

FRAGRANCE PRECURSORS

TECHNICAL FIELD

The present invention relates generally to fragrance precursors, which release odorant compounds. The invention also relates to fragrance compositions and consumer products containing said precursors. The invention further relates to methods of making said fragrance precursors, fragrance compositions and consumer products.

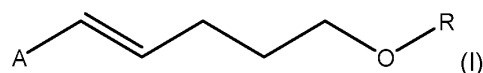
BACKGROUND

Consumer products such as fabric care products comprising fragrances are well-known in the art. However, since a few years, the interest in precursor technology has been renewed notably regarding claim support and customer's request for long-lastingness in challenging applications. Furthermore, some opportunities such as the future plastic legislation in Europe (potentially threatening the use of synthetic microcapsules) might benefit the precursor technology. Any new development should however consider customer's and consumer's request for "green" alternatives (considering sustainability, renewability and biodegradability).

The washing and softening of textiles are particular fields in which there is a constant need to enable the effect of active substances, in particular fragrance compositions, to be effective for a certain period of time after washing, softening and drying. Indeed, many fragrances which are particularly suitable for this type of application are known to lack tenacity on laundry, or do not remain on the laundry when rinsed, with the result that their perfuming effect is experienced only briefly and not very intensely. Given the importance of this type of application in the perfume industry, research in this field has been sustained, in particular with the aim of finding new, and more effective solutions to the aforementioned problems. Although use of fragrance precursors for consumer products are known, there still remains room for improvement with regard to odor profiles and /or deposition profiles. In particular, it is desirable to provide compounds that possess a long-lasting freshness.

SUMMARY

In accordance with a first aspect of the present invention there is provided a compound of formula (I)



wherein

A is selected from the group consisting of anisyl and naphthyl, and R is selected from C₆ – C₈ alkyl.

In accordance with a second aspect of the present invention there are provided fragrance compositions and consumer products comprising the compound of the first aspect of the invention.

- 5 In accordance with a third aspect of the present invention there is provided the use of the compound of the first aspect as fragrance precursor, in particular as a precursor which is capable of releasing watery, aldehydic, green olfactory impressions when exposed to ambient air.
- 10 In accordance with a fourth aspect of the present invention there is provided a method of manufacturing a consumer product comprising the incorporation of a compound of formula (I) to a consumer product base.

- In accordance with a fifth aspect of the present invention there is provided a method to
- 15 confer, enhance, improve or modify the hedonic properties of a substrate, which method comprises contacting said substrate with a product comprising a compound of the first aspect of the invention.

- Certain embodiments of any aspect of the present invention may provide one or more of the
- 20 following advantages:

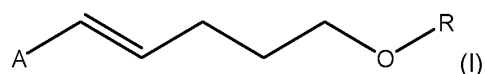
- well balanced odor profile
- good deposition properties on substrates
- biodegradable
- stable in aggressive media

- 25 The details, examples and preferences provided in relation to any particular one or more of the stated aspects of the present invention will be further described herein and apply equally to all aspects of the present invention. Any combination of the embodiments, examples and preferences described herein in all possible variations thereof is encompassed by the present
- 30 invention unless otherwise indicated herein, or otherwise clearly contradicted by context.

DETAILED DESCRIPTION

- The present invention is based on the surprising finding that compounds of formula (I) as
- herein defined can serve as fragrance precursors able to release over a long period watery,
- 35 aldehydic, green odor profiles when exposed to ambient air. This odor profile is equated with freshness, an odor impression which is very much sought after, in particular in fabric care products.

There is therefor provided herein a compound of formula (I)



wherein

- 5 A is selected from the group consisting of anisyl and naphthyl, and
R is selected from C₆ – C₈ alkyl (linear or branched).

In one particular embodiment the compound of formula (I) is a compound wherein A is anisyl.

- 10 In another particular embodiment the compound of formula (I) is a compound wherein A is naphthyl.

In another particular embodiment the compound of formula (I) is a compound wherein R is selected from 6-methyl-hept-2-yl, n-hexyl and n-heptyl.

