

ALKOXYBENZALDEHYDE DERIVATIVES AND PRECURSORS THEREOF

This disclosure relates to alkoxybenzaldehyde derivatives possessing long lasting citrus odor characteristics. The invention furthermore refers to methods of their production,
5 and to fragrance compositions containing these.

With constantly changing commercial and regulatory requirements, there is a constant search for new molecules that enhance fragrance notes or possess newly-available fragrance notes, in particular long lasting citrus-like odor notes.

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Compounds possessing citrus-like odor notes are of particular interest, since they are associated by the consumer with freshness and/or cleanliness.

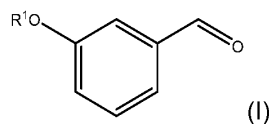
Alkoxybenzaldehydes, such as para-methoxy benzaldehyde (also known as anisic aldehyde), and their use as fragrance ingredients are known. They are described to
15 possess very typical benzaldehyde-like odors, which are described in general as aromatic, anisic, with spicy gourmand nuances.

Whereas meta alkoxybenzaldehydes of formula (I) are reported in the literature, e.g. as
20 intermediates for the preparation of pharmaceuticals, to the best of our knowledge, for none of them it has been reported or suggested any organoleptical properties, or any use as fragrance ingredient.

It has now surprisingly been found that meta alkoxybenzaldehydes of formula (I) as
25 herein below defined do possess citrus-like odor profiles, essentially free of spicy gourmand side notes which would reduce the desired impression of freshness.

There is therefore provided in one aspect the use as fragrance of a compound of formula (I)

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wherein R¹ is selected from linear or branched C₃-, C₄- and C₅- alkyl and C₃-, C₄- and C₅- alkenyl (e.g. butyl, pentyl, but-2-yl).

As a specific example of compounds of formula (I) one may cite, as non-limiting example, 3-butoxybenzaldehyde, which possesses a fresh citrus odor with a green nuance. This type of odor note combines particular well with other green and/or floral-aldehydic notes to create or improve an impression of cleanliness and/or freshness.

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Further, non-limiting examples are compounds of formula (I) selected from

3-(sec-butoxy)benzaldehyde,

3-pentyloxybenzaldehyde,

3-((2-methylallyl)oxy)benzaldehyde, and

10 3-isopropoxybenzaldehyde.

The compounds of formula (I) may be added to a fragrance composition, that is, a formulation that combines individual fragrance ingredients to provide a desirable hedonic effect. These may be selected from any of the large range of such materials

15 available to the art.

Typical, non-limiting examples of fragrance ingredients include

- 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 mandarine oil, myrtle oil, palmarose oil, patchouli oil, petitgrain oil, jasmine oil, rose oil, sandalwood oil, wormwood oil, lavender oil and/ or ylang-ylang oil;
 - 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;
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- 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);

5 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); 3-(4-isobutyl-2-methylphenyl)propanal; maltol; methyl cedryl ketone; methylionone; verbenone;

10 2,6,10-trimethylundeca-5,9-dienal; 3-(4-ethylphenyl)-2,2-dimethylpropanal ; 1-methyl-4-(4-methylpent-3-en-1-yl)cyclohex-3-ene-1-carbaldehyde; hex-2-enal and/or vanillin;
- 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);

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- 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

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- heterocycles, e.g. isobutylquinoline (2-isobutylquinoline).

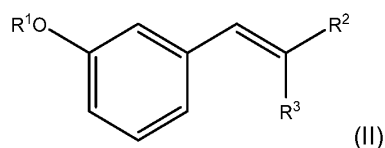
The compounds of formula (I) may be employed into a fragrance application simply by directly mixing the compound as such or the fragrance composition comprising it with

the fragrance application, and/or they may, in an earlier step, be entrapped with an entrapment material such as polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, and/or they may be chemically bonded to substrates, which are adapted to release the fragrance molecule upon application of an external stimulus such as light, air, moisture, elevated temperature, enzyme, or the like, and then mixed with the application.

While the compounds of formula (I) as hereinabove defined may not in themselves possess a particular strong odour, they combine usefully with other fragrance ingredients to provide useful fragrance profiles with long lasting citrus effects.

Thus, in one particular embodiment, the compounds of formula (I) may be added in the form of a precursor which is adapted to release two fragrance ingredients upon application of an external stimulus, one of which is a compound of formula (I).

In one particular embodiment the precursor has the general formula (II)



wherein

R^1 has the same meaning as defined for formula (I), and

R^2 is selected from the group consisting of

$C_4 - C_{14}$ alkyl, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkyl;

$C_4 - C_{14}$ alkyl, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkyl, substituted with one $-OH$ group and/or up to two (i.e. 0, 1 or 2) ether groups (e.g. R^2 is 6-methoxy-6-methyloctan-2-yl);

$C_4 - C_{14}$ alkenyl, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkenyl comprising, e.g. one or two carbon-to-carbon double bonds;

$C_4 - C_{14}$ alkenyl substituted with one $-OH$ group or an ether group, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkenyl substituted with one $-OH$ group or an ether group

comprising, e.g. one or two carbon-to-carbon double bonds (e.g. R² is (*E*)-8-hydroxy-4,8-dimethylnon-3-en-1-yl, or , pent-2-enyl);

C₅ – C₆ cycloalkyl such as cyclohexyl, or cyclopentyl;

- 5 C₅ – C₈ cycloalkyl (e.g. cyclohexyl, cyclopentyl) substituted with 1, 2, or 3 groups selected from C₁ – C₆ alkyl (e.g. ethyl, isopropyl, tert-pentyl) and C₂ – C₄ alkylidene (e.g. isopropenyl);

C₅ – C₈ cycloalkenyl, e.g. C₆ cycloalkenyl such as cyclohexa-2,4-dienyl, cyclohex-1-enyl, cyclooct-3-enyl;

- 10 C₅- C₈ cycloalkenyl, such as cyclooct-3-enyl, wherein the cycloalkenyl-ring is substituted with 1, 2, or 3 groups selected from C₁ – C₄ alkyl (e.g. ethyl, or isopropyl), C₂ – C₄ alkylidene (e.g. isopropenyl), and C₃-C₅ cycloalkyl (e.g. R² is 7-methyl-spiro[4.5]dec-8-en-6-yl, spiro[4.5]dec-7-en-7-yl, 5,5-dimethylcyclohex-1-enyl, 2,6,6-trimethylcyclohex-1,3-dienyl, 2,4-dimethylcyclohex-3-enyl, or 4-isopropenyl(cyclohex-1-en-1-yl);
- 15 1-en-1-yl);

- (C₁ – C₃)alkyl(C₅ – C₆)cycloalkyl wherein the cycloalkyl-ring is optionally substituted with one group selected from –OH group and =O group, and/or one or two ether group(s), and/or up to four C₁-C₅ alkyl groups (e.g. R² is (3-tertbutylcyclohexyl)ethyl, or (4-(1,1-dimethylpropyl)cyclohexyl)methyl, (3-oxo-2-pentylcyclopentyl)methyl);
- 20 dimethylpropyl)cyclohexyl)methyl, (3-oxo-2-pentylcyclopentyl)methyl);

- (C₁ – C₄)alkyl(C₅ – C₆)cycloalkenyl wherein the cycloalkenyl-ring is optionally substituted with one –OH group, and/or one or two ether group(s), and/or up to four (i.e. 0, 1, 2, 3 or 4) C₁-C₅ alkyl groups (e.g. R² is (2,6,6-trimethylcyclohex-1-en-1-yl)ethyl, 1-(2,6,6-trimethylcyclohex-2-en-1-yl)butan-3-yl);
- 25 (2,6,6-trimethylcyclohex-2-en-1-yl)butan-3-yl);

- (C₂ – C₃)alkenyl(C₅ – C₆)cycloalkenyl wherein the cycloalkenyl-ring is optionally substituted with one –OH group, and/or one or two ether group(s), and/or up to four (i.e. 0, 1, 2, 3, or 4) C₁-C₅ alkyl groups (e.g. R² is (2,6,6-trimethylcyclohex-1-en-1-yl)ethenyl, (2,6,6-trimethylcyclohex-2-en-1-yl)ethenyl, (2,6,6-trimethylcyclohex-2-en-1-yl)prop-2-en-2-yl, (2,6,6-trimethylcyclohex-1-en-1-yl)prop-2-en-2-yl);
- 30 (2,6,6-trimethylcyclohex-2-en-1-yl)ethenyl, (2,6,6-trimethylcyclohex-2-en-1-yl)prop-2-en-2-yl, (2,6,6-trimethylcyclohex-1-en-1-yl)prop-2-en-2-yl);

