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Fragrance Precursors

The present invention relates to fragrance precursors for a fragrant ketone and a fragrant ester.

5

A principal strategy currently employed in imparting odors to consumer products is the admixing of the fragrance directly into the product. There are, however, several drawbacks to this strategy. The fragrance material can be too volatile and/or too soluble, resulting in fragrance loss during manufacturing, storage, and use. Many fragrance materials are also unstable over time. This again results in loss during storage.

15 In many consumer products it is desirable for the fragrance to be released slowly over time. Micro-encapsulation and inclusion complexes with cyclodextrins have been used to help decrease volatility, improve stability and provide slow-release properties. However, these methods are for a number of reasons often not successful. In addition, cyclodextrins can be too expensive.

25 It is therefore desirable to have a fragrance delivery system which is capable of releasing the fragrant compound or compounds in a controlled manner, maintaining a desired smell over a prolonged period of time.

30 Precursors for the delivery of organoleptic compounds, especially for flavors, fragrances and masking agents, is described in EP-A 0 936 211. This delivery system releases one or more odoriferous compounds upon exposure to light

and/or UV irradiation. Using this system in various consumer products leads to a prolonged perception of the fragrant compound(s) to be released.

- 5 WO 99/60990 describes fragrance precursors which release fragrant alcohols, aldehydes or ketones upon exposure to light. Perfuming compositions comprising these fragrance precursors can be used in various consumer products such as detergents, fabric softeners, household products, hair-
10 care products etc..

Many fragrant compounds with odors accepted by the public are esters of high volatility resulting in a short period of perceivable odor. Such esters are fast hydrolyzed in
15 alkaline environment, thereby loosing the fragrant characteristic. Therefore, they are of limited use for laundry products.

Object of the present invention is to provide non volatile
20 precursors for volatile fragrant esters.

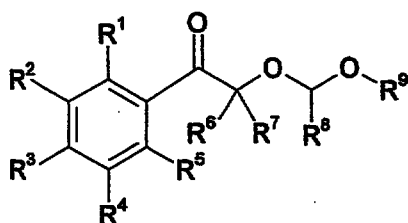
A further object of the present invention is to provide fragrance precursors which are stable in alkaline environment, especially in laundry products.
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Also an object of the present invention is to provide fragrance precursors with high substantivity.

A further object of the present invention is to provide
30 fragrance precursors which are activated and cleaved by light.

Also an object of the present invention is to provide fragrance precursors with slow release properties.

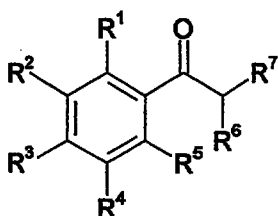
The present invention relates to fragrance precursors of
5 formula I



(I)

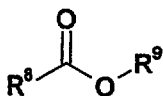
which upon exposure to light, and in particular daylight,
release a fragrant ketone of formula II

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(II)

and a fragrant ester of formula III



(III)

15

wherein

R¹ to R⁵ represent independently H, -NO₂, branched or
linear C₁-C₆-alkyl, C₁-C₆-alkenyl, C₁-C₆-alkynyl or C₁-C₄-
20 alkoxy,

R¹ and R², R² and R³, R³ and R⁴ and R⁴ and R⁵ may form together one or two aliphatic or aromatic rings, these rings may optionally contain branched or linear C₁-C₄-alkyl, C₁-C₄-alkenyl or C₁-C₄-alkinyl residues, and the above rings
5 and residues may comprise one or more oxygen atoms,

R⁶ and R⁷ are independently H, branched or linear C₁-C₆-alkyl, C₁-C₆-alkenyl, C₁-C₆-alkinyl, and R⁶ or R⁷ may form with either R¹ or R⁵ a carbocyclic ring optionally
10 substituted by an aliphatic residue.

R⁸ and R⁹ are the residues of an acid R⁸-COOH and an alcohol R⁹OH respectively forming the fragrant ester of formula
15 III.

Branched carbon chains also comprise multiple branched chains.

The present invention also relates to the compounds of
20 formula I.

The fragrance precursors of formula I release upon exposure to light volatile fragrant esters of formula III and fragrant ketons of formula II. Since the precursors of
25 the invention are stable in alkaline environment and show high substantivity, they are excellently adapted for detergent and laundry use.

