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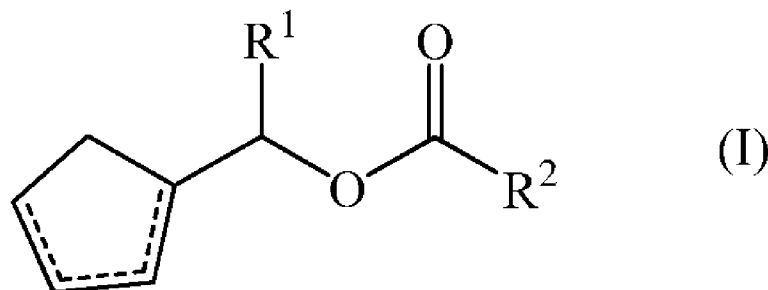
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(54) Title: ESTERS AS PERFUMING INGREDIENTS



(57) Abstract: The present invention relates to some perfuming ingredients, capable to a green note, which are esters of formula (I) wherein two dotted lines represent a carbon-carbon single bond and the other a carbon-carbon single bond or double bond; R¹ represents a hydrogen atom or a methyl or ethyl group; and R² represents a C₄-C₈ alkenyl group.

ESTERS AS PERFUMING INGREDIENTS

Technical field

The present invention relates to the field of perfumery. More particularly, it concerns some esters of cyclopentylmethanol or cyclopentenylmethanol and their methyl substituted derivatives as defined herein below. The present invention concerns the use of said compounds in the perfumery industry as well as the compositions or articles containing said compounds.

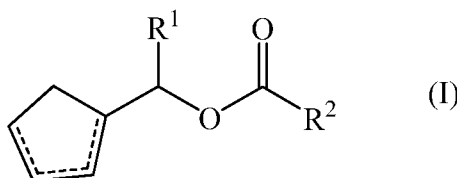
Prior art

To the best of our knowledge, very few compounds of formula (I) are reported in the prior art. Said compounds are 1-cyclopentylethyl hexanoate and 1-cyclopentylethyl octanoate (mentioned in CAS as reported in mass spectral library), 1-cyclopenten-1-ylmethyl 5-hexenoate (mentioned in Eur. J. Org. Chem., **2010**, 937), 1-cyclopentylmethyl octanoate (mentioned in J. Agric. Food Chem., **1988**, 36, 856), and 1-cyclopentylmethyl 2-ethyl-butanoate (mentioned in Polymer Communications **1984**, 25, 66) all mentioned as simple chemical compounds or intermediates. These prior art documents do not report or suggest any organoleptic properties of the compounds of formula (I), or any use of said compounds in the field of perfumery.

One may also cite an analogue of the present invention's compounds which is described as having interesting perfuming properties. This compound is levo-1-(3-isopropylcyclopentyl)-1-ethyl acetate reported in US 2946823 as having a bergamot (citrus) odor. This prior art document does not report, suggest or anticipate any organoleptic properties of the compounds of formula (I), or any use of said compounds in the field of perfumery.

Description of the invention

We have now surprisingly discovered that a compound of formula



in the form of any one of its stereoisomers or of a mixture thereof, and wherein two dotted lines represent a carbon-carbon single bond and the other a carbon-carbon single bond or double bond;

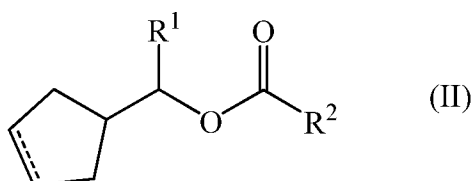
R^1 represents a hydrogen atom or a methyl or ethyl group; and

5 R^2 represents a C_4 - C_8 alkenyl group;

can be used as perfuming ingredient, for instance to impart an odor characterized by a green note, which may be associated with an onion/garlic tonality.

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

According to a particular embodiment of the invention, said compounds (I) are those of formula



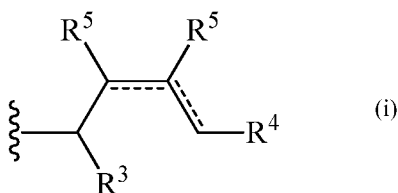
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in the form of any one of its stereoisomers or of a mixture thereof, and the dotted line represents a carbon-carbon single bond or double bond, R^1 and R^2 being as defined above.

According to any one of the above embodiments of the invention, R^2 represents a
20 C_5 - C_8 alkenyl group. Said compounds are generally new compounds, except those mentioned above in the prior art.