C₆ – C₁₄ aryl, e.g. phenyl;

- C₆ – C₁₄ aryl wherein the aryl ring is substituted with up to 3 (i.e. 0, 1, 2, or 3) groups selected from C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), – O – CH₂ – O –, and –
- 35 selected from C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), – O – CH₂ – O –, and –

OR¹¹ wherein R¹¹ is independently selected from hydrogen and C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl);

(C₁ – C₄)alkyl(C₆ – C₁₄)aryl, e.g. benzyl, 2-phenylethyl;

- 5 (C₁ – C₄)alkyl(C₆ – C₁₄)aryl, such as benzyl or 2-phenylethyl wherein the aryl-ring is substituted with up to 2 groups (e.g. 1 group) selected from C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), – O – CH₂ – O –, and –OR¹² wherein R¹² is independently selected from hydrogen and C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl);

- 10 (C₂ – C₈)alkenyl(C₆ – C₁₄)aryl, e.g. 2-phenylethylene-1-yl, 1-phenylhept-1-en-2-yl;
(C₂ – C₈)alkenyl(C₆ – C₁₄)aryl wherein the aryl-ring is substituted with up to 2 groups (e.g. 1 group) selected from C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), – O – CH₂ – O –, and –OR¹³ wherein R¹³ is independently selected from hydrogen and C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl);

- 15 bi-, tri, or tetracyclic hydrocarbon ring comprising C₈ – C₁₂ carbon atoms optionally substituted with up to 6 groups selected from C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), – O – CH₂ – O –, and –OR¹⁴ wherein R¹⁴ is independently selected from hydrogen and C₁ – C₄ alkyl (e.g. ethyl, iso-propyl, tert-butyl), e.g. R² is 1,1,6,7-tetramethyl-1,2,3,4,5,6,7,8-octahydronaphthalen-7-yl, 2-((1,1-dimethyl-(2,3-dihydro-1H-indene))-6-yl)-eth-1-yl, 3,6,8,8-tetramethyl-2,3,4,7,8,8a-hexahydro-1H-3a,7-methanoazulen-5(4H)-ylidene, or 1,1,2,4,4,7-hexamethyl-1,2,3,4-tetrahydronaphthalene-6-yl;

- 25 R³ is selected from hydrogen, C₁ – C₅ alkyl, and C₂ – C₅ alkenyl (e.g. but-3-enyl).

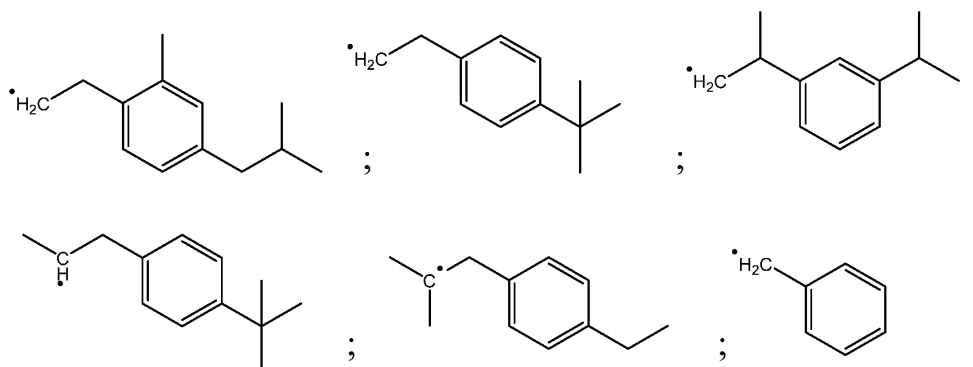
- As used in relation to compounds of formula (II) unless otherwise indicated “alkyl” refers to straight chain or branched-chain hydrocarbon group; “alkenyl” refers to straight chain or branched-chain hydrocarbon group comprising at least one carbon-to-carbon double bond, e.g. 2 or 3 double bonds; “hydrocarbon ring” refers to saturated and unsaturated ring systems, preferably containing up to two carbon-to-carbon double bonds per ring, wherein the ring may be substituted with up to 3 (e.g. one or two) C₁-C₃ alkyl; and “ether group” refers to an oxygen atom connected to two carbon atoms.

In certain embodiments R^3 is hydrogen.

In particular embodiments R^3 is hydrogen and R^2 is selected from

- 5 $C_4 - C_{14}$ alkyl, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkyl; $C_4 - C_{14}$ alkenyl, for example $C_5 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkenyl comprising, e.g. one or two carbon-to-carbon double bonds; (E)-4,8-dimethylnon-3-en-8-ol-1-yl; and 6-methoxy-6-methyloctan-2-yl.
- 10 In other particular embodiments, R^3 is hydrogen and R^2 is $C_5 - C_{12}$ alkenyl comprising one carbon-to-carbon double bond, e.g. R^2 is selected from Z-pent-2-en-1-yl, Z-oct-5-en-1-yl, dodec-1-en-1-yl, non-3-en-1-yl (e.g. E-non-3-en-1-yl), dec-8-en-1-yl.

- 15 In further particular embodiments, R^3 is hydrogen and R^2 is $(C_1 - C_4)$ alkyl(C_6)aryl such as benzyl, 2-phenylethyl or 3-phenylpropyl wherein the aryl-ring is substituted with up to 2 groups (e.g. 1 group) selected from $C_1 - C_4$ alkyl (e.g. ethyl, iso-propyl, tert-butyl, iso-butyl), e.g., R^2 is



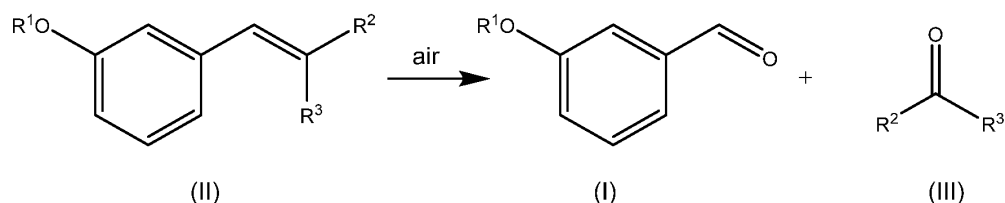
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In further particular embodiments, R^1 is selected from butyl, pentyl, (1-methyl)propenyl, and 2-methylbut-2-enyl, R^2 is selected from $C_4 - C_{14}$ alkyl, for example $C_6 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkyl; and $C_5 - C_{14}$ alkenyl, for example $C_6 - C_{12}$ such as C_8 , C_9 , C_{10} or C_{11} alkenyl comprising, e.g. one or two carbon-to-carbon double bonds, and R^3 is

25 hydrogen.

In a further particular embodiment R^2 is pent-2-enyl (e.g. Z-pent-2-enyl) and R^3 is hydrogen.

The compounds of formula (II) act as precursors for the release, by spontaneous air oxidation, of an alkoxybenzaldehyde of formula (I) and a fragrant ketone or aldehyde of formula (III) ($R^2-C(O)-R^3$ wherein R^2 and R^3 have the same meaning as defined for the compounds of formula (II)).



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The compounds of formula (II) are very stable when not exposed to the ambient air, i.e. when stored as such, or in a diluent conventionally used in conjunction with odorants, such as dipropylene glycol (DPG), isopropylmyristate (IPM), triethylcitrate (TEC), pentane-1,2-diol, and alcohol (e.g. ethanol), and known fragrance ingredients. Very good storage stability has been proven also when incorporated in consumer products such as detergent, shampoo and fabric conditioner. Thus the compounds of formula (II) may find use in a broad range of consumer products in which a prolonged and defined release of fragrant compounds is desired.

20 The concentration of oxygen in the air is sufficient for cleaving the compound of formula (II) in such a way, that the cleavage products can be detected in the ambient air, e.g. by olfaction or GC-MS analysis of headspace samples.

