

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
29 November 2007 (29.11.2007)

PCT

(10) International Publication Number
WO 2007/135582 A1

(51) International Patent Classification:

C07C 35/36 (2006.01) C07C 69/14 (2006.01)
C07C 69/06 (2006.01) C11B 9/00 (2006.01)

(21) International Application Number:

PCT/IB2007/051654

(22) International Filing Date: 3 May 2007 (03.05.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

PCT/IB2006/051622 22 May 2006 (22.05.2006) IB

(71) Applicant (for all designated States except US): **FIRMENICH SA** [CH/CH]; 1, route des Jeunes, P.O. Box 239, CH-1211 Geneva 8 (CH).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **MORETTI, Robert** [CH/CH]; 148, route de Gy, CH-1251 GY (CH).

(74) Agent: **CARINA, Riccardo**; Firmenich SA, 1, route des Jeunes, P.O. Box 239, CH-1211 Geneva 8 (CH).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

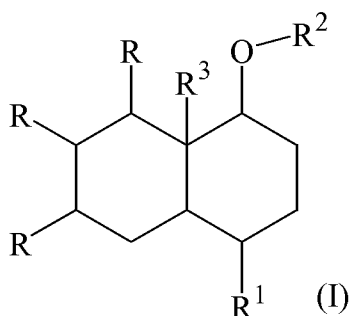
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PATCHOULI ODORANT



(57) Abstract: The present invention relates the use as perfuming ingredients of some derivatives of perhydro-1-naphthalenol of formula (I) wherein, in particular, each R represents a hydrogen atom or a methyl group, R¹ and R³ represent a methyl or ethyl group, and R² represents a hydrogen atom or a lower acyl group.



WO 2007/135582 A1

PATCHOULI ODORANT

Technical field

The present invention relates to the field of perfumery. More particularly, it
5 concerns some derivatives of perhydro-1-naphthaleneol as defined further below and their
use in perfumery to confer patchouli type odors. The present invention concerns also the
compositions or articles containing said compound.

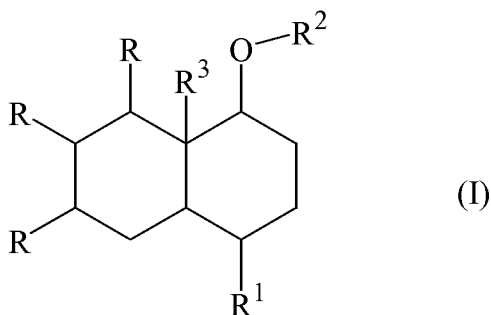
Prior art

10 To the best of our knowledge, none of the invention's compounds is known.

Some unsaturated alcohols or ketones, having a similar structure, are known in
perfumery as being useful ingredients (see EP 1605035, and the discussion further below).
However, nowhere in the prior art it is suggested or anticipated that the present saturated
alcohols/esters could be used as perfuming ingredients, and in particular to confer their
15 particular fragrance.

Description of the invention

We have now surprisingly discovered that a compound of formula



20

in the form of any one of its stereoisomers or of a mixture thereof; and wherein each R,
simultaneously or independently, represents a hydrogen atom or a methyl group;

R¹ represents a methyl or ethyl group;

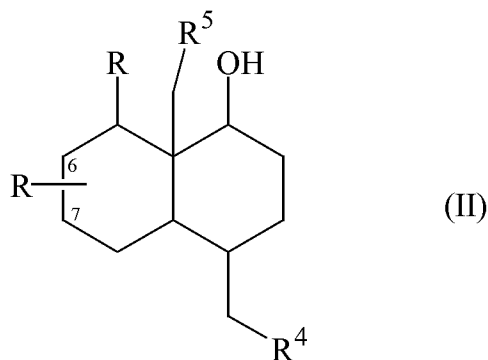
25 R² represents a hydrogen atom or a formyl or acetyl group; and

R³ represents a C₁₋₃ alkyl group;

can be used as perfuming ingredient, for instance to impart odor of the woody type, having

in particular patchouli and/or ambery connotations.