According to any one of the above embodiments of the invention, R^2 represents:

a) a C_5 - C_8 group of formula



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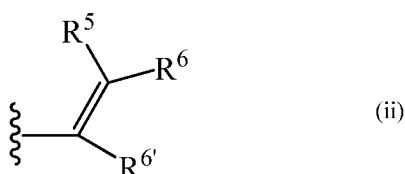
wherein one dotted line represents a carbon-carbon double bond and the other a carbon-carbon single bond;

R^4 represents a C_{1-4} alkyl or alkenyl group;

R^3 represents a hydrogen atom or a methyl group; and

each R^5 , taken separately, represents a hydrogen atom or a methyl group, or two R^5 , taken together, represent a CH_2 group (in such a case clearly both dotted lines represent a single bond); or R^4 and one R^5 , taken together, represent a C_{3-4} hydrocarbon group; or

b) a C_5-C_8 group of formula



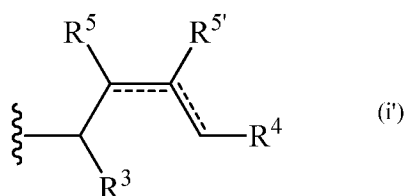
wherein R^6 represents a C_{3-4} alkyl or alkenyl group, $R^{6'}$ represents a hydrogen atom or a methyl or ethyl group, and R^5 is defined as above.

According to any one of the above embodiments of the invention, $R^{6'}$ represents a hydrogen atom or a methyl or ethyl group. Alternatively, $R^{6'}$ represents a hydrogen atom.

According to any one of the above embodiments of the invention, R^1 represents a hydrogen atom or a methyl group. Alternatively, R^1 represents a hydrogen atom.

According to any one of the above embodiments of the invention, said compounds (I) are those wherein R^2 represents:

aⁱ) a C_5-C_7 group of formula



wherein one dotted line represents a carbon-carbon double bond and the other a carbon-carbon single bond;

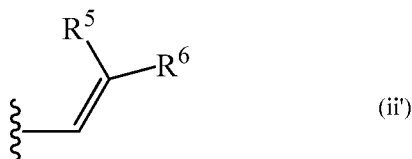
R^4 represents a C_{1-3} alkyl or alkenyl group, preferably alkyl;

R^3 and R^5 represent each a hydrogen atom or a methyl group; and

$R^{5'}$, taken alone, represents a hydrogen atom or taken together with R^5 represents a CH_2 group (in such a case clearly both dotted lines represent a single bond);

or

bⁱ) a C₅-C₇ group of formula



wherein R⁵ represents a hydrogen atom or a methyl group and R⁶ represents a C₃ alkyl or alkenyl group.

According to a particular embodiment, said invention's compounds are those wherein R² represents a group as defined under a), said compounds having a green note with a fruity character.

According to a particular embodiment of the invention, said compounds (I) are those of formula (I) wherein R² represents a group as defined under aⁱ) or bⁱ).

According to any one of the above embodiments of the invention, said compounds (I) are those wherein R² represents a group of formula CHR⁸R⁹, R⁸ representing a hydrogen atom or a methyl group; and R⁹ representing a C₄₋₆ linear alkenyl or alkadienyl group or a 2-R¹¹-cycloprop-1-yl group, R¹¹ representing a methyl, ethyl or propyl group.

According to any one of the above embodiments of the invention, said compounds (I) or (II) are C₁₂-C₁₆ compounds.

As mentioned above, the compounds of formula (I) possess very interesting odors which allow to distinguish them from other structurally related prior art perfuming ingredients. In particular compounds (I) distinguish themselves by associating a strong green note. Said invention's compounds distinguish themselves also by lacking or by not possessing a citrusy note.

As specific examples of the invention's compounds, one may cite, as non-limiting example, cyclopentylmethyl (3Z)-3-hexenoate which possesses a nice green note, with garlic/onion and apple tonalities as well as slightly powdery, sweet, wine aspects. This compound represents a complex notes which can be used in a variety of different perfuming compositions.

As other example one may cite (Z)-cyclopent-3-enylmethyl hex-3-enoate, which possesses an odor characterized by a typical green, grassy note, somehow reminding of the odor of (Z)-3-hexen-1-ol but less aggressive.

As other example one may cite cyclopentylmethyl 3-methylhex-2-enoate, which possesses a green, allylic, sulfury odor.

According to a particular embodiment of the invention, the compound of formula (I) is cyclopentylmethyl (3Z)-3-hexenoate or (Z)-cyclopent-3-enylmethyl hex-3-enoate.