Compounds of formula (II) wherein R^2 is pent-2-enyl and R^3 is hydrogen releases, by spontaneous air oxidation, hex-3-enal (e.g., cis-3-hexenal), which is unstable as such, and thus not usable as such in perfumery.

As a specific example of precursors of compounds of formula (I) one may cite a compound of formula (II) wherein R^1 is C_4-C_5 alkyl (e.g. butyl), R^2 is hydrogen and R^3 is pent-2-en-1-yl (e.g. Z-pent-2-en-1yl) which gives rise to a precursor with particularly desirable properties, in that, in cleavage on exposure to air, it provides both a citrus

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note and a green note, a combination that is highly desirable in many commercial products, such as laundry detergents.

In a further particular embodiment the precursor of formula (II) are selected from

- 5 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene;
1-butoxy-3-((1E,7Z)-deca-1,7-dien-1-yl)benzene;
1-(4-(3-butoxyphenyl)but-3-en-1-yl)-4-isobutyl-2-methylbenzene;
1-(4-(3-butoxyphenyl)but-3-en-1-yl)-2-isobutyl-4-methylbenzene;
1-(sec-butoxy)-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene;
10 1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-(pentyloxy)benzene;
1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-((2-methylallyl)oxy)benzene;
1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-isopropoxybenzene;
1-butoxy-3-(4-(4-(tert-butyl)phenyl)but-1-en-1-yl)benzene;
1-butoxy-3-(4-(4-(tert-butyl)phenyl)-3-methylbut-1-en-1-yl)benzene;
15 1-butoxy-3-(4-(3-isopropylphenyl)pent-1-en-1-yl)benzene;
11-(3-butoxyphenyl)-2,6-dimethylundeca-6,10-dien-2-ol;
1-butoxy-3-(3-methyldodec-1-en-1-yl)benzene;
5-(4-(3-butoxyphenyl)-2-methylbut-3-en-1-yl)benzo[d][1,3]dioxole;
1-butoxy-3-(tetradeca-1,3-dien-1-yl)benzene;
20 1-butoxy-3-(3-phenylprop-1-en-1-yl)benzene;
1-butoxy-3-((5E)-undeca-1,5-dien-1-yl)benzene;
5-(5-(3-butoxyphenyl)pent-4-en-1-ylidene)octahydro-1H-4,7-methanoindene;
1-butoxy-3-(4-(4-ethylphenyl)-3,3-dimethylbut-1-en-1-yl)benzene;
1-butoxy-3-(7-methoxy-3,7-dimethylnon-1-en-1-yl)benzene; and
25 1-butoxy-3-(4-(4-isobutylphenyl)but-1-en-1-yl)benzene.

There is further provided a method of fragancing a consumer product, comprising the addition to a consumer product base a compound of formula (I) or precursor thereof, e.g., a compound of formula (II).

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The compounds according to formula (I) or its precursor, e.g., a compound of formula (II) may be used in a broad range of fragrance applications, e.g. in any field of fine and functional perfumery, such as perfumes, household products, laundry products, body care products and cosmetics.

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The compounds of formula (I) or a precursor thereof (e.g., a compound of formula (II)) can be employed in widely varying amounts, depending upon the specific application and on the nature and quantity of other odorant ingredients. The proportion is typically from 0.0001 to 2 weight percent of the application. In one embodiment, the compounds
5 may be employed in a fabric softener in an amount of from 0.0001 to 0.005 weight percent. In another embodiment, the compounds may be used in an alcoholic solution in amounts of from 0.01 to 3 weight percent, more particularly between 0.5 and 2 weight percent. 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
10 or higher concentrations, e.g. up to about 20 weight percent based on the fragrance composition.

The compounds of formula (I) or a precursor thereof (e.g. a compound of formula (II)) may be employed in a consumer product base simply by directly mixing the compound
15 of formula (I) or a precursor thereof (e.g. a compound of formula (II)), or a fragrance composition comprising a compound of formula (I) or a precursor thereof (e.g. a compound of formula (II)) 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
20 or zeolites, cyclic oligosaccharides and mixtures thereof, and then mixed with the consumer product base.

Thus, the invention additionally provides a method of manufacturing a fragranced article, comprising the incorporation of a compound of formula (I) or a precursor thereof
25 (e.g. a compound of formula (II)), as a fragrance ingredient, either by directly admixing it to the consumer product base or by admixing a fragrance composition comprising the compound of formula (I) or a precursor thereof (e.g. a compound of formula (II)), which may then be mixed with a consumer product base, using conventional techniques and methods. Through the addition of an olfactory acceptable amount of the compound of of
30 formula (I) or a precursor thereof (e.g. a compound of formula (II)) the odor notes of a consumer product base will be improved, enhanced, or modified.

Thus, the invention furthermore provides a method for improving, enhancing or modifying a consumer product base by means of the addition thereto of an olfactorily

acceptable amount of the compound of formula (I) or a precursor thereof (e.g. a compound of formula (II)).

The invention also provides a fragranced article comprising:

- 5 a) as odorant the compound of formula (I), a mixture thereof, or a precursor thereof (e.g. a compound of formula (II)); and
 b) a consumer product base.

As used herein, 'consumer product base' means a composition for use as a consumer
10 product to fulfil specific actions, such as cleaning, softening, and caring or the like.
 Examples of such products include fine perfumery, e.g. perfume and eau de toilette;
 fabric care, household products and personal care products such as cosmetics, laundry
 care detergents, rinse conditioner, personal cleansing composition, detergent for
 dishwasher, surface cleaner; laundry products, e.g. softener, bleach, detergent; body-
15 care products, e.g. shampoo, shower gel; air care products (includes products that
 contain preferably volatile and usually pleasant-smelling compounds which
 advantageously can even in very small amounts mask unpleasant odors). Air
 fresheners for living areas contain, in particular, natural and synthetic essential oils
 such as pine needle oils, citrus oil, eucalyptus oil, lavender oil, and the like, in amounts
20 for example of up to 50% by weight. As aerosols they tend to contain smaller amounts
 of such essential oils, by way of example less than 5% or less than 2% by weight, but
 additionally include compounds such as acetaldehyde (in particular, <0.5% by weight),
 isopropyl alcohol (in particular, <5% by weight), mineral oil (in particular, <5% by
 weight), and propellants.

25 In one particular embodiment the consumer product base (e.g. bleach products) are
 essentially free of aromatic imides.

30 This list of products is given by way of illustration, and is not to be regarded as being in
 any way limiting.

The compounds of formula (I) may be prepared by etherification reaction of 3-hydroxy
benzaldehyde with an alkyl halide R^1-X , X being a chloride, bromide, iodide or a
toluenesulfonate, in a suitable solvent, such as tetrahydrofuran or dimethyl formamide,
35 and in the presence of a base, such as potassium or sodium carbonate or hydroxide.

Other conditions for the formation of phenyl ethers can be employed which are known to the person skilled in the art of organic synthesis.

The compounds of formula (II) may be prepared by a Grignard reaction between -
5 $R^2R^3CHMgBr$ and an alkoxybenzaldehyde of formula (I) in a solvent like tetrahydrofuran or diethyl ether, followed by standard workup under conditions known to the person skilled in the art and dehydration of the resulting secondary benzyl alcohol in the presence of a catalyst, e.g. p-toluene sulfonic acid. Other double bond forming reactions might be employed, such as the Wittig reaction.

10

The disclosure is further described with reference to the following non-limiting examples, which depict particular embodiments.

15 Example 1: 3-butoxybenzaldehyde and a precursor thereof

1.1: 3-butoxybenzaldehyde

A solution of 3-hydroxybenzaldehyde (20 g, 164 mmol, 1.0 equiv.) in DMF (100 mL) was treated with potassium carbonate (27.2 g, 197 mmol, 1.2 equiv.). The resulting mixture was heated to 80 °C and then slowly treated with 1-bromobutane (21.2 ml,
20 197 mmol, 1.2 eq.). The mixture was stirred at 80 °C for 1 h then cooled to 25 °C, filtered to remove solids, diluted with MTBE (500 mL) and washed with water (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered and concentrated. The resulting oil was vacuum-distilled over a 5 cm Vigreux column, collecting at 135 – 137 °C at 25 mbar to give 3-butoxybenzaldehyde (25.3 g, 142 mmol, 87%) as a clear,
25 colorless liquid.

