, 2C), 21.0 (t).

Example 2Preparation of a perfuming composition

5

An Eau de Cologne for man, of the woody-citrus type, was prepared by admixing the following ingredients:

	<u>Parts by weight</u>	<u>Ingredient</u>
10	10	1,1-Dimethyl-2-phenylethyl acetate
	10	Geranyl acetate
	200	Bergamot essential oil
	10	10%* 4-(4-Hydroxy-1-phenyl)-2-butanone
	30	Citral
15	500	Lemon essential oil
	90	10%* Galbanum essential oil
	90	Clove essential oil
	100	Habanolide ^{® 1)}
	200	Lavender essential oil
20	70	Linalol
	120	Marjoram essential oil
	50	50%* Moss Base - 184017 F ²⁾
	150	Nutmeg essential oil
	120	Paradisone ^{® 3)}
25	250	Sandela ^{® 4)}
	400	Sclareolate ^{® 5)}
	700	Vertofix Cœur ^{® 6)}
	200	Wolfwood ^{® 7)}
	<u>100</u>	Ylang oil
30	3400	

* in dipropyleneglycol

1) pentadecenolide; origin: Firmenich SA, Geneva, Switzerland

2) compounded perfumery base; origin: Firmenich SA, Geneva, Switzerland

- 3) methyl (1R)-cis-3-oxo-2-pentyl-1-cyclopentaneacetate; origin: Firmenich SA, Geneva, Switzerland
- 4) 5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol; origin: Givaudan SA, Vernier, Switzerland
- 5) 5) propyl (S)-2-(1,1-dimethylpropoxy)propanoate; origin: Firmenich SA, Geneva, Switzerland
- 6) methyl cedryl ketone; origin: International Flavors & Fragrances, USA
- 7) (1S,2S,3S)-2,6,6-trimethyl-bicyclo[3.1.1]heptane-3-spiro-2'-cyclohexen-4'-one; origin: Firmenich SA, Geneva, Switzerland

10

The addition of 400 parts by weight of Composition 1 (as described in Example 1) to the above-described composition imparted to the latter a diffusiveness and a “moist” effect, associated with the white flowers aspect of the composition, highly comparable to the effect provided when Lyrall[®] was added instead of the invention’s composition of matter.

15

Example 3

Preparation of a perfuming composition

20 A perfuming composition, of the floral, fruity, violet type, was prepared by admixing the following ingredients:

	<u>Parts by weight</u>	<u>Ingredient</u>
	60	Benzyl acetate
25	30	Cinnamyl acetate
	30	Citronellyl acetate
	30	Geranyl acetate
	80	1%* Para Cresol acetate
	120	Phenylethyl acetate
30	20	10%* (Z)-3-hexen-1-yl acetate
	30	Hexyl acetate
	20	Cinnamic alcohol
	100	Hexylcinnamic aldehyde
	60	Ambrettolide ^{® 1)}

	10	Anethol
	50	Benzyl benzoate
	10	Methyl benzoate
	50	2-Methyl-4-phenyl-2-butanol
5	100	Citronellol
	20	Coumarine
	30	3-(4-Isopropylphenyl)-2-methylpropanal
	40	10%* Estragole
	40	Eugenol
10	200	Exaltolide ^{® 2)} Total
	200	Florol ^{® 3)}
	30	10%* Phenylethyl formiate
	2000	70%** Galaxolide ^{® 4)}
	50	Geraniol
15	800	Habanolide ^{® 5)}
	1500	Hedione ^{® 6)} HC
	200	Helvetolide ^{® 7)}
	50	10%* Hivernal ^{® 8)}
	40	Iralia ^{® 9)}
20	30	Methyl jasmonate
	600	Lilial ^{® 10)}
	500	Linalol
	40	Methylisoeugenol
	30	10%* Methylnaphthylcetone
25	20	10%* Methylparacresol
	200	Muscenone ^{® 11)} Delta
	50	Muscone Laevo
	20	Nirvanol
	10	10%* Gamma nonalactone
30	20	10%* (Z)-3-Hexen-1-ol
	60	10%* Benzyl propionate
	50	Rose essential oil
	160	Benzyl salicylate

	50	Sclareolate ^{® 12)}
	500	Tonalide ^{® 13)}
	20	10%* 2,4-Dimethyl-3-cyclohexene-1-carbaldehyde
	40	Vanilline
5	<u>100</u>	Vertofix ^{® 14)} Cœur
	8500	

* in dipropylenglycol

** in isopropyle myristate

- 10 1) 16-hexadecanolide; origin: Firmenich SA, Geneva, Switzerland
- 2) pentadecanolide; origin: Firmenich SA, Geneva, Switzerland
- 3) tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin: Firmenich SA, Geneva,
Switzerland
- 4) 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta-g-2-benzopyrane; origin:
15 International Flavors & Fragrances, USA
- 5) pentadecenolide; origin: Firmenich SA, Geneva, Switzerland
- 6) cis methyl dihydrojasmonate; origin: Firmenich SA, Geneva, Switzerland
- 7) (1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate;
origin: Firmenich SA, Geneva, Switzerland
- 20 8) 3-(3,3/1,1-dimethyl-5-indanyl)propanal; origin: Firmenich SA, Geneva, Switzerland
- 9) mixture of methylionones isomers; origin: Firmenich SA, Geneva, Switzerland
- 10) 3-(4-tert-butylphenyl)-2-methylpropanal; origin: Givaudan SA, Vernier,
Switzerland
- 11) 3-methyl-(5)-cyclopentadecenone; origin: Firmenich SA, Geneva, Switzerland
- 25 12) propyl (S)-2-(1,1-dimethylpropoxy)propanoate; origin: Firmenich SA, Geneva,
Switzerland
- 13) 3,3-dimethyl-5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-4-penten-2-ol; origin:
Firmenich SA, Geneva, Switzerland
- 14) methyl cedryl ketone; origin: International Flavors & Fragrances, USA