As mentioned above, the invention concerns the use of a compound of formula (I) 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 at least a compound of formula (I). By "use of a compound of formula (I)" it has to be understood here also the use of any composition containing compound (I) and which can be advantageously employed in perfumery industry as active ingredients.

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

Therefore, another object of the present invention is a perfuming composition comprising:

- i) as perfuming ingredient, at least one invention's compound 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.

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 detailed description of the nature and type of solvents commonly used in perfumery cannot be exhaustive. However, one can cite as non-limiting example solvents such as dipropyleneglycol, diethyl phthalate, isopropyl myristate, benzyl benzoate, 2-(2-ethoxyethoxy)-1-ethanol or ethyl citrate, which are the most commonly used.

As solid carrier 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, Hydrokolloids : Stabilisatoren, Dickungs- und Geliermittel in Lebensmittel, Band 2 der Schriftenreihe Lebensmittelchemie, Lebensmittelqualität, Behr's VerlagGmbH & 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 techniques.

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

Said perfuming co-ingredient is not of the formula (I). Moreover, by "perfuming co-ingredient" it is meant here a compound, which is used in perfuming preparation or 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 its 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.

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).

By “perfumery adjuvant” we mean here an ingredient capable of imparting additional added benefits 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 one compound of formula (I) and at least one perfumery carrier represents a particular embodiment of the invention as well as a perfuming composition comprising at least one compound of formula (I), at least one perfumery carrier, at least one perfumery base, and optionally at least one perfumery adjuvant.

It is useful to mention here that the possibility to have, in the compositions mentioned above, more than one compound of formula (I) is important as it enables the perfumer to prepare accords, perfumes, possessing the odor tonality of various compounds of the invention, creating thus new tools for their work.

Preferably, any mixture resulting directly from a chemical synthesis, e.g. without an adequate purification, in which the compound 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.

Furthermore, the invention’s compound 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 compound (I) is added. Consequently, a perfuming consumer product which comprises:

- i) as perfuming ingredient, at least one compound of formula (I), as defined above; and
- ii) a perfumery consumer base;

is also an object of the present invention.

The invention’s compound 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 perfuming

effect, in other words it is a perfumed consumer product. For the sake of clarity, it has to be mentioned that, by “perfumery consumer base” we mean here the functional formulation, as well as optionally additional benefit agents, corresponding to a consumer product which is compatible with perfuming ingredients and is expected to deliver a pleasant odor 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 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 compound.

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 compound, 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 compounds 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 0.01% to 3% by weight, or even more, of the compounds of the invention based on the weight of the composition into which they are incorporated. Concentrations
5 lower than these, such as in the order of 0.001% to 2% by weight, can be used when these compounds are incorporated into perfumed articles, percentage being relative to the weight of the article.

The invention's compounds can be prepared according to a method involving an trans esterification of an appropriate ester of the acid R^2COOH , e.g. a methyl or ethyl
10 ester of R^2COOH , with an appropriate alcohol, such as cyclopentylmethanol. Alternatively the compounds (I) can be obtained by a direct esterification of an acid R^2COOH with an appropriate alcohol. Typical examples are provided herein below in the Example section.

15 **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 ($^{\circ}C$) ; the NMR spectral data were recorded in $CDCl_3$ (if not stated otherwise) with a 360 or 400 MHz machine for 1H and ^{13}C , the chemical
20 shifts δ are indicated in ppm with respect to TMS as standard, the coupling constants J are expressed in Hz.

Example 1

25 Synthesis of compounds of formula (I)

General procedure for obtaining the invention's compounds

Ester preparation

30 The methyl carboxylate (116 mmol), the cycloaliphatic alcohol (234 mmol), dioctyl tin oxide (1.0 g; 2.8 mmol) and n-heptane (20 g) were charged in a 100 ml round bottom flask and heated to reflux. The methanol formed by the reaction was removed using a Dean Stark trap. The reaction progress was monitored by GC. After 24 hours the solvent

was distilled off to yield the crude ester in quantitative yield. Distillation through a 15 cm Vigreux column under reduced pressure gave the pure ester.

Using the above general procedure where prepared the following compounds:

5 Cyclopentylmethyl (3Z)-3-hexenoate

Prepared from (Z) methyl hex-3-enoate and cyclopentanemethanol according to general procedure.

Bp.: 72°C/1 mbar

10 ¹³C NMR: 14.0 (q), 20.8 (t), 25.3 (t), 29.4 (t), 33.0 (t), 38.6 (d), 68.6 (t), 120.4 (d), 135.0 (d), 172.2 (s).