- 15 As specific examples of compounds of formula (I) one may cite 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene, 1-methoxy-4-(5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene, 2-(5-(hexyloxy)pent-1-en-1-yl)naphthalene, and 1-(5-(heptyloxy)pent-1-en-1-yl)-4-methoxybenzene.

- 20 The compounds of formula (I) exist as two different isomers. In one particular embodiment the compound of formula (I) is a compound wherein the double bond is in *E*-configuration.

- Furthermore, the compounds of formula (I) can have one or more stereo centers and in
25 consequence exist as different stereoisomers (e.g. diastereomers or enantiomers), all of which are encompassed by the present invention. Chiral compounds of formula (I) can be enantiomerically pure, enriched or racemic. If more than one stereo center is present, the compounds are either diastereomeric mixtures, diastereomerically enriched or pure diastereomers.

- 30 Inventors surprisingly found that the compounds of formula (I) as herein defined possess very good deposition properties, in particular on fabrics and are therefore substantially retained on the fabric for the complete washing cycle. In other words, they do not get lost in larger quantities during rinse-off procedure, e.g., in a washing machine.

- 35 Thus there is provided in a further aspect of the present invention a method to confer, enhance, improve or modify the hedonic properties of a substrate which method comprises

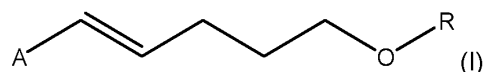
contacting said substrate with a rinse-off product comprising a compound of formula (I) as herein defined.

The term "rinse-off products" as used herein are products that only come into contact with the substrate to be treated for a short time and are then washed off with water. As an examples one may cite cleaning products such as detergents (e.g. laundry detergent in liquid or powder form), and finishing agents including fabric softeners. Further examples are typically cosmetic products such as shower baths, shampoos and cleaning agents, which come into contact with the skin for a short time and are then washed off with water.

In one specific embodiment the substrate to be treated is a fabric.

Due to their good deposition properties the compound of formula (I) does not get lost in larger quantities during rinse-off procedure remains on the substrate (being it fabric, skin, or hair) to which the rinse-off product was applied. And when the substrate to which the rinse-off product comprising a compound of formula (I) was applied is then exposed to ambient air a noticeable watery, aldehydic, green olfactory impression is observed.

Thus there is provided in a further aspect of the present invention the use of the compound of formula (I)



wherein

A is selected from the group consisting of anisyl and naphthyl, and

R is selected from C₆ – C₈ alkyl (linear or branched),

as fragrance precursor, in particular as a precursor which is capable of releasing watery, aldehydic, green olfactory impressions when exposed to ambient air.

Exposure to ambient air means exposure to molecular oxygen which might be responsible for the oxidative cleavage of the compound of formula (I). The concentration of oxygen in the air is sufficient for cleaving the compound of formula (I) so that the cleavage products can be detected in the ambient air, e.g. by olfaction or GC-MS analysis of collected organic volatiles from the precursor headspace.

The cleavage products of the compound of formula (I) was noticeable over a long period (at least 3 days and longer (e.g. 4, 5, 6, or 7 days). The watery, aldehydic, green olfactory impression was still very well perceived even after 4 days after the washing of the fabric.

The compounds of formula (I) are very stable when stored in neat form in appropriate containers protected from air, or when stored in proper solvents. For example, in ethanol, isopropanol, diethylene glycol monoethyl ether, glycerol, propylene glycol, 1,2-butylene glycol, dipropylene glycol, isopropyl myristate, triethyl citrate, diethyl phthalate, triacetine and/or diacetine. The compounds of formula (I) show a high degree of stability, even when they are admixed into aggressive consumer product bases, such as liquid detergents and/or liquid fabric softener. Thus the compounds of formula (I) may find use in a broad range of consumer products.

- 10 By "aggressive media" we mean in the context of the present invention compositions having a non-neutral pH, for example, compositions having a pH lower than 5 or a higher than 9.

The compound of formula (I) may be used alone or in combination with further fragrance precursors and/or odorants well known in the art.

- 15 The odorant(s) may be selected from the extensive range of natural products, and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture with one or more ingredients or excipients conventionally used in conjunction with odorants in perfume compositions, for example, carrier materials, and other auxiliary agents commonly used in the art.