1H NMR ($CDCl_3$, 400MHz): δ = 9.99 (s, 1H), 7.44-7.47 (m, 2H), 7.39-7.42 (m, 1H), 7.17-7.21 (m, 1H), 4.04 (t, J =6.5 Hz, 2H), 1.76-1.85 (m, 2H), 1.46-1.58 (m, 2H), 1.00 ppm (t, J =7.3 Hz, 3H).

30 ^{13}C NMR ($CDCl_3$, 101MHz): δ = 192.3, 159.7, 137.8, 130.0, 123.3, 122.0, 112.8, 68.0, 31.2, 19.2, 13.8 ppm.

MS (EI, 70 eV): 178 (30, $[M]^+$), 123 (11), 122 (100), 121 (100), 77 (9), 65 (13), 41 (18), 39 (12), 29 (22), 27 (9).

Odor description (10% solution in DPG on paper blotter, 24h): fresh citrus, citral, lemongrass, verbena, green, slightly hot iron, slightly fatty.

5 1.2: 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene

In a flask flushed with nitrogen were placed magnesium turnings (0.750 g, 31 mmol, 1.3 equiv.) and THF (2 mL). (Z)-1-chlorohex-3-ene (3.66 g, 31 mmol, 1.3 equiv.) in THF (60 mL) was added dropwise at reflux, the reaction mixture further heated to reflux for 12 h and then cooled to 0 °C. 3-Butoxybenzaldehyde (4.00 g, 22 mmol, 1.0 equiv.) was
10 added, the reaction mixture was stirred at 25 °C for 30 min and poured on ice-cold 1 M aq. HCl-solution (100 mL). The aqueous layer was extracted with MTBE (2 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over MgSO₄, filtered and concentrated. The resulting oil was dissolved in Toluene (50 mL), treated at 25 °C with p-Toluenesulfonic acid monohydrate (0.21 g, 1.12 mmol, 0.05 equiv.) and
15 heated to reflux on a Dean-Stark apparatus for 3 h. The resulting mixture was cooled to 25 °C, diluted with MTBE (100 mL), washed with saturated aqueous NaHCO₃ solution (50 mL), brine (50 mL), the organic layer was dried over MgSO₄, filtered and concentrated. The resulting crude material was purified by flash column chromatography eluting with a gradient of 1-7% MTBE in Hexanes to give 1-butoxy-3-
20 ((1E,4Z)-hepta-1,4-dien-1-yl)benzene (2.06 g, 8.43 mmol, 37.6%) as a clear, colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ = 7.22 (dd, J=8.2, 7.6 Hz, 1H), 6.90-6.98 (m, 2H), 6.77 (ddd, J=8.2, 2.6, 0.7 Hz, 1H), 6.39 (dt, J=15.9, 1.5 Hz, 1H), 6.22 (dt, J=15.9, 6.4 Hz, 1H), 5.39-5.58 (m, 2H), 3.99 (t, J=6.5 Hz, 2H), 2.94-3.01 (m, 2H), 2.08-2.18 (m, 2H),
25 1.75-1.84 (m, 2H), 1.46-1.56 (m, 2H), 1.02 (t, J=7.6 Hz, 6H), 1.00 ppm (t, J=7.6 Hz, 3H).

¹³C-NMR (CDCl₃, 101MHz): δ = 159.4, 139.2, 133.0, 129.9, 129.4, 129.3, 126.0, 118.5, 113.1, 111.9, 67.6, 31.4, 30.6, 20.6, 19.3, 14.3, 13.9 ppm

30 MS (EI, 70 eV): 244 (34, [M]⁺), 159 (49), 145 (100), 133 (16), 131 (24), 128 (18), 120 (39), 115 (27), 41 (20), 29 (21).

Odour description (1% solution in EtOH on paper blotter, 24 h): green, citrus, apple, lime, crushed leaves

1.3: 1-butoxy-3-((1E,7Z)-deca-1,7-dien-1-yl)benzene

The procedure described in Example 1.2. was repeated with the Grignard reagent derived from *Z*-9-bromonon-3-ene (13.8 g, 67 mmol, 1.2 equiv.) and magnesium (1.64 g, 67 mmol, 1.2 equiv.) in THF (150 mL) and 3-butoxybenzaldehyde (Example 1.1),
5 followed by dehydration of the crude product with *p*-toluene sulfonic acid (500 mg) in toluene (100 mL). The crude product was purified by flash chromatography on silica gel with a gradient heptane 100% to heptane/MTBE 50:1 to yield (2.18 g, 28%) as a slightly yellow liquid.

10 ¹H-NMR (CDCl₃, 400MHz): δ = 7.18 (t, *J*=7.9 Hz, 1 H), 6.86 - 6.94 (m, 2 H), 6.73 (ddd, *J*=8.2, 2.4, 0.7 Hz, 1 H), 6.29 - 6.37 (m, 1 H), 6.14 - 6.26 (m, 1 H), 5.28 - 5.48 (m, 2 H), 3.96 (t, *J*=6.5 Hz, 2 H), 2.15 - 2.25 (m, 2 H), 1.94 - 2.10 (m, 4 H), 1.72 - 1.82 (m, 2 H), 1.33 - 1.57 (m, 6 H), 0.96 (td, *J*=7.5, 6.4 Hz, 6 H).
¹³C-NMR (CDCl₃, 101MHz): δ = 159.4 (s), 139.4 (s), 131.8 (s), 131.3 (s), 129.8 (s),
15 129.4 (s), 129.0 (s), 118.5 (s), 113.0 (s), 112.9 - 113.0 (m), 111.9 (s), 67.6 (s), 32.9 (s), 31.4 (s), 29.3 (s), 29.0 (s), 27.0 (s), 20.5 (s), 19.3 (s), 14.4 (s), 13.9 (s).
MS (EI, 70 eV): 286(16), 257(13), 230(6), 176(18), 164(46), 145(69), 127(100), 108(58), 107(58), 55(54), 41(92), 29(50).

20 Odour description (1% solution in EtOH on paper blotter, 24 h): melon, green, citrus, floral.

1.4: 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-4-isobutyl-2-methylbenzene and 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-2-isobutyl-4-methylbenzene25 A) (3-butoxyphenyl)methanol

3-Butoxybenzaldehyde (18.5 g, 104 mmol, 1.0 equiv.) in THF (80 mL) was added dropwise to a suspension of LiAlH₄ (1.26 g, 31.5 mmol, 0.304 eq.) in THF (120 mL) at 25 °C. After 1 h, the mixture was cooled to 0 °C and treated carefully with water (1.25 mL) followed by 15% aq. NaOH (1.25 mL) and finally water (3.75 mL). The mixture was
30 warmed to 40 °C and treated with MgSO₄ then filtered. The filtrate was concentrated to give (3-butoxyphenyl)methanol (17.3 g, 96 mmol, 92%) as a pale yellow oil.

¹H-NMR (CDCl₃, 400MHz): δ = 7.23-7.30 (m, 1H), 6.89-6.95 (m, 2H), 6.82-6.87 (m, 1H), 4.62 (s, 2H), 3.98 (t, *J*=6.6 Hz, 2H), 2.64 (br s, 1H), 1.74-1.84 (m, 2H), 1.46-1.59 (m, 2H), 1.02 ppm (t, *J*=7.3 Hz, 3H).

^{13}C -NMR (CDCl_3 , 101MHz): δ = 159.4, 142.6, 129.5, 118.9, 113.7, 112.9, 67.7, 65.1, 31.4, 19.3, 13.9 ppm.

MS (EI, 70 eV): 180 (52, $[\text{M}]^{+}$), 124 (100), 123 (39), 107 (19), 106 (37), 105 (25), 95 (50), 78 (18), 77 (20), 41 (13).