¹H-NMR: 0.98 (t, J= 7.5Hz, 3H); 1.21-1.29 (m, 2H); 1.51-1.66 (m, 4H); 1.71-1.79 (m, 2H); 2.03-2.10 (m, 2H); 2.15-2.26 (m, 1H); 3.08 (d, J= 6.3Hz, 2H); 3.97 (d, J= 7.2Hz, 2H); 5.49-5.60 (m, 2H).

15 (Z)-Cyclopent-3-enylmethyl hex-3-enoate

Prepared from (Z) methyl hex-3-enoate and cyclopent-3-enylmethanol according to general procedure.

Purified by bulb to bulb distillation at 120°C/1 mbar

20 ¹³C NMR: 13.9 (q), 20.7 (t), 33.0 (t), 35.7 (t), 36.0 (d), 68.3 (t), 120.3 (d), 129.4 (d), 135.0 (d), 172.2 (s).

¹H-NMR: 0.98 (t, J= 7.5Hz, 3H); 2.03-2.14 (m, 4H); 2.44-2.53 (m, 2H); 2.56-2.66 (m, 1H); 3.09 (d, J= 6.2Hz, 2H); 4.00 (d, J= 7.3Hz, 2H); 5.49-5.61 (m, 2H); 5.63-5.67 (m, 2H).

25 Cyclopentylmethyl 3-methylhex-2-enoate

Prepared from (E/Z) methyl 3-methylhex-2-enoate and cyclopentanemethanol according to general procedure. Bp.: 61°C/0.2 mbar

E isomer (61%)

30 ¹³C NMR: 13.7 (q), 18.7 (q), 20.6 (t), 25.4 (t), 29.5 (t), 38.7 (d), 43.0 (t), 67.6 (t), 115.8 (d), 159.7 (s), 167.1 (s).

¹H-NMR: 0.91 (t, J=7.3Hz, 3H); 1.22-1.32 (m, 2H); 1.46-1.66 (m, 6H); 1.71-1.80 (m, 2H); 2.11 (t, J=7.6Hz, 2H); 2.15 (d, J=0.7Hz, 3H); 2.17-2.25 (m, 1H); 3.98 (D, J=3.6Hz, 2H); 5.66-5.68 (m, 1H);

Z isomer (35%)

¹³C NMR: 14.1 (q), 21.5 (t), 25.1 (q), 25.4 (t), 29.5 (t), 35.3 (t), 38.7 (d), 67.6 (t), 116.4 (d), 160.2 (s), 166.6 (s).

¹H-NMR: 0.95 (t, J=7.3Hz, 3H); 1.22-1.32 (m, 2H); 1.46-1.66 (m, 6H); 1.71-1.80 (m, 2H); 1.88 (d, J=0.7Hz, 3H); 2.17-2.25 (m, 1H); 2.58-5.62 (m, 2H); 3.97 (d, J=3.6Hz, 2H); 5.66-5.68 (m, 1H).

(E)-cyclopentylmethyl hex-2-enoate

Prepared from cyclopentylmethyl (3Z)-3-hexenoate (2 g, 10.19 mmol) by heating for 120 h at 80°C in the presence of 12% weight 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine. Workup (hydrolysis with aq. sodium citrate solution followed by extraction with MTBE, washing with brine, distillation of the solvent) yielded the crude product (1.9 g). Bulb to bulb distillation (85°C/1 mbar) yielded 1.6 g of a mixture containing the desired compound (79%) and some starting material (21%).

¹³C NMR: 13.7 (q), 21.3 (t), 25.3 (t), 29.4 (t), 34.2 (t), 38.7 (d), 68.2 (t), 121.5 (d), 149.1 (d), 166.9 (s).

¹H-NMR: 0.94 (t, J=7.5Hz, 3H); 1.23-1.31 (m, 2H); 1.46-1.66 (m, 6H); 1.71-1.79 (m, 2H); 2.16-2.26 (m, 3H); 4.02 (d, J= 7.0Hz, 2H); 5.83 (d, J= 15.9Hz, 1H); 6.93-6.99 (m, 1H).