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

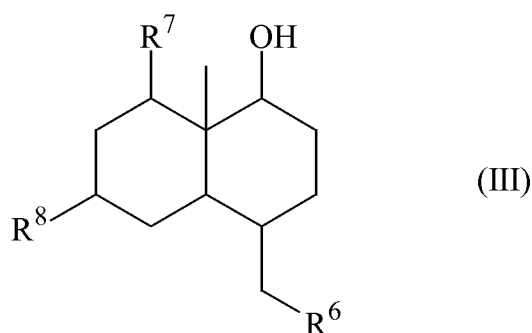


i.e. with a R group in the position 6 or 7, wherein each R, simultaneously or independently, represents a hydrogen atom or a methyl group;

R⁴ represents a hydrogen atom or a methyl group; and

R⁵ represents a hydrogen atom or a methyl or ethyl group.

According to another particular aspect of the invention, said compounds of formula (I) are of formula



wherein R⁶, R⁷ and R⁸, simultaneously or independently, represent a hydrogen atom or a methyl group.

In particular in said formula (III), one may cite the ones wherein R⁶, R⁷ and R⁸ are all hydrogen atoms or the ones wherein R⁷ is a methyl group and one of R⁶ and R⁸ is a hydrogen atom and the other a methyl group.

Amongst the invention's compounds, one may cite perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol, one of the most appreciated by the perfumer. This compound

possesses an odor of the woody type with a strong patchouli character. In fact the olfactive note of this compound belongs to the same family, and is close to, as the one of patchouli oil, and could be used as replacer of the known ingredient 2,6,10,10-tetramethyl-1-oxaspirol[4.5]decan-6-ol in a synthetic patchouli. Its overall fragrance can be described as being of the patchouli type with a rooty and ambery aspect.

Others compounds of formula (I) are also described in Table (I) hereinbelow, together with their odors :

Table 1 : Structure and odor characteristics of the invention's compounds

Structure of compound (I)	Odor
perhydro-4-ethyl-8a-methyl-1-naphthalenol	cedar-patchouli odor with a dried leaves aspect
perhydro-4,8a-dimethyl-1-naphthalenol	woody-rooty patchouli and camphoraceous note having a quite natural overall impression
perhydro-4,6,8,8a-tetramethyl-1-naphthalenol	patchouli, earthy note quite similar to the one of 2,6,10,10-tetramethyl-1-oxaspirol[4.5]decan-6-ol, but distinguish from the latter by being more woody and a bit less patchouli
perhydro-4,6,8a-trimethyl-1-naphthalenol	patchouli, borneol and cellar note
perhydro-4,6,8,8a-tetramethyl-1-naphthalenyl acetate	woody-ambery and dry odor which develops its strength over the time
perhydro-4,6,8a-trimethyl-1-naphthalenyl formate	woody-ambery and methylionone odor
perhydro-4,6,8a-trimethyl-1-naphthalenyl acetate	woody-ambery and with a cedar aspect

The odor of these compounds distinguishes from the ones of the prior art structural analogues (and in particular the ones disclosed in EP 1605035) by lacking, or by not possessing a significant, citrus-grapefruit notes and/or the cedar, leather, ozone and/or

agarwoods notes which are characteristic of the prior art compounds. 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.

For example perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol differs from perhydro-
5 4-ethyl-8,8a-dimethyl-1-naphthalenone, the structurally closest analogue disclosed in EP 1605035, by lacking the typical grapefruit note of said prior art compound. Similarly, perhydro-4,6,8,8a-tetramethyl-1-naphthalenol distinguishes itself from the prior art compounds by lacking the citrus-grapefruit.

As mentioned above, the invention concerns the use of a compound of formula (I)
10 as perfuming ingredient, and in particular to confer an odor of the woody-patchouli and/or ambery type. 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
15 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
20 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.

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 detailed
30 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-
5 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 Gehermittel in Lebensmittel*, Band 2 der Schriftenreihe Lebensmittelchemie, Lebensmittelqualität, Behr's Verlag GmbH & Co.,
10 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.

Generally speaking, by "perfumery base" we mean here a composition comprising
15 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
20 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
25 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, aldehydes, ketones, esters, ethers, acetates, nitriles, terpene hydrocarbons, 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
30 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
5 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).

10 Generally speaking, 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.

15 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.

20 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 or 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
25 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 to positively impart or modify the odor of a consumer product
30 into which said compound (I) is added. Consequently, a perfumed article comprising:

i) as perfuming ingredient, at least one compound of formula (I), as defined above, or an

invention's perfuming composition; and
ii) a consumer product base ;
is also an object of the present invention.