5

B) 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-4-isobutyl-2-methylbenzene and 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-2-isobutyl-4-methylbenzene

(3-butoxyphenyl)methanol (17.0 g, 94 mmol, 1.0 equiv.) was combined with triphenylphosphine hydrobromide (32.4 g, 94 mmol, 1.0 equiv.) and acetonitrile (100 mL) and the resulting mixture heated to reflux under nitrogen atmosphere for 20 h. The resulting mixture was concentrated then suspended in Et_2O (70 mL) and placed in the fridge (4 °C) for 5 h. The precipitated solid was filtered and washed with Et_2O (2x 50 mL) and then dried under high vacuum at 25 °C for 2 h. The resulting solid was suspended in THF (350 mL), cooled to 5 °C and treated portion-wise with KOtBu (10.38 g, 92 mmol, 0.98 equiv.), maintaining the temperature between 0 – 5 °C. The resulting bright red mixture was stirred for 20 min at 5 °C then treated dropwise over 40 min with a solution of 3-(4-isobutyl-2-methylphenyl)propanal (16.1 g, 78 mmol, 0.83 equiv.) and 3-(2-isobutyl-4-methylphenyl)propanal (2.84 g, 14 mmol, 0.15 equiv.) in THF (50 mL). The resulting mixture was allowed to warm to 25 °C and stirred for 2 h. The mixture was then poured onto a mixture of acetic acid (20 mL) and ice-water (500 mL), extracted with heptane (2x 200 mL), the extracts washed successively with 70% methanol (3x 100 mL), sat. aq. KHCO_3 (2x 100 mL), water (2x 100 mL), dried over MgSO_4 , filtered and evaporated. The resulting crude material was purified by flash column chromatography eluting with a gradient of 1-7% MTBE in Hexanes to give an isomeric mixture of 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-4-isobutyl-2-methylbenzene and 1-(4-(3-butoxyphenyl)but-3-en-1-yl)-2-isobutyl-4-methylbenzene (22.3 g, 63.6 mmol, 68%) as a clear, pale green liquid (isomers 1 to 4 obtained in ratio 3 : 25 : 9 : 63 (GC) (isomer 1 : isomer 2 : isomer 3 : isomer 4))

^1H NMR (CHLOROFORM-d , 400MHz): δ = 7.11-7.23 (m), 7.01-7.09 (m), 6.86-6.98 (m), 6.67-6.84 (m), 6.34-6.44 (m), 6.21-6.33 (m), 5.66-5.75 (m), 3.89-3.99 (m), 2.67-2.77 (m), 2.54-2.64 (m), 2.36-2.50 (m), 2.31 (s), 2.30 (s), 2.28 (s), 2.25 (s), 1.69-1.90 (m), 1.42-1.56 (m), 0.86-1.01 ppm (m)

^{13}C NMR (BENZENE-d_6 , 101MHz): δ = 159.7, 159.7, 159.5, 159.4, 139.3, 139.4, 139.3, 139.3, 139.1, 139.1, 139.0, 139.0, 137.1, 136.9, 136.6, 136.5, 135.3, 135.2, 134.8,

35

134.8, 132.1, 131.0, 131.0, 130.9, 130.9, 130.5, 130.5, 130.1, 129.6, 129.4, 129.2, 129.2, 129.1, 129.1, 128.7, 128.7, 128.7, 128.7, 126.8, 126.8, 126.7, 126.7, 121.3, 121.1, 118.6, 115.4, 115.1, 115.0, 113.2, 113.1, 112.8, 112.8, 112.3, 111.5, 67.1, 67.1, 67.1, 67.0, 45.0, 41.9, 41.9, 34.9, 33.8, 33.0, 32.8, 32.4, 32.2, 31.3, 31.3, 30.4, 30.2, 5 30.2, 30.1, 29.9, 29.8, 29.3, 22.4, 22.4, 22.2, 21.2, 20.8, 20.8, 19.2, 19.2, 19.1, 19.1, 13.6, 13.6 ppm.

MS (EI, 70 eV) (Isomer 1): 350 (12, [M]⁺), 189 (9), 161 (58), 133 (29), 120 (10), 119 (100), 117 (9), 115 (9), 105 (17), 55 (15).

10 MS (EI, 70 eV) (Isomer 2): 350 (8, [M]⁺), 189 (6), 162 (13), 161 (100), 133 (19), 119 (25), 118 (9), 117 (5), 115 (6), 105 (11).

MS (EI, 70 eV) (Isomer 3): 350 (11, [M]⁺), 189 (10), 162 (8), 161 (62), 133 (35), 120 (10), 119 (100), 115 (8), 105 (18), 55 (16).

15 MS (EI, 70 eV) (Isomer 4): 350 (9, [M]⁺), 189 (8), 162 (13), 161 (100), 133 (23), 119 (25), 118 (9), 115 (6), 105 (11), 43 (5).

Odour description (1% solution in EtOH on paper blotter, 24 h): citrus, aldehydic, muguet, slightly fatty.

20 Example 2: 3-(sec-butoxy)benzaldehyde and a precursor thereof

2.1: 3-(sec-butoxy)benzaldehyde

The procedure described in Example 1.1. was repeated with 3-hydroxybenzaldehyde (6.0 g, 49.1 mmol, 1 equiv.), potassium carbonate (13.6 g, 98 mmol, 2 equiv.) and 2-bromobutane (10.1 g, 73.7 mmol, 1.5 equiv.) in DMF (60 mL). The crude product was 25 purified by flash chromatography on silica gel with hexane/MTBE 93:7 followed by vacuum bulb-to-bulb distillation at 114°C/0.03 mbar to yield 3-(sec-butoxy)benzaldehyde (6.8 g, 77%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ = 9.80 - 10.16 (m, 1 H), 7.42 - 7.46 (m, 2 H), 7.38 - 7.41 30 (m, 1 H), 7.14 - 7.20 (m, 1 H), 4.40 (sxt, J=6.0 Hz, 1 H), 1.61 - 1.84 (m, 2 H), 1.33 (d, J=5.9 Hz, 3 H), 1.00 (t, J=7.5 Hz, 3 H).

¹³C-NMR (CDCl₃, 101MHz): δ 192.2 (d), 158.8 (s), 137.8 (s), 130.1 (d), 123.1 (d), 123.0 (d), 114.2 (d), 75.3 (d), 29.1 (t), 19.1 (q), 9.7 (q).

MS (EI, 70 eV): 178 (15, M⁺), 122 (100), 121 (95), 93 (8), 77 (7), 65 (11), 57 (7), 41 (9), 35 29 (18).

Odour description (10% solution in DPG on paper blotter, 4h): citrus, fruity, phenolic.

5 2.2: 1-(sec-butoxy)-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene

The procedure described in Example 1.2. was repeated with (Z)-hex-3-en-1-ylmagnesium chloride (0.65 M in THF, 26 mL, 16.9 mmol, 1.2 equiv.) and 3-(sec-butoxy)benzaldehyde (2.5 g, 14.3 mmol, 1 equiv.) in THF (50 mL), followed by dehydration of the crude product with p-toluene sulfonic acid (286 mg, 1.5 mmol, 0.1 equiv.) in toluene (100 mL). The crude product was purified by flash chromatography on silica gel with hexane/MTBE 100:1 to yield 1-(sec-butoxy)-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene (1.43 g, 39%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ = 7.22 (t, J=7.8 Hz, 1 H), 6.91 - 6.98 (m, 2 H), 6.78 (ddd, J=8.1, 2.5, 0.9 Hz, 1 H), 6.36 - 6.44 (m, 1 H), 6.18 - 6.27 (m, 1 H), 5.41 - 5.59 (m, 2 H), 4.34 (sxt, J=6.1 Hz, 1 H), 2.99 (br. t, J=6.7 Hz, 2 H), 2.14 (quind, J=7.4, 1.2 Hz, 2 H), 1.60 - 1.85 (m, 2 H), 1.33 (d, J=6.1 Hz, 3 H), 1.03 (q, J=7.6 Hz, 3 H), 1.00 (q, J=7.3 Hz, 3 H).

¹³C-NMR (CDCl₃, 101MHz): δ 158.4 (s), 139.3 (s), 133.0 (d), 129.9 (d), 129.4 (d), 129.2 (d), 126.0 (d), 118.5 (d), 114.4 (d), 113.6 (d), 75.0 (d), 30.6 (t), 29.3 (t), 20.6 (t), 19.3 (q), 14.3 (q), 9.8 (q).

MS (EI, 70 eV): 244 (16, M⁺), 159 (62), 146 (17), 145 (100), 131 (22), 120 (56), 115 (27), 81 (19), 41 (18), 29 (16).