The following non limiting list comprises examples of known odorants, which may be combined with the compound of formula (I) in a fragrance composition:

- 25 • Essential oils and extracts, e.g. castoreum, costus root oil, oak moss absolute, geranium oil, tree moss absolute, basil oil, fruit oils, such as bergamot oil and mandarin oil, myrtle oil, palmarose oil, patchouli oil, petitgrain oil, jasmine oil, rose oil, sandalwood oil, wormwood oil, lavender oil and/ or ylang-ylang oil;
- 30 • Alcohols, e.g. cinnamic alcohol ((E)-3-phenylprop-2-en-1-ol); cis-3-hexenol ((Z)-hex-3-en-1-ol); Citronellol (3,7-dimethyloct-6-en-1-ol); dihydro myrcenol (2,6-dimethyloct-7-en-2-ol); Ebanol™ ((E)-3-methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pent-4-en-2-ol); eugenol (4-allyl-2-methoxyphenol); ethyl linalool ((E)-3,7-dimethylnona-1,6-dien-3-ol); farnesol ((2E,6Z)-3,7,11-trimethyldodeca-2,6,10-trien-1-ol); geraniol ((E)-3,7-dimethylocta-2,6-dien-1-ol); Super Muguet™ ((E)-6-ethyl-3-methyloct-6-en-1-ol); linalool (3,7-dimethylocta-1,6-dien-3-ol); menthol (2-isopropyl-5-methylcyclohexanol); Nerol (3,7-dimethyl-2,6-octadien-1-ol); phenyl ethyl alcohol (2-phenylethanol); Rhodinol™ (3,7-dimethyloct-6-en-1-ol); Sandalore™ (3-methyl-5-(2,2,3-

trimethylcyclopent-3-en-1-yl)pentan-2-ol); terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-ol); or Timberol™ (1-(2,2,6-trimethylcyclohexyl)hexan-3-ol); 2,4,7-trimethylocta-2,6-dien-1-ol, and/or [1-methyl-2(5-methylhex-4-en-2-yl)cyclopropyl]-methanol;

- 5 • Aldehydes and ketones, e.g. anisaldehyde (4-methoxybenzaldehyde); alpha amyl cinnamic aldehyde (2-benzylideneheptanal); Georgywood™ (1-(1,2,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-2-yl)ethanone); Hydroxycitronellal (7-hydroxy-3,7-dimethyloctanal); Iso E Super® (1-(2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-2-yl)ethanone); Isoraldeine® ((E)-3-methyl-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one); Hedione® (methyl 3-oxo-2-pentylcyclopentaneacetate); Nympeal (3-(4-isobutyl-2-methylphenyl)propanal); Mahonial (5,9-dimethyl-9-hydroxy-decen-4-al); maltol; methyl cedryl ketone; methylionone; verbenone; and/or vanillin;
- 10 • Ether and acetals, e.g. Ambrox® (3a,6,6,9a-tetramethyl-2,4,5,5a,7,8,9,9b-octahydro-1H-benzo[e][1]benzofuran); geranyl methyl ether ((2E)-1-methoxy-3,7-dimethylocta-2,6-diene); rose oxide (4-methyl-2-(2-methylprop-1-en-1-yl)tetrahydro-2H-pyran); and/or Spirambrene® (2',2',3,7,7-pentamethylspiro[bicyclo[4.1.0]heptane-2,5'-[1,3]dioxane]);
- 15 • Esters and lactones, e.g. benzyl acetate; cedryl acetate ((1S,6R,8aR)-1,4,4,6-tetramethyloctahydro-1H-5,8a-methanoazulen-6-yl acetate); γ-decalactone (6-pentyltetrahydro-2H-pyran-2-one); Helvetolide® (2-(1-(3,3-dimethylcyclohexyl)ethoxy)-2-methylpropyl propionate); γ-undecalactone (5-heptyloxolan-2-one); and / or vetiveryl acetate ((4,8-dimethyl-2-propan-2-ylidene-3,3a,4,5,6,8a-hexahydro-1H-azulen-6-yl) acetate
- 20 • Macrocycles, e.g. Ambrettolide ((Z)-oxacycloheptadec-10-en-2-one); ethylene brassylate (1,4-dioxacycloheptadecane-5,17-dione); and / or Exaltolide® (16-oxacyclohexadecan-1-one); and
- 25 • Heterocycles, e.g. isobutylquinoline (2-isobutylquinoline).