For the sake of clarity, it has to be mentioned that, by "consumer product base" we
5 mean here a consumer product which is compatible with perfuming ingredients. In other
words, a perfumed article according to the invention comprises the functional formulation,
as well as optionally additional benefit agents, corresponding to a consumer product, e.g. a
detergent or an air freshener, and an olfactive effective amount of at least one invention's
compound.

10 The nature and type of the constituents of the 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 its general knowledge and according to the
nature and the desired effect of said product.

Examples of suitable consumer product bases include solid or liquid detergents and
15 fabric softeners as well as all the other articles common in perfumery, namely perfumes,
colognes or after-shave lotions, perfumed soaps, shower or bath salts, mousses, oils or
gels, hygiene products or hair care products such as shampoos, body-care products,
deodorants or antiperspirants, air fresheners and also cosmetic preparations. As detergents
there are intended applications such as detergent compositions or cleaning products for
20 washing up or for cleaning various surfaces, e.g. intended for textile, dish or hard-surface
treatment, whether they are intended for domestic or industrial use. Other perfumed
articles are fabric refreshers, ironing waters, papers, wipes or bleaches.

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
25 the latter from premature decomposition, for example by encapsulation.

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
30 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 0.001 % to 15 % by weight, or even more, of the compounds 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 10% by weight, can be used when these
5 compounds are incorporated into perfumed articles, percentage being relative to the weight of the article.

The invention's compounds can be prepared by hydrogenation/reduction of the corresponding unsaturated alcohol, or the corresponding ketone, described in EP 1605035. A typical example of such manner to prepare the invention's compounds is
10 exposed hereinbelow.

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
15 displacements δ are indicated in ppm with respect to TMS as standard, the coupling constants J are expressed in Hz. The NMR spectra are for the mixtures of isomers, unless specified.

Example 1

20

Synthesis of compounds of formula (I) by using the aldol derivative of α -damascone as starting material

General procedures:

25 **I) *General procedure for the Diels-Alder coupling***

In a 500 ml reactor were introduced the AlEtCl₂, or the AlCl₃, 0.1 g of BHT and toluene, or CH₂Cl₂. Then, under vigorous stirring, was added the appropriate cyclohexenone dropwise, so as to maintain the temperature below 30°C. Afterwards was added the diene dropwise and when the reaction ended the reaction mixture was
30 hydrolyzed with 5% aqueous HCl, extracted twice with Et₂O. The organic layer was then washed with a saturated NaHCO₃ aqueous solution, water, brine and then dried

over Na_2SO_4 . Evaporation of the solvents, chromatography (SiO_2 , elution heptane/AcOEt 98:2) and distillation provided the end product.

II) General procedure for the reduction of the ketone into the alcohol

5 In a 100 ml flask, maintained under Ar atmosphere, were introduced 2 molar equivalents, with respect of the ketone, of LiAlH_4 in Et_2O . Then the appropriate naphthalenone was added dropwise, so as to maintain the reflux. After completion of the reaction the mixture was stirred for 30 minutes at reflux. Afterwards the reaction mixture was hydrolyzed with a stoichiometric amount of aqueous NaOH and the
10 organic layer was dried over Na_2SO_4 . Evaporation of the solvents and distillation provided the end product.

III) General procedure for the hydrogenation of the naphthalenone into the perhydro naphthalenone

15 In a 100 ml flask were introduced the appropriate naphthalenone, ethyl acetate and 10% w/w, relative to the naphthalenone, of Pd/C 5%. The mixture was thus stirred under H_2 , at a room temperature, until consumption of the theoretical amount of hydrogen. Afterwards, the reaction mixture was filtered over Nylon 6/6. Evaporation of the solvents and distillation provided the end product.

20

IV) General procedure for the esterification of the alcohol

In a 250 ml flask were introduced the appropriate alcohol, CH_2Cl_2 , dimethylaminopyridine, pyridine and the appropriate carboxylic anhydride. The mixture was thus stirred 24 hours at room temperature. When the reaction has
25 finished the reaction mixture was hydrolyzed with 5% aqueous HCl, extracted twice with Et_2O . The organic layer was then washed an aqueous solution of CuSO_4 , a saturated NaHCO_3 aqueous solution, water, brine and then dried over Na_2SO_4 . Evaporation of the solvents provided the end product.