25 Odour description (1% solution in EtOH on paper blotter, 24 h): green, citrus, crushed leaves

Example 3: 3-Pentyloxybenzaldehyde and precursor thereof

3.1: 3-Pentyloxybenzaldehyde

30 The procedure described in Example 1.1. was repeated with 3-hydroxybenzaldehyde (6.0 g, 49.1 mmol, 1 equiv.), potassium carbonate (13.6 g, 98 mmol, 2 equiv.) and 1-bromopentane (8.9 g, 59.0 mmol, 1.2 equiv.) in DMF (60 mL). The crude product was purified by flash chromatography on silica gel with hexane/MTBE 93:7 followed by vacuum bulb-to-bulb distillation at 130°C/0.03 mbar to yield 3-Pentyloxybenzaldehyde
35 (8.0 g, 84%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ 9.98 (s, 1 H), 7.43 - 7.47 (m, 2 H), 7.38 - 7.42 (m, 1 H), 7.15 - 7.22 (m, 1 H), 4.03 (t, *J*=6.6 Hz, 2 H), 1.78 - 1.88 (m, 2 H), 1.35 - 1.52 (m, 4 H), 0.96 (t, *J*=7.3 Hz, 3 H).

5 ¹³C-NMR (CDCl₃, 101MHz): δ 192.2 (d), 159.7 (s), 137.8 (s), 130.0 (d), 123.3 (d), 121.9 (d), 112.8 (d), 68.3 (t), 28.8 (t), 28.2 (t), 22.4 (t), 14.0 (d).

MS (EI, 70 eV): 192 (21, M⁺), 122 (100), 121 (78), 105 (5), 93 (6), 77 (9), 71 (3), 70 (8), 65 (9), 55 (10), 43 (30), 29 (23).

10 Odour description (10% solution in DPG on paper blotter, 4h): floral, watery, citrus, fatty.

3.2: 1-((1*E*,4*Z*)-hepta-1,4-dien-1-yl)-3-(pentyloxy)benzene

The procedure described in Example 1.2. was repeated with (*Z*)-hex-3-en-1-ylmagnesium chloride (0.65 M in THF, 38.4 mL, 25.0 mmol, 1.2 equiv.) and 3-(pentyloxy)benzaldehyde (4.0 g, 20.8 mmol, 1 equiv.) in THF (50 mL), followed by dehydration of the crude product with *p*-toluene sulfonic acid (432 mg, 2.3 mmol, 0.1 equiv.) in toluene (100 mL). The crude product was purified by flash chromatography on silica gel with hexane/MTBE 100:1 to yield 1-((1*E*,4*Z*)-hepta-1,4-dien-1-yl)-3-(pentyloxy)benzene (2.84 g, 47%) as a colorless liquid.

25 ¹H-NMR (CDCl₃, 400MHz): δ 7.18 - 7.32 (m, 1 H), 6.87 - 7.00 (m, 2 H), 6.78 (ddd, *J*=8.2, 2.4, 0.9 Hz, 1 H), 6.34 - 6.47 (m, 1 H), 6.16 - 6.29 (m, 1 H), 5.40 - 5.61 (m, 2 H), 3.99 (t, *J*=6.6 Hz, 2 H), 2.99 (br. t, *J*=6.7 Hz, 2 H), 2.10 - 2.20 (m, 2 H), 1.77 - 1.87 (m, 2 H), 1.37 - 1.54 (m, 4 H), 1.04 (t, *J*=7.6 Hz, 3 H), 0.98 (t, *J*=7.1 Hz, 3 H).

¹³C-NMR (CDCl₃, 101MHz): δ 159.4 (s), 139.2 (s), 133.0 (d), 129.9 (d), 129.4 (d), 129.3 (d), 126.0 (d), 118.5 (d), 113.1 (d), 112.0 (d), 67.9 (t), 30.6 (t), 29.1 (t), 28.3 (t), 22.5 (t), 20.6 (t), 14.3 (q), 14.1 (q).

30 MS (EI, 70 eV): 258(21, M⁺), 159(48), 145(100), 133(18), 131(22), 128(18), 120(41), 115(27), 43(25), 41(20).

Odour (1% solution in EtOH on paper blotter, 24 h): green, citrus, geranium leaves

Example 4: 3-((2-methylallyl)oxy)benzaldehyde and precursor thereof

35 4.1: 3-((2-methylallyl)oxy)benzaldehyde

The procedure described in Example 1.1. was repeated with 3-hydroxybenzaldehyde (5.0 g, 40.9 mmol, 1 equiv.), potassium carbonate (11.3 g, 82 mmol, 2 equiv.) and 3-Bromo-2-methylpropene (6.63 g, 49.1 mmol, 1.2 equiv.) in DMF (60 mL). The crude product was purified by flash chromatography on silica gel with hexane/MTBE 93:7
5 followed by vacuum bulb-to-bulb distillation at 129°C/0.03 mbar to yield 3-((2-methylallyl)oxy)benzaldehyde (5.2 g, 72%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ 9.98 (s, 1 H), 7.40 - 7.50 (m, 3 H), 7.21 (dt, *J*=7.0, 2.5 Hz, 1 H), 5.10 - 5.15 (m, 1 H), 5.02 (td, *J*=2.1, 1.0 Hz, 1 H), 4.50 (s, 2 H), 1.85 (br. d, *J*=0.7
10 Hz, 3 H).

¹³C-NMR (CDCl₃, 101MHz): δ 192.1 (d), 159.3 (s), 140.3 (s), 137.8 (s), 130.0 (d), 123.5 (d), 122.0 (d), 113.3 (d), 113.1 (t), 71.9 (t), 19.4 (q).

MS (EI, 70 eV): 176 (11, M⁺), 161 (31), 158 (8), 147 (11), 133 (10), 121 (18), 105 (5), 92 (5), 77 (8), 65 (12), 55 (100), 39 (33), 29 (29).

15

Odour description (10% solution in DPG on paper blotter, 4h): fresh, floral, citrus, anisic.

4.2: 1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-((2-methylallyl)oxy)benzene

The procedure described in Example 1.2. was repeated with (*Z*)-hex-3-en-1-ylmagnesium chloride (0.65 M in THF, 52.4 mL, 25.0 mmol, 1.2 equiv.) and 3-((2-methylallyl)oxy)benzaldehyde (5.0 g, 28.4 mmol, 1 equiv.) in THF (50 mL), followed by dehydration of the crude product with *p*-toluene sulfonic acid (584 mg, 2.3 mmol, 0.1 equiv.) in toluene (100 mL). The crude product was purified by flash chromatography on silica gel with hexane/MTBE 100:1 to yield 1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-((2-methylallyl)oxy)benzene (1.49 g, 20%) as a colorless liquid.
20

¹H-NMR (CDCl₃, 400MHz): δ 7.23 (t, *J*=7.8 Hz, 1 H), 6.94 - 7.02 (m, 2 H), 6.81 (ddd, *J*=8.3, 2.5, 1.0 Hz, 1 H), 6.41 (dt, *J*=15.9, 1.5 Hz, 1 H), 6.24 (dt, *J*=15.7, 6.6 Hz, 1 H), 5.41 - 5.61 (m, 2 H), 5.12 - 5.18 (m, 1 H), 4.98 - 5.06 (m, 1 H), 4.48 (br. s, 2 H), 3.00 (t, *J*=6.7 Hz, 2 H), 2.09 - 2.22 (m, 2 H), 1.88 (br. s, 3 H), 1.04 (t, *J*=7.6 Hz, 3 H).
30

¹³C-NMR (CDCl₃, 101MHz): δ 159.0 (s), 141.0 (s), 139.2 (s), 133.1 (d), 129.8 (d), 129.4 (d), 129.4 (s), 126.0 (d), 118.8 (d), 113.4 (d), 112.7 (t), 112.3 (d), 71.7 (t), 30.6 (t), 20.6 (t), 19.5 (q), 14.3 (q).

MS (EI, 70 eV): 242(15, M⁺), 174(15), 159(32), 145(61), 131(44), 129(43), 128(42),
35 117(41), 115(60), 91(33), 55(100), 29(35).