30 Whereas the compounds of formula (I) are particular suitable for the use in rinse-off products as defined herein above, they may of course find use in any type of consumer products.

Thus there is provided in a further aspect of the present invention a consumer product comprising a compound of formula (I) and a consumer product base.

35

For example, the consumer product according to the invention is selected from the group consisting of detergents and cleaning agents, hygiene or care products, preferably in the field

of body and hair care, cosmetics and household, preferably from the group consisting of perfume extracts, eau de perfumes, eau de toilettes, aftershave lotions, eau de colognes, pre-shave products, splash colognes, perfumed refreshing wipes, acidic, alkaline or neutral detergents, textile fresheners, ironing aids, liquid detergents, powder detergents, laundry pre-treatments, fabric softeners, laundry sheets, washing soaps, washing tablets, dish bar soaps, disinfectants, surface disinfectants, air fresheners, aerosol sprays, waxes and polishes, body care products, hand creams and lotions, foot creams and lotions, depilatory creams and lotions, after-shave creams and lotions, tanning creams and lotions, hair care products (in liquid or solid form), dry shampoo, deodorants, antiperspirants, decorative cosmetic products, candles, lamp oils, incense sticks, insecticides, repellents and fuels.

The consumer product for example is selected from fine fragrance, personal care products (body care products, hair care products, cosmetic products) fabric care products, home care products and air care products. As used herein, "consumer product base" means a composition for use as a consumer product to fulfill specific actions, such as cleaning, softening, and caring or the like.

Personal care products to which the compound of formula (I) can be added include, for example, all kinds of body care products. Especially interesting products are hair care products, for example shampoos, conditioners and hairsprays, and skin care products, like lotions or creams. Furthermore, the compound of formula (I) may be added to soaps, bath and shower gels and deodorants.

Home care products to which the compound of formula (I) can be added include all kinds of detergents, window cleaners, hard surface cleaners, all-purpose cleaners and furniture polishes. In one particular embodiment said products are liquids, e.g. fabric detergent or conditioner compositions.

The compound of formula (I) may be used in a broad range of consumer products, e.g. in any field of fine and functional perfumery, such as perfumes, air care products, household products, laundry products, body care products and cosmetics. The compound can be employed in widely varying amounts, depending upon the specific article and on the nature and quantity of other odorant ingredients. The proportion of the formula (I) is typically from 0.001 to 5 weight% of the article. In one embodiment, the compound of formula (I) may be employed in a fabric softener in an amount from 0.01 to 0.5 weight % (e.g. 0.05 to 0.1 including 0.2 weight%). In another embodiment, the compound of formula (I) may be employed in laundry detergent in an amount from 0.01 to 0.5 weight % (e.g. 0.1 to 0.3 including 0.2 weight%) based on the final

product. In another embodiment, the compound of formula (I) may be used in fine perfumery in amounts from 0.001 to 30 weight% (e.g. up to about 10 or up to 20 weight%), more preferably between 0.01 and 5 weight%. However, these values are given only by way of example, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.

The compound of formula (I) may be employed in a consumer product base simply by directly mixing the compound of the present invention, or a fragrance composition comprising the compound of formula (I), with the consumer product base, or it may, in an earlier step, be entrapped with an entrapment material, for example, polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, and then mixed with the consumer product base. The consumer product base might further contain entrapment material able to release other fragrant compounds.

Thus, there is provided a method of manufacturing a consumer product, comprising the incorporation of a compound of formula (I) either by directly admixing it to the consumer product base or by admixing a fragrance composition comprising the compound of formula (I), which may then be mixed with a consumer product base, using conventional techniques and methods.