Odor : green, pear, slightly onion odor

Example 2Preparation of a perfuming composition

25

A shower gel perfuming composition, of the gourmand, fruity, musky type, was prepared by admixing the following ingredients:

	<u>Ingredient</u>	<u>Parts by weight</u>
30	Benzyl acetate	350
	Anisic aldehyde	290
	Hexylcinnamic aldehyde	450
	10%* Ethyl 2-methyl-pentanoate ¹⁾	50

	Gamma undecalactone	150
	Allyl cyclohexylpropionate	10
	Cis-2-pentyl-1-cyclopentanol ¹⁾	20
	(1'R,E)-2-ethyl-4-(2',2',3'-trimethyl-3'-cyclopenten-1'-yl)-	
5	2-buten-1-ol ¹⁾	50
	Ethylpraline	35
	Ethylvanilline	60
	1,3-Benzodioxole-5-carbaldehyde ¹⁾	100
	Helvetolide ^{® 2)}	500
10	Melonal ^{® 3)}	5
	Lilly of the valley composition ¹⁾	20
	Hedione ^{® 4)}	50
	Octanolide-1,4	270
	Orange essential oil	100
15	Hexyl salicylate	380
	Vertofix Cœur ^{® 5)}	<u>90</u>
		2980

* in dipropyleneglycol

- 20 1) origin: Firmenich SA, Geneva, Switzerland
- 2) (1S,1'R)-2-[1-(3',3'-dimethyl-1'-cyclohexyl)ethoxy]-2-methylpropyl propanoate;
origin: Firmenich SA, Geneva, Switzerland
- 3) 2,6-dimethyl-5-heptenal; origin: Givaudan-Roure SA, Vernier, Switzerland
- 4) methyl dihydrojasmonate; origin: Firmenich SA, Geneva, Switzerland
- 25 5) methyl cedryl ketone; origin: International Flavors & Fragrances, USA

The addition of 20 parts by weight of cyclopentylmethyl (3Z)-3-hexenoate to the above-described composition imparted to the latter an elegant and delicate green and green apple connotation, reminding of a juicy green apple. This effect was not obtained with the

30 addition of other derivatives of cis-3-hexenol which are known ingredients imparting green notes.

Example 3Preparation of a perfuming composition

- 5 A perfuming composition, of the linden type, was prepared by admixing the following ingredients:

	<u>Ingredient</u>	<u>Parts by weight</u>
	Benzyl acetate	55
10	Dodecyl acetate	270
	Hydratropyl alcohol	205
	Anisic aldehyde	20
	Cuminic aldehyde	2
	Dihydro eugenol	20
15	1,3-Benzodioxole-5-carbaldehyde ¹⁾	15
	Hivernal ^{® 2)}	10
	Isoeugenol	5
	Mayol ^{® 3)}	275
	Methylacetophenone	5
20	(1'R)-2-[2-(4'-methyl-3'-cyclohexen-1'-yl)propyl]	
	Cyclopentanone ¹⁾	3
	10%* Neobutenone [®] Alpha ⁴⁾	5
	Methyl octin carbonate	5
	1%* Nonadienal	5
25	Phenethylol	30
	Methyl salicylate	5
	Terpineol	20
	Undecavertol ^{® 5)}	5
	Ionone alpha	20
30	10%** Violettyne ⁶⁾	<u>15</u>
		995

* in dipropyleneglycol

** in isopropyle myristate

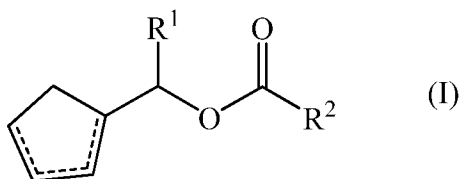
- 1) origin: Firmenich SA, Geneva, Switzerland
- 2) 3-(3,3-dimethyl-5-indanyl)propanal; origin: Firmenich SA, Geneva, Switzerland
- 3) cis-7-P-menthanol; origin: Firmenich SA, Geneva, Switzerland
- 4) 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one; origin: Firmenich SA, Geneva,
5 Switzerland
- 5) 4-methyl-3-decen-5-ol; origin: Givaudan-Roure SA, Vernier, Switzerland
- 6) 1,3-undecadien-5-yne; origin: Firmenich SA, Geneva, Switzerland

The addition of 5 parts by weight of cyclopentylmethyl (3Z)-3-hexenoate to the above-
10 described composition conferred a nice green, connotation and imparted to the latter also
a fruity aspect.

The effect obtained was similar to the one obtained by the addition of classical (Z)-3-hexen-1-ol esters, such as (acetate, propionate or isobutyrate).