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

5 Example 5: 3-isopropoxybenzaldehyde and precursor thereof

5.1: 3-isopropoxybenzaldehyde

The procedure described in Example 1.1. was repeated with 3-hydroxybenzaldehyde (6.0 g, 49.1 mmol, 1 equiv.), potassium carbonate (13.6 g, 98 mmol, 2 equiv.) and 2-bromopropane (7.25 g, 59 mmol, 1.2 equiv.) in DMF (60 mL). The crude product was
10 purified by flash chromatography on silica gel with hexane/MTBE 93:7 followed by vacuum bulb-to-bulb distillation at 120°C/0.03 mbar to yield 3-isopropoxybenzaldehyde (5.88 g, 73%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ = 9.98 (s, 1 H), 7.38 - 7.46 (m, 3 H), 7.13 - 7.19 (m, 1 H),
15 4.64 (spt, *J*=6.1 Hz, 1 H), 1.37 (d, *J*=6.1 Hz, 6 H).

¹³C-NMR (CDCl₃, 101MHz): δ = 192.2 (d), 158.5 (s), 137.8 (s), 130.1 (d), 123.1 (d),
123.0 (d), 114.2 (d), 70.2 (d), 21.9 (2q).

MS (EI, 70 eV): 164 (13, M⁺), 122 (73), 121 (100), 93 (9), 77 (4), 65 (11), 43 (11), 39
(13), 27 (7).

20

Odour description (10% solution in DPG on paper blotter, 4h): green, phenolic, citrus, medicinal.

5.2: 1-((1E,4Z)-hepta-1,4-dien-1-yl)-3-isopropoxybenzene

25 The procedure described in Example 1.2. was repeated with (*Z*)-hex-3-en-1-ylmagnesium chloride (1.3 M in THF, 29 mL, 37.5 mmol, 1.5 equiv.) and 3-isopropoxybenzaldehyde (4.0 g, 24.4 mmol, 1 equiv.) in THF (50 mL), followed by dehydration of the crude product with *p*-toluene sulfonic acid (432 mg, 2.3 mmol, 0.1 equiv.) in toluene (100 mL). The crude product was purified by flash chromatography on
30 silica gel with hexane/MTBE 100:1 to yield 1-((1*E*,4*Z*)-hepta-1,4-dien-1-yl)-3-isopropoxybenzene (1.54 g, 29%) as a colorless liquid.

¹H-NMR (CDCl₃, 400MHz): δ = 7.22 (t, *J*=7.8, 1 H), 6.90 - 6.98 (m, 2 H), 6.78 (ddd, *J*=8.1, 2.5, 0.9 Hz, 1 H), 6.39 (dt, *J*=15.7, 1.2, 1 H), 6.22 (dt, *J*=15.9, 6.6 Hz, 1 H), 5.42 -

5.59 (m, 2 H), 4.59 (spt, $J=5.6$ Hz, 1 H), 2.99 (br. t, $J=6.8$ Hz, 2 H), 2.10 - 2.20 (m, 2 H), 1.37 (d, $J=5.9$ Hz, 6 H), 1.04 (t, $J=7.6$ Hz, 3 H).

^{13}C -NMR (CDCl_3 , 101MHz): δ = 158.1 (s), 139.3 (s), 133.0 (d), 129.9 (d), 129.4 (d), 129.3 (d), 126.0 (d), 118.6 (d), 114.4 (d), 113.6 (d), 69.8 (d), 30.6 (t), 22.1 (2q), 20.6 (t), 14.3 (q).

MS (EI, 70 eV): 230(18), 159(60), 145(100), 131(26), 120(54), 115(29), 107(18), 81(20), 43(21), 41(19).

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

Example 6a- 6m:

6a: 1-butoxy-3-(4-(4-(tert-butyl)phenyl)but-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(4-(tert-butyl)phenyl)propanal to prepare the title product 1-butoxy-3-(4-(4-(tert-butyl)phenyl)but-1-en-1-yl)benzene.

6b: 1-butoxy-3-(4-(4-(tert-butyl)phenyl)-3-methylbut-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(4-(tert-butyl)phenyl)-2-methylpropanal to prepare the title product 1-butoxy-3-(4-(4-(tert-butyl)phenyl)-3-methylbut-1-en-1-yl)benzene.

6c: 1-butoxy-3-(4-(3-isopropylphenyl)pent-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(3-isopropylphenyl)butanal to prepare the title product 1-butoxy-3-(4-(3-isopropylphenyl)pent-1-en-1-yl)benzene.

6d: 11-(3-butoxyphenyl)-2,6-dimethylundeca-6,10-dien-2-ol

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 9-hydroxy-5,9-dimethyldec-4-enal to prepare the title product 11-(3-butoxyphenyl)-2,6-dimethylundeca-6,10-dien-2-ol.

6e: 1-butoxy-3-(3-methyldodec-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 2-methylundecanal to prepare the title product 1-butoxy-3-(3-methyldodec-1-en-1-yl)benzene.

6f: 5-(4-(3-butoxyphenyl)-2-methylbut-3-en-1-yl)benzo[d][1,3]dioxole

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(benzo[d][1,3]dioxol-5-yl)-2-methylpropanal to prepare the title product 5-(4-(3-butoxyphenyl)-2-methylbut-3-en-1-yl)benzo[d][1,3]dioxole.

6g: 1-butoxy-3-(tetradeca-1,3-dien-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of tridec-2-enal to prepare the title product 1-butoxy-3-(tetradeca-1,3-dien-1-yl)benzene.

6h: 1-butoxy-3-(3-phenylprop-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 2-phenylacetaldehyde to prepare the title product 1-butoxy-3-(3-phenylprop-1-en-1-yl)benzene.

6i: 1-butoxy-3-((5E)-undeca-1,5-dien-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of (E)-dec-4-enal to prepare the title product 1-butoxy-3-((5E)-undeca-1,5-dien-1-yl)benzene.

6j: 5-(5-(3-butoxyphenyl)pent-4-en-1-ylidene)octahydro-1H-4,7-methanoindene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF

with a corresponding solution of 4-(octahydro-5H-4,7-methanoinden-5-ylidene)butanal to prepare the title product 5-(5-(3-butoxyphenyl)pent-4-en-1-ylidene)octahydro-1H-4,7-methanoindene.

5 6k: 1-butoxy-3-(4-(4-ethylphenyl)-3,3-dimethylbut-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(4-ethylphenyl)-2,2-dimethylpropanal to prepare the title product 1-butoxy-3-(4-(4-ethylphenyl)-3,3-dimethylbut-1-en-1-yl)benzene.

10

6l: 1-butoxy-3-(7-methoxy-3,7-dimethylnon-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 6-methoxy-2,6-dimethyloctanal to prepare the title product 1-butoxy-3-(7-methoxy-3,7-dimethylnon-1-en-1-yl)benzene.

15

6m: 1-butoxy-3-(4-(4-isobutylphenyl)but-1-en-1-yl)benzene

The procedure described in example 1.4 can be repeated by replacing the solution of 3-(4-isobutyl-2-methylphenyl)propanal and 3-(2-isobutyl-4-methylphenyl)propanal in THF with a corresponding solution of 3-(4-isobutylphenyl)propanal to prepare the title product 1-butoxy-3-(4-(4-isobutylphenyl)but-1-en-1-yl)benzene.

20

Example 7: fragrance comprising a compound of formula (I)

25

Compound / Ingredient	parts by weight 1/1000
Benzyl acetate	15
2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl acetate	60
(E)-2-Benzylideneoctanal	30
30 Decanal	18
Allyl 2-(isopentyloxy)acetate	3
CASSYRANE (2-(tert-butyl)-5-methyl-2-propyl-2,5-dihydrofuran)	0.5
Triethylcitrate (TEC)	6.3
Citronellol	20
35 CYCLAL C (2,4-dimethylcyclohex-3-ene-1-carbaldehyde)	5