30 **Perhydro-4,6,8a-trimethyl-1-naphthalenol**

Step 1: 4,6,8a-Trimethyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone

Prepared according to the general procedure # I, with the following quantities:

2,4-Dimethyl-2-cyclohexen-1-one (40 g, 0.32 mmol), Aluminium trichloride (10.7 g, 0.08 mmol), Isoprene (326 g, 4.8 mol), Toluene (500 ml)

The compound was obtained as a mixture of isomers (87/4/9) in 83 % yield.

B.p. = 78 °C/0.003 mbar

5 ¹³C-NMR (major isomer): 215.68; 130.73; 117.13; 47.83; 46.86; 37.29; 35.02; 32.14; 29.76; 28.82; 23.84; 20.15; 20.04.

¹H-NMR (major isomer): 0.93 (d, J = 7 Hz, 3 H); 1.07 (s, 3 H); 1.27-1.43 (m, 2 H); 1.60-1.86 (m, 2 H); 1.68 (broad s, 3 H); 1.92-2.15 (m, 3 H); 2.22-2.45 (m, 2 H); 2.70-2.80 (m, 1 H); 5.32 (broad s, 1 H).

10

Step 2: *Perhydro-4,6,8a-trimethyl-1-naphthalenone*

Prepared according to the general procedure # III, with the following quantities:

Naphthalenone obtained in step 1 (10 g; 0.052 mol), 5 % Pd-C (1 g), EtOAc (200 ml), H₂ (1.16 l)

15 The product was obtained in 98 % yield as a mixture of isomers (4/16/80).

B.p. = 85 °C/0.017 mbar

¹H-NMR: 0.81-0.98 (m, 6H); 1.12-1.78 (m, 11H); 1.85-2.30 (m, 4H); 2.52-2.72 (m, 1H).

20 Step 3: *Perhydro-4,6,8a-trimethyl-1-naphthalenol*

Prepared according to the general procedure # II, with the following quantities:

Naphthalenone obtained in step 2 (4.0 g; 0.0206 mol), Lithium aluminium hydride (0.39 g; 0.0103 mol), Ether (40 ml)

The title compound was obtained in 91 % yield as a mixture of isomers (8/67/6/15).

25 B.p. = 79 °C/0.004 mbar

¹H-NMR: 0.80-0.92 (m, 7H); 0.94-1.15 (m, 6H); 1.20-2.05 (m, 10H); 3.22-3.56 (m, 1H).

Perhydro-4,6,8a-trimethyl-1-naphthalenyl acetate

30 The title compound was obtained according to the general procedure IV, with the following quantities:

Perhydro-4,6,8a-trimethyl-1-naphthalenol ((1.8 g, 0.0094 mol), Acetic anhydride (1.43 g, 0.014 mol), Pyridine (1.26 g, 0.016 mol), Dimethylaminopyridine (0.11 g, 0.54 mmol), Dichloromethane (20 ml).

The title compound was obtained in 72 % yield as a mixture of isomers (10/70/15).

5 B.p. = 72 °C/0.004 mbar

¹H-NMR: 0.80-1.18 (m, 12H); 1.20-1.90 (m, 10H); 2.00-2.07 (m, 3H); 4.57 (m, 1H)

Perhydro-4,6,8a-trimethyl-1-naphthalenyl formate

Prepared according to the general procedure IV, with the following quantities:

10 Perhydro-4,6,8a-trimethyl-1-naphthalenol (2.0 g, 0.01 mol), Acetic anhydride (3.06 g, 0.03 mol) and formic acid (1.66 g, 0.036 mol) heated together at 55 °C for 2 hours, Dichloromethane (20 ml)

The title compound was obtained in 93 % yield as a mixture of isomers (15/56/8/3/18).

B.p. = 64 °C/0.002 mbar

15 ¹H-NMR: 0.80-1.20 (m, 11 H); 1.23-2.10 (m, 11 H); 4.65-4.72 (m, 1 H); 8.09 (m, 1 H).

Perhydro-4,6,8,8a-tetramethyl-1-naphthalenol

Step 1: *4,6,8,8a-Tetramethyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone*

Prepared according to the general procedure # I, with the following quantities:

20 2,4-Dimethyl-2-cyclohexen-1-one (7.25 g, 0.0585 mol), Ethyl aluminium dichloride (1 molar solution in hexane, 29.2 ml, 0.0292 mol), Methylpentadiene (70 % chemical purity, 16.7 g, 0.117 mol), Dichloromethane (150 ml)

The compound was obtained in 90 % yield as a mixture of isomers (89/11).