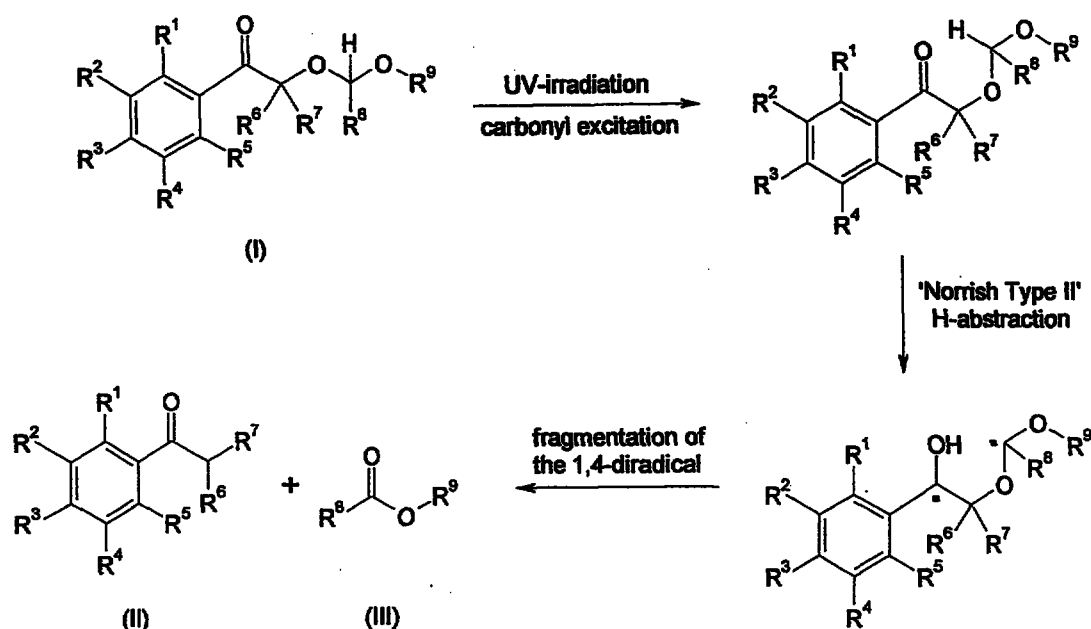
The fragrance precursors of the present invention are
30 slowly cleaved when exposed to light, in particular daylight. Upon absorption of energy from said light, the phenacyl acetals undergo a Norrish Type II photoreaction

which leads to the release of a fragrant ketone of formula II and a fragrant ester of formula III.

The release of the above mentioned fragrant compounds occurs for example upon exposure to sunlight penetrating through ordinary windows and being not particularly rich in UV irradiation. It is needless to say that upon exposure to bright sunlight, in particular outdoors, the release of the fragrant compounds of formula II and III will occur faster and to a greater extent than upon exposure to room light inside a building. The cleavage of the precursors of the present invention can also be initiated by an appropriate lamp, for example a sun tanning lamp.

It is known that phenacyl glycosides undergo a Norrish Type II photoreaction leading to gluconolactones and the corresponding phenacyl compound (Crich et al., Tetrahedron, 1995, 51, 11945-11952). However, it has not been described or suggested to use such phenacyl acetals as fragrance precursors, which are capable of releasing a fragrant ketone and a fragrant ester over a prolonged period.

The photoreaction of the fragrance precursors of formula I involves in a first step the absorption of light by the keto-group followed by abstraction of the acetal-H atom and subsequent cleavage of the resulting 1,4-diradical (Scheme A). It has been found that the aromatic residue of the fragrance precursors plays an important role in this photoreaction as it influences the absorption maximum $\lambda_{\max}$ of the keto-group. Therefore, the cleavage properties of the fragrance precursors can be modified by variation of the substituents R^1 to R^5 .



Scheme A

Fragrant aryl alkyl ketones of formula II are well known to those skilled in the art. A fragrant ketone of formula II is a compound known to a person skilled in the art as being a useful ingredient for the formulation of perfumes or perfumed articles. Non-limiting examples of said aryl alkyl ketones are acetanisole (1-(4-methoxyphenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], acetophenone (1-phenyl-ethanone) [Haarmann & Reimer GmbH, Germany], Crysolide® (4-acetyl-6-tert-butyl-1,1-dimethyl-indan) [Givaudan Roure (International) SA, Vernier, Switzerland], dimethyl acetophenone (1-(2,4-dimethylphenyl)-ethanone) [Fluka AG, Buchs, Switzerland], Fixolide® (1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone) [Givaudan Roure (International) SA, Vernier, Switzerland], Florantone T® (1-(5,6,7,8-tetrahydro-2-naphthalenyl)-ethanone) [Takasago Perfumery Co., Japan], Grassenone 34® (3-methyl-1-(4-methylphenyl)-4-hexen-1-one) [Keemia Institute, Tallin USSR],

isopropylindanone (2-(1-methylethyl)-indanone) [Givaudan
Roure (International) SA, Vernier, Switzerland], Lavonax®
(1-phenyl-4-penten-1-one) [International Flavors &
Fragrances, USA], Musk F (5-acetyl-1,1,2,3,3-pentamethyl-
5 indane) [CNNP], Musk ketone® (4-tert-butyl-3,5-dinitro-
2,6-dimethyl-acetophenone) [Givaudan Roure (International)
SA, Vernier, Switzerland], Novalide® (1,6,7,8-tetrahydro-
1,4,6,6,8,8-hexamethyl-indacen-3(2H)-one) [Givaudan Roure
(International) SA, Vernier, Switzerland], Oranger
10 Crystals® (1-(2-naphthalenyl)-ethanone) [Givaudan Roure
(International) SA, Vernier, Switzerland], Orinox® (1-[4-
(1,1-dimethylethyl)-2,6-dimethylphenyl]-ethanone) [Polak's
Frutal Works BV, Netherlands], Phantolide® (1-(2,3-
dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl)-ethanone)
15 [Polak's Frutal Works BV, Netherlands], propiophenone (1-
phenyl-propanone) [Haarmann & Reimer GmbH, Germany],
Traseolide 100® (1-[2,3-dihydro-1,1,2,6-tetramethyl-3-(1-
methylethyl-1H-inden-5-yl)-ethanone) [Quest International,
Netherlands], Vernolide® (1-(5,6,7,8-tetrahydro-
20 3',5',5',8',8'-pentamethyl-2-naphthalenyl)-ethanone)
[Givaudan Roure (International) SA, Vernier, Switzerland],
Versalide® (1-(5,6,7,8-tetrahydro-3'-ethyl,5',5',8',8'-
tetramethyl-2-naphthalenyl)-ethanone) [Givaudan Roure
(International) SA, Vernier, Switzerland], Vitalide® (1-
25 (hexahydrodimethyl-1H-benzindenyl)-ethanone) [Takasago
Perfumery, Japan].