	Delta Damascone	1
	(E)-dec-4-enal	0.2
	DIHYDRO MYRCENOL	60
	DPG	296.3
5	EUCALYPTUS essential oil	10
	FLORALOZONE (3-(4-ethylphenyl)-2,2-dimethylpropanal)	3
	FLORHYDRAL (3-(3-isopropylphenyl)butanal)	2
	FRESKOMENTHE (2-(sec-butyl)cyclohexan-1-one)	5
	GALBANONE (1-(3,3/5,5-dimethylcyclohex-1-en-1-yl)pent-4-en-1-one)	4
10	ISO E SUPER	20
	ISOBUTAVAN (4-formyl-2-methoxyphenyl isobutyrate)	0.2
	ISORALDEINE	10
	JAVANOL	1
	LABIENOXIME ¹⁾ 1%/IPM-TEC @ 10% DPG	3
15	LEMONILE (3,7-dimethylnona-2,6-dienenitrile)	35
	Terpinolene (1-methyl-4-(propan-2-ylidene)cyclohex-1-ene)	20
	Linalol	90
	MANZANATE (ethyl 2-methylpentanoate)	2
	METHYL PAMPLEMOUSSE (6,6-dimethoxy-2,5,5-trimethylhex-2-ene)	5
20	MYRALDENE (4-(4-methylpent-3-en-1-yl)cyclohex-3-ene-1-carbaldehyde)	10
	NYMPHEALTM (3-(4-isoputyl-2-methylpehnyl)propanal)	8
	Orange terpenes	240
	Petalia (2-cyclohexylidene-2-(o-tolyl)acetonitrile)	7
	RHUBAFURAN (2,4-dimethyl-4-phenyltetrahydrofuran)	0.5
25	ROSYFOLIA® (1-methyl-2-(5methylhex-4-en-2-yl)cyclopropyl)methanol	3
	SYLKOLIDE	5
	((E)-2-((3,5-dimethylhex-3-en-2-yl)oxy)-2-methylpropyl cyclopropanecarboxylate)	
	<u>TOSCANOL (1-(cyclopropylmethyl)-4-methoxybenzene)</u>	<u>1</u>
	Total:	1000
30		
	1) 3E,6E)-2,4,4,7-tetramethylnona-6,8-dien-3-one oxime	

The fragrance composition above possesses a classical fresh green lemon character. This fragrance can be applied to, e.g., all-purpose cleaner (APC), at 0.1 – 1.5 wt% (e.g. 0.3 wt%).

- 5 By replacing 40 parts of DPG of the accord above by 3-butoxybenzaldehyde, i.e. a compound of formula (I), the overall odor character is now softer, more floral, rounder, and over all, the perception is easier, fresher, more comfortable.

- By replacing 40 parts of DPG of the accord above by 3-butoxybenzaldehyde, i.e. a
 10 compound of formula (I), and replacing 110 parts of DPG of the accord above by a mixture comprising 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene (60 parts) and two additional precursors (4-(dodecylthio)-4-methylpentan-2-one (10 parts) and ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate (40 parts)), the longlastingness of the accord is greatly improved, delivering a pleasant and very natural
 15 combination.

Example 8: fragrance comprising a compound of formula (II)

20	Compound / Ingredient	parts by weight 1/1000
	Nerolex ((Z)-3,7-dimethylocta-2,6-dien-1-ol)	11
	PETALIA (2-cyclohexylidene-2-(o-tolyl)acetonitrile)	20
	LABIENOXIME 1%/IPM-TEC @ 10% DPG (3E,6E)-2,4,4,7-tetramethylnona-6,8-dien-3-one oxime)	5
25	Benzyl acetate	15
	(Z)-hex-3-en-1-yl acetate	2
	Myraldyle acetate	20
	((4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)methyl acetate)	
	2-phenylethan-1-ol	100
30	(E)-2-benzylideneheptanal	40
	(E)-2-benzylideneoctanal	100
	dodecanal	3
	ROSYFOLIA® (1-methyl-2-(5methylhex-4-en-2-yl)cyclopropyl)methanol	4
	NYMPHEAL™ (3-(4-isoputyl-2-methylpehnyl)propanal)	20
35	Cyclamen aldehyde (3-(4-isopropylphenyl)-2-methylpropanal)	30

	Indol @ 10% TEC	7
	Prunolide (5-pentylidihydrofuran-2(3H)-one)	2
	Peach Pure (5-heptyldihydrofuran-2(3H)-one)	3
	Nectaryl (2-(2-(4-methylcyclohex-3-en-1-yl)propyl)cyclopentan-1-one)	5
5	Citronellol	40
	Dipropylene glycol (DPG)	195
	ESTRAGOLE (1-allyl-4-methoxybenzene)	1
	HEDIONE (methyl 2-(3-oxo-2-pentylcyclopentyl)acetate)	60
	Grapefruit oil	20
10	Isoeugenol	9
	Citral	3
	Linalol	180
	FLOROCYCLEN (3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-6-yl propionate)	10
	Geraniol	45
15	<u>PEONILE® (2-cyclohexylidene-2-phenylacetonitrile)</u>	<u>50</u>
		Total: 1000

20 The fragrance composition above is a fresh floral green accord, reminiscent of fresh green muguet. This fragrance can be applied, e.g. in high density liquid detergent (HDLD), at 0.3 – 1.5 wt% (e.g. 0.6 wt%).

25 By replacing 30 parts of DPG of the accord above by 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene, i.e. a precursor of a compound of formula (I), the fresh green effect on wet fabric is clearly enhanced. And, in particular, the longlastingness of the accord on dry fabric is clearly enhanced when the dry fabric is assessed after one or three days.

30 By replacing 70 parts of DPG of the accord above by 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene, the green freshness becomes very present and brings a surprising and unusual freshness on dry fabric, reminiscent of green leaf and fresh apple skin.

Example 9: fragrance comprising a compound of formula (II)

	Compound / Ingredient	parts by weight 1/1000
	2-methyl-1-phenylpropan-2-yl acetate	20
5	4-(tert-butyl)cyclohexyl acetate	50
	(2-(1-ethoxyethoxy)ethyl)benzene	2
	AGRUMEX (2-(tert-butyl)cyclohexyl acetate)	25
	2-phenylethan-1-ol	10
	(E)-2-benzylideneoctanal	100
10	2-methylundecanal	1
	AMBROFIX (3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan)	1
	methyl 2-aminobenzoate	2
	AUBEPINE PARA CRESOL (4-methoxybenzaldehyde)	3
	lemon terpens	10
15	Citronellol	80
	delta damascone	2
	DIHYDRO MYRCENOL	100
	DIPHENYL OXIDE	10
	DUPLICAL (4-(octahydro-5H-4,7-methanoinden-5-ylidene)butanal)	2
20	EUCALYPTOL NATUREL	3
	FLOROCYCLEN (3a,4,5,6,7,7a-hexahydro-1H-4,7-methanoinden-6-yl propionate)	75
	GARDENOL (1-phenylethyl acetate)	20
	ISO E SUPER	100
	ISORALDEINE	25
25	JAVANOL @ 10% DPG	5
	LEMONILE (3,7-dimethylnona-2,6-dienenitrile)	2
	METHYL ACETOPHENONE (1-(p-tolyl)ethan-1-one)	2
	4-(tert-butyl)cyclohexan-1-ol	10
	PATCHOULI ESS SANS FER INDONESIE ORPUR	3
30	PHARAONE (2-cyclohexylhepta-1,6-dien-3-one) 10%/DPG	5
	Hexyl salicylate	75
	SERENOLIDE	
	(2-(1-(3,3-dimethylcyclohexyl)ethoxy)-2-methylpropyl cyclopropanecarboxylate)	30
	SPIROGALBANONE (1-(spiro[4.5]dec-6/7-en-7-yl)pent-4-en-1-one)	1
35	STEMONE ((Z)-5-methylheptan-3-one oxime)	1

TETRAHYDRO LINALOL	50
UNDECAVERTOL	10
<u>Dipropylen glycol (DPG)</u>	<u>165</u>
Total: 1000	

5

The fragrance composition above is a fresh floral green accord, reminiscent of fresh green muguet. This fragrance can be applied, e.g. in high density powder detergent (HDPD), at 0.1 – 1.5 wt% (e.g. 0.3 wt%).

10

By replacing 100 parts of DPG of the accord above by 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene, i.e. a precursor of a compound of formula (I), the performance and diffusion on wet towels is enhanced with a fresh green pleasant character. And on dry fabric, the substantivity is noticeably improved, with an unusual and very pleasant fresh green character.

15

By replacing 110 parts of DPG of the accord above by a mixture comprising 1-butoxy-3-((1E,4Z)-hepta-1,4-dien-1-yl)benzene (70 parts) and two additional precursors (4-(dodecylthio)-4-methylpentan-2-one (10 parts) and ethyl N,S-bis(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate (30 parts)), a very unusual and pleasant fresh green juicy fruity character is delivered on dry fabric. This fresh green juicy fruity character will last for few days, which is also novel and surprising.

20