The compounds of formula (I) may be prepared starting from an aldehyde A-CHO, wherein A has the same meaning as given for formula (I), reacting it with a Grignard reagent prepared from the chloride Cl-CH₂CH₂CH₂CH₂OR, wherein R has the same meaning as given for formula (I), using methods known to the person skilled in the art, such as reacting the halide with magnesium turnings in an appropriate solvent (e.g. THF (tetrahydrofuran)) at elevated temperatures (e.g. 60°C) followed by slow addition of the aldehyde (A-CHO) at low temperature (e.g. -20°C). The resulting carbinol A-CH(OH)CH₂CH₂CH₂CH₂OR can be converted to the compound of formula (I) by dehydration, which can be effected for example by treating it with a catalytic amount of acid (e.g. para-Toluenesulfonic acid or sulfuric acid) in an appropriate solvent (e.g. Toluene) optionally at elevated temperature (e.g. 110°C), optionally removing the generated water by azeotropic distillation (e.g. using a Dean-Stark apparatus). Other methods of synthesis of compound of formula (I) exist and will be clear to someone skilled in the art.

The invention is now further described with reference to the following non-limiting examples. These examples are for the purpose of illustration only and it is understood that variations and modifications can be made by one skilled in the art.

Example 1: 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene

5 A flask was charged with magnesium turnings (7.23 g, 297 mmol) and slowly treated with a solution of 1-(4-chlorobutoxy)hexane (57.3 g, 297 mmol) in THF (tetrahydrofuran) (148 mL) over a period of 30 min, ensuring that the Grignard reaction starts. The resulting mixture was heated to reflux (oil bath at 120°C) and the reaction was continued for 12 h. The resulting solution was cooled to room temperature and slowly added to a cooled (-20°C) solution of
10 anisaldehyde (40.4 g, 297 mmol) in THF (35 mL), keeping the temperature below -15°C and then stirred for 1 h. The resulting mixture was poured onto iced 2N H₂SO₄ solution (pH 1), stirred for 10 min, extracted with MTBE (methyl tert-butyl ether), washed with brine, dried over MgSO₄ and evaporated. The resulting mixture was taken up in toluene (300 mL) and treated with 62% H₂SO₄ (0.47 g, 2.97 mmol) and refluxed using a Dean-Stark apparatus to
15 remove water. After completion of the dehydration (30 min), the mixture was cooled to room temperature, poured onto saturated aqueous NaHCO₃ solution, extracted 2x with MTBE, dried over MgSO₄ and evaporated to give a crude that was purified by wipe-film distillation to give 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene (64.7 g, 75% yield, 96% purity) as a pale yellow oil.

20 ¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm) = 7.30 - 7.23 (m, 2H), 6.86 - 6.80 (m, 2H), 6.34 (d, J = 15.9 Hz, 1H), 6.07 (td, J = 7.0, 15.8 Hz, 1H), 3.79 (s, 3H), 3.44 (t, J = 6.5 Hz, 2H), 3.40 (t, J = 6.7 Hz, 2H), 2.31 - 2.20 (m, 2H), 1.79 - 1.68 (m, 2H), 1.63 - 1.51 (m, 2H), 1.39 - 1.25 (m, 6H), 0.95 - 0.84 (m, 3H).
25 ¹³C NMR (101 MHz, CDCl₃, 298 K) δ (ppm) = 158.7, 130.7, 129.5, 128.2, 127.0, 113.9, 71.0, 70.1, 55.3, 31.7, 29.8, 29.6, 29.5, 25.9, 22.7, 14.1.
MS (EI, 70eV): 276 (15, [M⁺]), 176 (33), 174 (62), 159 (54), 147 (100), 121 (59).

Odour description (1% solution in EtOH on paper blotter, 24 h): floral, watery, aldehydic,
30 green, powdery.

Example 2: 1-methoxy-4-(5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene

Example 2a: 2-(4-chlorobutoxy)-6-methylheptane: A flask was charged with tetrahydrofuran (15.0 g, 208 mmol) and 6-methylheptan-2-ol (27.1 g, 208 mmol). The mixture was cooled to
35 5°C and then treated dropwise with thionyl chloride (SOCl₂) (29.7 g, 18 mL, 250 mmol). After the addition the cooling bath was removed and the reaction mixture was slowly heated up to 120°C for 6h then cooled to room temperature. The reaction mixture was poured into iced 2M

NaOH and extracted 2x with MTBE, washed with water and brine until neutral, dried over MgSO_4 , filtered and concentrated. The crude material was purified by Kugelrohr distillation to give 2-(4-chlorobutoxy)-6-methylheptane (13.26 g, 60.1 mmol, 29% yield) as a colorless oil.