B.p. = 85 °C/0.065 mbar

25 ¹H-NMR: 0.72-1.02 (m, 6H); 1.15-1.47 (m, 4H); 1.58-2.78 (m, 11H); 5.08-5.38 (m, 1H).

Step 2: *perhydro-4,6,8,8a-tetramethyl-1-naphthalenone*

Prepared according to general procedure # III, with the following quantities:

30 Unsaturated ketone obtained in step 1 (4.5 g; 0.022 mol), 5 % Pd-C (0.45 g), EtOAc (40 ml), H₂ (0.55 l)

The compound was obtained in 95 % yield as a mixture of isomers (2/3/63/18/7/3/2/3).

B.p. = 74 °C/0.008 mbar

¹H-NMR: 0.60-1.10 (m, 7H); 1.10-1.80 (m; 13 H); 1.90-2.70 (m, 4 H).

Step 3: *perhydro-4,6,8,8a-tetramethyl-1-naphthalenol*

5 Prepared according to the general procedure # III, with the following quantities:

Ketone obtained in step 2 (3.05 g, 0.0147 mol), Lithium aluminium hydride (0.28 g, 0.0073 mol), Diethylether (20 ml)

The title compound was obtained in 92 % yield as a mixture of isomers (4/2/77/10/2/3).

B.p. = 74 °C/0.034 mbar

10 ¹H-NMR: 0.78-1.10 (m, 10H); 1.12-1.50 (m, 9H); 1.50-2.12 (m, 6H); 3.30-3.80 (m, 1H).

Perhydro-4,6,8,8a-tetramethyl-1-naphthalenyl acetate

Prepared according to the general procedure # IV, with the following quantities:

15 Perhydro-4,6,8,8a-tetramethyl-1-naphthalenol (0.90 g, 0.0043 mol), Acetic anhydride (0.66 g, 0.0064 mol), Pyridine (0.58 g, 0.0073 mol), Dimethylaminopyridine (0.052 g, 0.43 mmol), Dichloromethane (20 ml)

The title compound was obtained in 76 % yield as a mixture of isomers (2/4/53/30/6).

B.p. = 78 °C/0.034 mbar

20 ¹H-NMR: 0.80-0.98 (m, 9 H); 1.90-1.95 (m, 16 H); 2.00-2.20 (m, 3 H).

Perhydro-4,8a-dimethyl-1-naphthalenol

Step 1: *4,8a-Dimethyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone*

Prepared according the general procedure # I, with the following quantities:

25 2,4-Dimethyl-2-cyclohexen-1-one (10.0 g, 0.081 mol), Butadiene (8.75 g, 0.162 mol), Ethyl aluminium dichloride (1 molar solution in hexane, 40 ml, 0.040 mol), Dichloromethane (100 ml)

The compound was obtained in 43 % yield as a mixture of isomers (55/45).

B.p = 85 °C/1.1 mbar

30 ¹H-NMR: 0.95 (m, 3H); 1.12-1.45 (m, 4H); 1.60-2.45 (m, 7H); 2.60-2.80 (m, 2H); 5.55-5.68 (m, 2H).

Step 2: *perhydro-4,8a-dimethyl-1-naphthalenone*

Prepared according to the general procedure # III, with the following quantities:

Unsaturated ketone obtained in step 1 (3.0 g, 0.017 mol), 5 % Pd-C (0.3 g), EtOAc (30 ml), H₂ (0.38 l)

5 The compound was obtained in 89 % yield as a mixture of isomers (44.4/55.6).

B.p. = 85 °C/0.017 mbar

¹H-NMR: 0.80-0.98 (m, 4H); 1.10-2.00 (m, 12H); 2.07-2.30 (m, 2H); 2.45-2.70 (m, 2H).

10 Step 3: *Perhydro-4,8a-dimethyl-1-naphthalenol*

Prepared according to general procedure # II, with the following quantities:

Ketone obtained in step 2 (2.0 g, 0.011 mol), Lithium aluminium hydride (0.21 g, 0.0055 mol), Diethyl ether (20 ml)

The title compound was obtained in 83 % yield as a mixture of isomers (23/50/26).

15 B.p. = 93 °C/0.97 mbar

¹H-NMR: 0.78-1.12 (m, 8H); 1.14-2.08 (m, 13H); 3.22-4.02 (m, 1H).