Claims

1. A compound of formula



in the form of any one of its stereoisomers or of a mixture thereof, and wherein two dotted lines represent a carbon-carbon single bond and the other a carbon-carbon single bond or double bond;

- 10 R^1 represents a hydrogen atom or a methyl or ethyl group; and

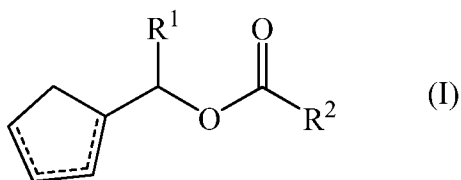
R^2 represents a C_5 - C_8 alkenyl group;

provided that

1-cyclopenten-1-ylmethyl 5-hexenoate, is excluded.

- 15 2. A compound according to claim 1, characterized in that it is cyclopentylmethyl (3Z)-3-hexenoate or (Z)-cyclopent-3-enylmethyl hex-3-enoate.

3. Use as perfuming ingredient of a compound of formula

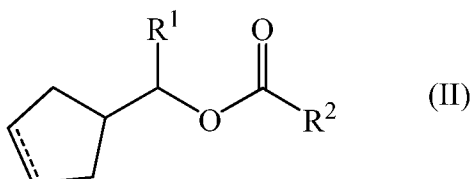


in the form of any one of its stereoisomers or of a mixture thereof, and wherein two dotted lines represent a carbon-carbon single bond and the other a carbon-carbon single bond or double bond;

- 25 R^1 represents a hydrogen atom or a methyl or ethyl group; and

R^2 represents a C_4 - C_8 alkenyl group.

4. Use according to claim 3, characterized in that said compound is of formula

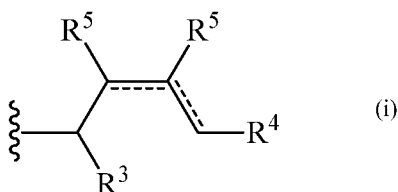


in the form of any one of its stereoisomers or of a mixture thereof, and the dotted line represents a carbon-carbon single bond or double bond; R^1 and R^2 being as defined in claim 3.

5. Use according to claim 3 or 4, characterized in that R^2 represents

a) a C_5 - C_8 group of formula

10



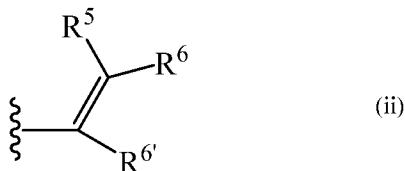
wherein one dotted line represents a carbon-carbon single or double bond and the other a carbon-carbon single bond;

R^4 represents a C_{1-4} alkyl or alkenyl group;

15 R^3 represents a hydrogen atom or a methyl group; and

each R^5 , taken separately, represents a hydrogen atom or a methyl group, or two R^5 , taken together, represent a CH_2 group (in such a case clearly both dotted lines represent a single bond); or R^4 and one R^5 , taken together, represent a C_{3-4} hydrocarbon group; or

20 b) a C_5 - C_8 group of formula



wherein R^6 represents a C_{3-4} alkyl or alkenyl group, $R^{6'}$ represent a hydrogen atom or a methyl or ethyl group, and R^5 is defined as above.

6. Use according to claim 3 or 4, characterized in that said compound is cyclopentylmethyl (3Z)-3-hexenoate or (Z)-cyclopent-3-enylmethyl hex-3-enoate.

- 5 7. A perfuming ingredient in the form of a composition comprising
- i) at least one compound of formula (I), as defined in claim 3;
 - 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.

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8. A perfuming consumer product:
- i) as perfuming ingredient, at least one compound of formula (I) as defined in claim 3; and
 - ii) a perfumery consumer base.

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

- 20 10. A perfuming consumer product according to claim 8, characterized in that the perfumery consumer base 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
- 25 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/EP2011/067218

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C69/533 C11B9/00
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)
C07C C11B

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 practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE CA [Online] CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; PODLEJSKI, JERZY ET AL: "Production of odoriferous substances by cyclization of .beta.-alkyl-.epsilon.-ketoaldehydes", XP002663196, retrieved from STN Database accession no. 1982:6878 abstract & PODLEJSKI, JERZY ET AL: "Production of odoriferous substances by cyclization of .beta.-alkyl-.epsilon.-ketoaldehydes", ZESZYTY NAUKOWE - POLITECHNIKA LODZKA, SERIA: CHEMIA SPOZYWCZA, 361(35), 341-52 CODEN: ZNLSAZ; ISSN: 0528-9254, 1980, -----	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

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"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

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"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

10 November 2011

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17/11/2011

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