5 ^1H NMR (400 MHz, CDCl_3 , 298 K) δ (ppm) = 3.62 - 3.56 (m, 2H), 3.55 - 3.50 (m, 1H), 3.42 - 3.33 (m, 2H), 1.94 - 1.84 (m, 2H), 1.76 - 1.67 (m, 2H), 1.61 - 1.46 (m, 2H), 1.42 - 1.27 (m, 3H), 1.22 - 1.15 (m, 2H), 1.14 (d, J = 6.4 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H).
 ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ (ppm) = 75.5, 67.4, 45.0, 39.0, 36.9, 29.7, 28.0, 27.6, 23.3, 22.6, 22.6, 19.7.

10

Example 2b: 1-methoxy-4-(5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene: Was prepared in a similar way as Example 1 using 2-(4-chlorobutoxy)-6-methylheptane (16.1 g, 72.7 mmol), magnesium turnings (1.77 g, 72.7 mmol) and anisaldehyde (9.0 g, 66 mmol), followed by dehydration with pTSA (para-toluenesulfonic acid – used instead of sulphuric acid used in example 1) (1.26 g, 6.6 mmol) to give 1-methoxy-4-(5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene (11.1 g, 98% purity, 54% yield) as a pale yellow oil.

15

^1H NMR (400 MHz, CDCl_3 , 298 K) δ (ppm) = 7.30 - 7.23 (m, 2H), 6.86 - 6.79 (m, 2H), 6.34 (d, J = 15.9 Hz, 1H), 6.07 (td, J = 6.9, 15.8 Hz, 1H), 3.79 (s, 3H), 3.52 (td, J = 6.4, 9.2 Hz, 1H), 3.43 - 3.30 (m, 2H), 2.31 - 2.22 (m, 2H), 1.77 - 1.63 (m, 2H), 1.59 - 1.47 (m, 2H), 1.46 - 1.26 (m, 4H), 1.22 - 1.14 (m, 2H), 1.12 (d, J = 6.1 Hz, 3H), 0.87 (d, J = 6.6 Hz, 6H).
 ^{13}C NMR (101 MHz, CDCl_3 , 298 K) δ (ppm) = 158.7, 130.7, 129.5, 128.3, 127.0, 113.9, 75.5, 67.7, 55.3, 39.1, 37.0, 29.9, 29.7, 28.0, 23.4, 22.7, 22.6, 19.8.
MS (EI, 70eV): 304 (2, $[\text{M}^{**}]$), 191 (11), 176 (39), 159 (22), 147 (100), 121 (56).

20

25

Odour description (1% solution in EtOH on paper blotter, 24 h): aldehydic, watery, green, metallic, marine, powdery.

Example 3: 2-(5-(hexyloxy)pent-1-en-1-yl)naphthalene

30 Was prepared similarly to Example 1, replacing anisaldehyde with 2-naphthaldehyde, to give 2-(5-(hexyloxy)pent-1-en-1-yl)naphthalene as a pale yellow oil.

^1H NMR (400 MHz, CDCl_3 , 298 K – ca. 1:1 mixture of E and Z isomers) δ (ppm) = 7.93 - 7.66 (m, 4H), 7.65 - 7.38 (m, 3H), 6.74 - 6.50 (m, 1H), 6.50 - 5.68 (m, 1H), 3.62 - 3.31 (m, 4H), 2.59 - 2.31 (m, 2H), 1.88 - 1.75 (m, 2H), 1.69 - 1.50 (m, 2H), 1.45 - 1.23 (m, 6H), 0.97 - 0.86 (m, 4H).

35

¹³C NMR (101 MHz, CDCl₃, 298 K – ca. 1:1 mixture of E and Z isomers) δ (ppm) = 135.3, 135.2, 133.7, 133.4, 132.9, 132.7, 132.2, 130.9, 130.3, 129.3, 128.0, 127.9, 127.8, 127.6, 127.6, 127.4, 127.2, 126.1, 126.0, 125.6, 125.5, 125.4, 123.6, 120.0, 71.1, 70.1, 31.9, 31.7, 31.7, 29.8, 29.8, 29.8, 25.9, 25.9, 25.4, 22.7, 22.7, 22.6, 14.1, 14.1, 14.1.