Perhydro-4-ethyl-8a-methyl-1-naphthalenolStep 1: *4-Ethyl-8a-methyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone*

20 Prepared according to the general procedure # I, with the following quantities:

4-Ethyl-2-methyl-2-cyclohexen-1-one (27.6 g, 0.20 mol), Butadiene (21.6 g, 0.040 mol), Ethyl aluminium dichloride (1 molar solution in hexane, 100 ml, 0.10 mol), Dichloromethane (300 ml)

The compound was obtained in 42 % yield as a mixture of isomers (61/39).

25 B.p. = 76 °C/0.021 mbar

¹H-NMR: 0.82-0.98 (m, 3H); 1.10-1.45 (m, 5H); 1.55-1.80 (m, 3H); 1.90-2.46 (m, 5H); 2.62-2.77 (m, 2H); 5.52-5.68 (m, 2H).

Step 2: *Perhydro-4-ethyl-8a-methyl-1-naphthalenone*

30 Prepared according to the general procedure # III, using the following quantities:

Unsaturated ketone obtained in step 1 (5.0 g, 0.026 mol), 5 % Pd-C (0.5 g), EtOAc (50 ml)

H₂ (0.6 l)

The compound was obtained in 97 % yield as a mixture of isomers (40/60).

B.p. = 84 °C/0.048 mbar

¹H-NMR: 0.82-0.95 (m, 3H); 1.08-1.75 (m, 14H); 1.80-2.36 (m, 4H); 2.52-2.63 (m, 1H).

Step 3: *Perhydro-4-ethyl-8a-methyl-1-naphthalenol*

Prepared according to the general procedure # II, with the following quantities:

Ketone obtained in step 2 (3.40 g, 0.0175 mol), Lithium aluminium hydride (0.33 g, 0.00875 mol), Diethyl ether (30 ml)

The title compound was obtained in 99 % yield as a mixture of isomers (11/21/4/64).

B.p. = 86 °C/0.055 mbar

¹H-NMR: 0.78-1.10 (m, 6H); 1.12-1.96 (m, 17H); 3.22-4.03 (m, 1H).

15 **Perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol**

Step 1: *4-Ethyl-8,8a-dimethyl-3,4,4a,5,8,8a-hexahydro-1(2H)-naphthalenone*

Prepared according to the general procedure I, with the following quantities:

4-Ethyl-2-methyl-2-cyclohexen-1-one (20.7 g, 0.15 mol), Piperylene (50 % chemical purity, 40.8 g, 0.30 mol), Ethyl aluminium dichloride (1 molar solution in hexane, 30 ml, 0.03 mol), Dichloromethane (200 ml)

The title compound was obtained in 72 % yield as a mixture of isomers (63/37).

B.p. = 81 °C/0.034 mbar

¹H-NMR: 0.76-1.30 (m, 9 H); 1.42-1.83 (m, 4 H); 1.90-2.37 (m, 6 H); 2.50-2.77 (m, 1 H); 5.37-5.62 (m, 2 H).

Step 2: *perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenone*

Prepared according to the general procedure # III, with the following quantities:

Unsaturated ketone obtained in step 1 (5.0 g, 0.025 mol), 5 % Pd-C (0.5 g), EtOAc (50 ml), H₂ (0.625 l).

The title compound was obtained in 98 % yield as a mixture of isomers (42/38/18).

B.p. = 86 °C/0.036 mbar

¹H-NMR: 0.60-1.20 (m, 7H); 1.20-1.90 (m, 13H); 1.95-2.40 (m, 3H); 2.50-2.70 (m, 1H).

Step 3: *Perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol*

5 Prepared according to the general procedure # II, with the following quantities:

Starting ketone obtained in step 2 (3.90 g, 0.018 mol), Lithiumaluminium hydride (0.34 g, 0.009 mol),

Diethyl ether (30 ml)

The title compound was obtained in 99 % yield as a mixture of isomers (33/7/40/17)

10 B.p. = 90 °C/0.032 mbar

¹H-NMR: 0.78-1.17 (m, 10 H); 1.20-2.12 (m, 15 H); 3.22-3.82 (m, 1 H).