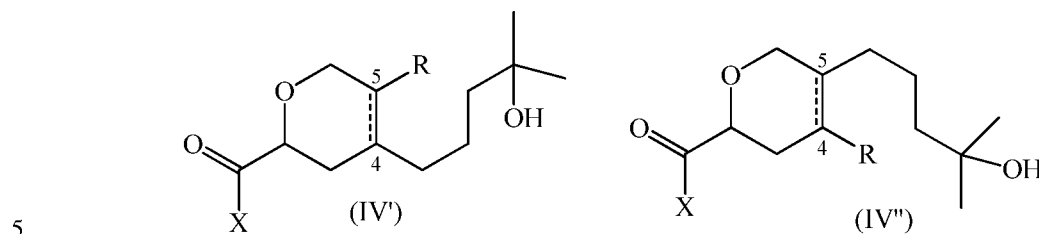
30

The addition of 1500 parts by weight Composition 1 (as described in Example 1) to the above-described composition imparted to the latter a floral, lily of the valley connotation having an outstanding tenacity and an exceptional powdery sweetness.

The addition of Lyr^{al}[®] to the above perfuming composition, instead of the invention's composition, provided the same effect despite the several physic-chemical differences between the two compounds.

Claims

1. A compound of formula (IV') or (IV'')



wherein X represent a hydrogen atom or a OR^1 group, R^1 being a C_{1-4} alkyl group; and R represents

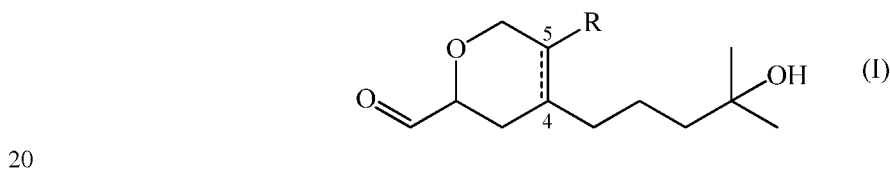
- 10
- a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or
 - a CH_2 group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond; and

said compound (IV') or (IV'') being in the form of any one of its stereoisomers or a mixture thereof.

15

2. Use as perfuming ingredient of a composition of matter comprising:

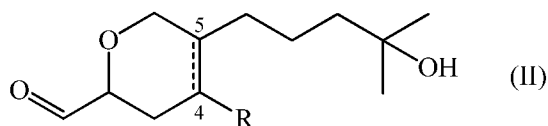
1) at least 70% of at least a compound of formula



in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents

- 25
- a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or
 - a CH_2 group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond;

2) at most 30% of at least a compound of formula



in the form of any one of its stereoisomers or a mixture thereof, and wherein R represents

- a hydrogen atom and the dotted line represents a carbon-carbon single or double bond; or
- 5 - a CH₂ group bonded with C4 and C5 and the dotted line represents a carbon-carbon single bond; and

wherein the percentages are w/w percentages relative to the total weight of the composition.

10 **3.** Use according to claim 2, characterized in that said dotted line and R have simultaneously the same meaning in formula (I) and (II).

4. Use according to claim 2, characterized in that R represents a hydrogen atom and the dotted line represents a carbon-carbon single or double bond.

15 **5.** Use according to claim 2, characterized in that the compounds of formula (I) represent at least 85%, and the compounds of formula (II) at most 15%, of the total weight of the composition.

20 **6.** Use according to claim 2, characterized in that said composition comprises 88% of 4-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde and 12% of 5-(4-hydroxy-4-methylpentyl)-3,6-dihydro-2H-pyran-2-carbaldehyde.

7. A perfuming composition comprising

- 25 i) a composition of matter, as defined in any one of claims 2 to 6;
- ii) at least one ingredient selected from the group consisting of a perfumery carrier and a perfumery base; and
- iii) optionally at least one perfumery adjuvant.

30 **8.** A perfuming consumer product comprising a composition of matter, as defined in any one of claims 2 to 6.

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

10. A perfuming consumer product according to claim 8, characterized in that 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
5 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-surface detergent.

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/052114

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C07D309/06 A61Q13/00 C07D309/26
 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)
 C07D A61Q
 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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 007 137 A (SANDERS JAMES MILTON ET AL) 8 February 1977 (1977-02-08) cited in the application the whole document -----	1-10
A	US 2 947 780 A (TEEGARDEN ROBERT W ET AL) 2 August 1960 (1960-08-02) cited in the application the whole document -----	1-10
A	KULA JOZEF ET AL: "Tetrahydrofuran and tetrahydropyran derivatives as odor substances", PERFUMER & FLAVORIST, ALLURED PUBLISHING CORP, vol. 17, no. 5, 1992, pages 77-92, XP009133547, ISSN: 0272-2666 the whole document -----	1-10

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 20 February 2014	Date of mailing of the international search report 04/03/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fazzi, Raffaella
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/052114

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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