5 MS (EI, 70eV): 296 (11, [M⁺]), 212 (1), 194 (56), 179 (100), 167 (66), 165 (81), 152 (36), 141 (45), 128 (38), 43 (31).

Odour description (1% solution in EtOH on paper blotter, 24 h): aldehydic, green, metallic, ozonic.

10

Example 4: 1-(5-(heptyloxy)pent-1-en-1-yl)-4-methoxybenzene

Was prepared similarly to Example 1, replacing 1-(4-chlorobutoxy)hexane with 1-(4-chlorobutoxy)heptane, to give 1-(5-(heptyloxy)pent-1-en-1-yl)-4-methoxybenzene as a pale yellow oil.

15

¹H NMR (400 MHz, CDCl₃, 298 K) δ (ppm) = 7.35 - 7.22 (m, 2H), 6.93 - 6.80 (m, 2H), 6.37 (d, J = 15.6 Hz, 1H), 6.10 (td, J = 6.9, 15.8 Hz, 1H), 3.89 - 3.77 (m, 3H), 3.47 (t, J = 6.5 Hz, 2H), 3.43 (t, J = 6.7 Hz, 2H), 2.35 - 2.22 (m, 2H), 1.85 - 1.70 (m, 2H), 1.67 - 1.53 (m, 2H), 1.50 - 1.23 (m, 8H), 0.97 - 0.84 (m, 3H).

20 ¹³C NMR (101 MHz, CDCl₃, 298 K) δ (ppm) = 158.7, 130.7, 129.5, 128.2, 127.0, 113.9, 71.0, 70.1, 55.3, 31.9, 29.8, 29.6, 29.5, 29.2, 26.2, 22.6, 14.1.

MS (EI, 70eV): 290 (12, [M⁺]), 192 (2), 174 (70), 159 (52), 147 (100), 121 (65).

Odour description (1% solution in EtOH on paper blotter, 24 h): aldehydic, green, floral, watery, muguet.

25

Example 5 (comparison): (6-(6-Methylheptan-2-yloxy)hex-2-enyl)benzene

A solution of phenethyltriphenylphosphonium bromide (2.20 g, 4.92 mmol, 1.0 equiv.) in THF (10 mL) was cooled to 0 °C. After adding n-BuLi (1.6 M in hexanes, 3.1 mL, 4.92 mmol, 1.0 equiv.) at 0 °C, the red solution was stirred at 60 °C for 1 h. The mixture was re-cooled to 0 °C, 4-(6-methylheptan-2-yloxy)butanal (0.86 g, 4.29 mmol, 0.9 equiv.) in THF (5 mL) was added, and the mixture was stirred at 70 °C for 20 h. After addition of H₂O, the aqueous layer was extracted with cyclohexane (2 x), the combined organic phases were washed with brine, dried (MgSO₄), filtered and the filtrate was concentrated. The residue was purified by flash chromatography on SiO₂ (cyclohexane/EtOAc 997:3) to yield 0.42 g (27%) of the title compound as a yellow oil.

35

Odour description (1% solution in EtOH on paper blotter, 24 h): weak, floral, hyacinth, warm, honey, animalic.

Example 6 (comparison): (E)-1-(dodec-1-en-1-yl)-4-methoxybenzene

- 5 Following the procedure described in WO2014/073003 the title compound was prepared from anisaldehyde and dodecyl aldehyde.

Odour description (1% solution in EtOH on paper blotter, 24 h): green, anisic, metallic, aldehydic.

10

Example 7: Application in liquid detergent

0.2% by weight of 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene (Example 1) was incorporated into unperfumed liquid detergent base by magnetic stirring at room temperature for 24 h.

15

A 40°C machine wash cycle was performed using 55 g of the above prepared liquid detergent sample and odour-neutral cotton/elastan mixed fabric T-shirts. The line-dried fabric (1 and 3 days) was assessed by a panel of 4-6 experts with regard to odour intensity and quality. The odour intensity was recorded on an intensity scale of 0 (odourless) to 5 (extremely strong).