Example 2

15 Preparation of a perfuming composition

A perfuming base was prepared by admixing the following ingredients :

	<u>Ingredient</u>	<u>Parts by weight</u>
20	Styrallyl acetate	10
	Allyl amyl glycolate	5
	10%* 4-Nonanolide	5
	Bergamote essential oil	100
	Coumarine	15
25	10%* Damascone delta	5
	3,7-Dimethyl-1,6-nonadien-3-ol	50
	10%* 2-Ethyl-3-hydroxy-4(4H)-pyranone	20
	Florol ^{® 1)}	100
	3-(4-Methoxyphenyl)-2-methylpropanal	30
30	Lilyflore ^{® 2)}	20
	Mandarine essential oil	10
	Nutmeg	10
	Hedione ^{® 3)}	300

	1,2,3,4,4a β ,5,8,8a β -Octahydro-2,2,6,8 α -tetramethyl-1 α -naphthalenol	5
	Portugal Bresil essential oil	20
	Romandolide ^{® 4)}	150
	Pipol salicylate	20
5	Vanilline	15
	10%* 2,4-Dimethyl-3-cyclohexene-1-carbaldehyde	<u>30</u>
		920

* in dipropyleneglycol

- 10 1) Tetrahydro-2-isobutyl-4-methyl-4(2H)-pyranol; origin: Firmenich SA, Geneva, CH
 2) 2,5-Dimethyl-2-indanmethanol; origin: Firmenich SA, Geneva, CH
 3) Methyl dihydrojasmonate; origin: Firmenich SA, Geneva, CH
 4) (1S,1'R)-[1-(3',3'-Dimethyl-1'-cyclohexyl)ethoxycarbonyl]methyl propanoate; origin:
 Firmenich SA, Geneva, CH

15

The addition of 80 parts by weight of perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol to the above-described perfuming composition imparted to the latter an excellent woody character very close to the one of patchouli. Furthermore a camphoraceous aspect is developed, which impart to the new fragrance a nice freshness in the head-notes. Upon
 20 evaporation of the perfuming composition, the ambery aspect of the invention's compounds became more perceivable, adding thus a new pleasant effect to the patchouli dimension.

When to the above-mentioned perfuming base was added the same amount of patchouli the new fragrance was earthier and less elegant than the one obtained with the invention's
 25 compound.

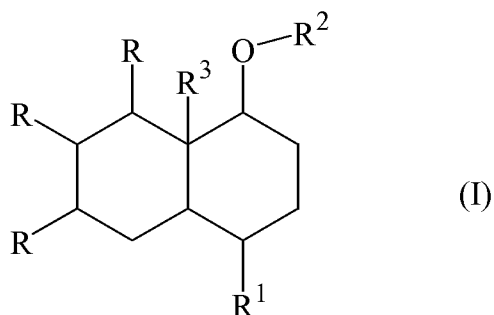
When to the above-mentioned perfuming base was added the same amount of 4-ethyl-6,8-dimethyl-1,2,3,4,4a,5,8,8a-octahydro-1-naphthalenol (a perfuming ingredient from the prior art) the base scent acquired a different woody character, which was of the vetiver type, furthermore it acquired also a grapefruit character which modified strongly the whole
 30 fragrance (less oriental type)

When to the above-mentioned perfuming base was added the same amount of perhydro-4-ethyl-8-methyl-1-naphthalenone (a perfuming ingredient from the prior art) the base scent acquired a powerful sweet-powdery woody note with a vetyver type connotation.

When to the above-mentioned perfuming base was added the same amount of perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenone (a perfuming ingredient from the prior art) the base
5 scent acquired a vetyver and grapefruit character, no patchouli note was perceivable.

Claims

1. A compound of formula



5

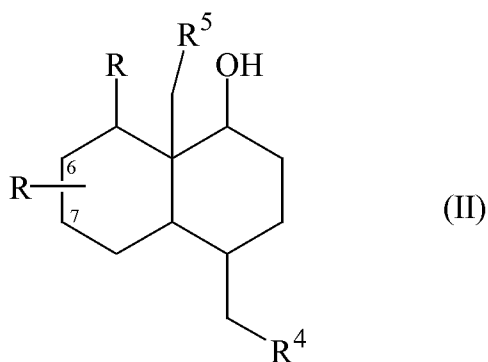
in the form of any one of its stereoisomers or of a mixture thereof; and wherein each R, simultaneously or independently, represents a hydrogen atom or a methyl group;

R¹ represents a methyl or ethyl group;

10 R² represents a hydrogen atom or a formyl or acetyl group; and

R³ represents a C₁₋₃ alkyl group.

2. A compound according to claim 2, characterized in that it is of formula



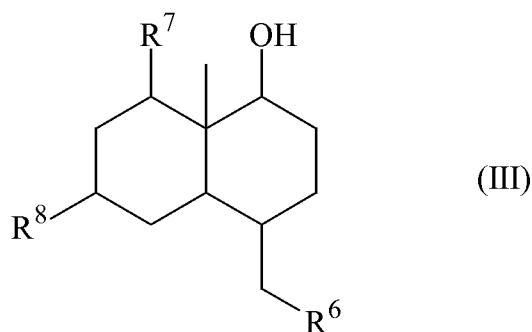
15

wherein each R, simultaneously or independently, represents a hydrogen atom or a methyl group;

R⁴ represents a hydrogen atom or a methyl group; and

20 R⁵ represents a hydrogen atom or a methyl or ethyl group.

3. A compound according to claim 2, characterized in that it is of formula



wherein R^6 , R^7 and R^8 , simultaneously or independently, represents a hydrogen atom or a methyl group.

4. As a compound according to claim 1, perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol, perhydro-4-ethyl-8a-methyl-1-naphthalenol, perhydro-4,8a-dimethyl-1-naphthalenol, perhydro-4,6,8,8a-tetramethyl-1-naphthalenol, perhydro-4 β ,6 β ,8a β -trimethyl-4a β H-1 α -naphthalenol, perhydro-4,6,8,8a-tetramethyl-1-naphthalenyl acetate, perhydro-4 β ,6 β ,8a β -trimethyl-4a α H-1 α -naphthalenyl formate or perhydro-4,6,8a-trimethyl-1-naphthalenyl acetate.

5. As a compound according to claim 1, perhydro-4-ethyl-8,8a-dimethyl-1-naphthalenol, perhydro-4-ethyl-8a-methyl-1-naphthalenol, perhydro-4,8a-dimethyl-1-naphthalenol, perhydro-4,6,8,8a-tetramethyl-1-naphthalenol, perhydro-4 β ,6 β ,8a β -trimethyl-4a β H-1 α -naphthalenol.

6. A perfuming ingredient in the form of a composition comprising

- i) at least an invention's compound as defined in any one of claims 1 to 5;
- 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.

7. A perfumed article comprising:

- i) as perfuming ingredient, at least one compound of formula (I), as defined in any one of claims 1 to 5; and
- ii) a consumer product base.

8. A perfumed article according to claim 7, characterized in that the consumer product base is a solid or liquid detergent, a fabric softener, a perfume, a cologne or after-shave lotion, a perfumed soap, a shower or bath salt, mousse, oil or gel, a hygiene product,
5 a hair care product, a shampoo, a body-care product, a deodorant or antiperspirant, an air freshener, a cosmetic preparation, a fabric refresher, an ironing water, a paper, a wipe or a bleach.

9. Use as perfuming ingredient of a compound of formula (I), as defined in
10 anyone of claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/051654

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C35/36 C07C69/06 C07C69/14 C11B9/00

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, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 605 035 A1 (FIRMENICH & CIE [CH]) 14 December 2005 (2005-12-14) cited in the application claims 1-11; examples 1-3 -----	1-9
A	EP 0 465 936 A2 (FIRMENICH & CIE [CH]) 15 January 1992 (1992-01-15) claims 1-9; examples 1-14 -----	1-9
A	EP 0 167 709 A2 (FIRMENICH & CIE [CH]) 15 January 1986 (1986-01-15) claims 1-7; examples 1-6 ----- -/--	1-9

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- * & * document member of the same patent family

Date of the actual completion of the international search

2 October 2007

Date of mailing of the international search report

16/10/2007

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

GRAMMENOUDI, S

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/051654

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	MEHTA, GOVERDHAN ET AL MEHTA, GOVERDHAN ET AL: "Terpenes and related systems. XIII. Regiospecific fragmentation of patchoulol . Short synthesis of .alpha.-bulnesene" TETRAHEDRON LETTERS, vol. 50, 1975, pages 4495-4498, XP002453448 page 4496, compound 6 -----	1-9

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2007/051654

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1605035	A1	14-12-2005	NONE	
EP 0465936	A2	15-01-1992	DE 69106957 D1 DE 69106957 T2 JP 4368352 A US 5114915 A	09-03-1995 14-06-1995 21-12-1992 19-05-1992
EP 0167709	A2	15-01-1986	DE 3574583 D1 JP 1464942 C JP 61040235 A JP 63012853 B US 4671798 A	11-01-1990 10-11-1988 26-02-1986 23-03-1988 09-06-1987