20

The T-shirt washed with 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene was found to exhibit aldehydic, watery, metallic and powdery smell with an intensity of 2.6 after 1 day and 3.2 after 3 days.

25

Example 8 (comparison): Application in liquid detergent

0.2% by weight of (E)-1-(dodec-1-en-1-yl)-4-methoxybenzene (Example 6) was incorporated into unperfumed liquid detergent base by magnetic stirring at room temperature for 24h.

- 30 A 40°C machine wash cycle was performed using 55 g of the above prepared liquid detergent sample and odour-neutral cotton/elastan mixed fabric T-shirts. The line-dried fabric (1 and 3 days) was assessed by a panel of 4-6 experts with regard to odour intensity and quality. The odour intensity was recorded on an intensity scale of 0 (odourless) to 5 (extremely strong).

35

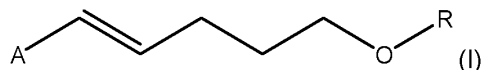
No significant odor was observed in the T-shirts, scoring consistently below 1 after 1 and 3 days, respectively.

Whereas (*E*)-1-(dodec-1-en-1-yl)-4-methoxybenzene was clearly perceived on paper blotter after 24 h (Example 6) but not on dry cloth after washing (Example 8), it is clear that it has been (mostly) lost during the wash cycle, confirming the good deposition properties of the

5 compounds of formula (I) as defined herein.

Claims

1. A compound of formula (I)



wherein

- 5 A is selected from the group consisting of anisyl and naphthyl, and
R is selected from C₆ – C₈ alkyl.
2. The compound according to claim 1 wherein the compound is selected from the
group consisting of 1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene, 1-methoxy-4-
10 (5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene, 2-(5-(hexyloxy)pent-1-en-1-
yl)naphthalene, and 1-(5-(heptyloxy)pent-1-en-1-yl)-4-methoxybenzene.
3. The compound according to claim 1 or 2 wherein the double bond is in *E*-
configuration.
- 15 4. The compound according to any of the preceding claims wherein the compound is
selected from the group consisting of 1-(5-(hexyloxy)pent-1-en-1-yl)-4-
methoxybenzene, (*E*)-1-(5-(hexyloxy)pent-1-en-1-yl)-4-methoxybenzene, 1-
methoxy-4-(5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene, (*E*)-1-methoxy-4-
20 (5-((6-methylheptan-2-yl)oxy)pent-1-en-1-yl)benzene, 2-(5-(hexyloxy)pent-1-en-1-
yl)naphthalene, (*E*)-2-(5-(hexyloxy)pent-1-en-1-yl)naphthalene, 1-(5-(heptyloxy)pent-
1-en-1-yl)-4-methoxybenzene, and (*E*)-1-(5-(heptyloxy)pent-1-en-1-yl)-4-
methoxybenzene.
- 25 5. A fragrance composition comprising a compound of formula (I) as define in claim 1
to 4, or a mixture thereof.
6. A consumer product comprising a compound of formula (I) as defined in claim 1 to 4
or a fragrance composition as define in claim 5, and a consumer product base.
- 30 7. The consumer product according to claim 6 wherein the product is selected from the
group consisting of rinse-off products.
8. The consumer product according to claim 7 wherein the rinse-off product is selected
35 from the group consisting of fabric care and personal care products.
9. The product according to claim 8 wherein the fabric care product is selected from
laundry detergent and fabric softener products.

10. A method to confer, enhance, improve or modify the hedonic properties of a fabric, which method comprises contacting said fabric with a rinse-off product comprising a compound of formula (I) as defined in claim 1 to 4, or a mixture thereof.
- 5 11. The method according to claim 10 wherein the rinse-off product is selected from the group consisting of fabric care and personal care products.
- 10 12. The use of a compound of formula (I) as defined in claim 1 to 4 as fragrance precursor.
13. The use according to claim 12, wherein the compound of formula (I) is capable of releasing watery, aldehydic, green olfactory impressions when exposed to ambient air.