It is obvious to the person skilled in the art that the
above list is illustrative and that the present invention
30 relates to many other fragrant ketones of formula II.
Additional fragrant ketones of formula II are e.g.

described in "Perfume and Flavor Chemicals", S. Arctander Ed. , Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 1994 and in K. Bauer, D. Garbe and H. Surburg, Eds., Common Fragrance and Flavor Materials, 5 Wiley-VCH, 3rd Edition, Weinheim, 1997.

Fragrance esters of formula III, represent an important class of perfumery raw materials and comprise compounds of a great structural variety. Fragrance esters of formula 10 III contribute to the odor and aroma of nearly all fruits and are known to be useful ingredients for the formulation of perfumes or perfumed articles. In the following a non-limiting list of such esters are given as examples.

15 Most of the aliphatic esters of formula III are either acetates or comprise ethanol as the alcohol component. Examples for such esters of formula III include amyl butyrate, butyl 2-methylpentanoate, 3,7-dimethyloctan-3-yl acetate, ethyl 2-methylbutyrate, hexyl acetate, hexyl 20 isobutyrate and isopropyl 2-methylbutyrate.

The lower fatty acid esters of acyclic terpene alcohols, e.g. geraniol, linalool and citronellol, and of cyclic terpene alcohols, e.g. menthol, α -terpineol, borneol and 25 guaiacol, are important both as fragrance and as flavor substances and are envisaged as esters of formula III.

Various cycloaliphatic esters of formula III are widely used perfumery chemicals, non-limiting examples are 30 Agrumex[®] (2-tert-butylcyclohexyl acetate) [Haarmann & Reimer GmbH, Germany], Vertenex[®] (4-tert-butylcyclohexyl acetate) [International Flavors & Fragrances, USA], Verdylacetate[®] (4,7-Methano-3a,4,5,6,7,7a-hexahydro-5(6)-

indenyl acetate) [Givaudan Roure (International) SA,
Vernier, Switzerland], Givescone® (ethyl 2-ethyl-6,6-
dimethyl-2-cyclohexenecarboxylate and ethyl 2,3,6,6-tetra-
methyl-2-cyclohexenecarboxylate) [Givaudan Roure
5 (International) SA, Vernier, Switzerland], Cyclogalbanat®
(allyl cyclohexyloxyacetate) [DRAGOCO Gerberding & Co. AG,
Germany], Methyl jasmonate® (3-oxo-2-(cis-pentenyl)cyclo-
pentaneacetic acid methyl ester) [Firmenich S.A.,
Switzerland] and Hedion® (methyl (3-oxo-2-pentyl-
10 cyclopentyl)acetate) [Firmenich S.A., Switzerland].

Other important esters of formula III used in perfumery
are those derived from araliphatic alcohols and aliphatic
acids. They have characteristic odor properties. Important
15 esters that fall into this category are e.g. benzyl
acetate, phenethyl acetate, α,α -dimethylphenethyl acetate
and cinnamyl acetate.

Many of the esters of formula III described above, which
20 are of pleasant odor, have a rather high volatility. This
is especially true for aliphatic esters exhibiting typical
fruity odors and for lower fatty acid esters of acyclic
terpene alcohols having pleasant citrusy, floral odors. An
example of such a volatile ester is e.g. cis-3-hexenyl
25 acetate. Cis-3-hexenyl acetate applied to a surface of,
for example, a fabric using a fabric softener in the
rinsing cycle of the washing process, can only be
perceived over a short period of time of one or two hours,
depending on the concentration of cis-3-hexenyl acetate in
30 the fabric softener.

The fragrance precursors of the present invention are not, or only slightly, volatile. The fragrant ketone of formula II and the fragrant ester of formula III are released only upon exposure to light, and especially daylight. The
5 photochemical cleavage provides over days and weeks perceptible amounts of the fragrant compounds. The period depends interalia on the amount or concentration of the precursor applied, the duration of exposure to light, its intensity and its wavelength.

10

Fragrance esters of formula III are prone to undergo hydrolysis into an acid of formula R^8COOH and an alcohol of formula R^9OH , especially in alkaline products. Therefore many fragrance accords comprising such esters, e.g. fruity
15 accords, cannot be imparted to such products.

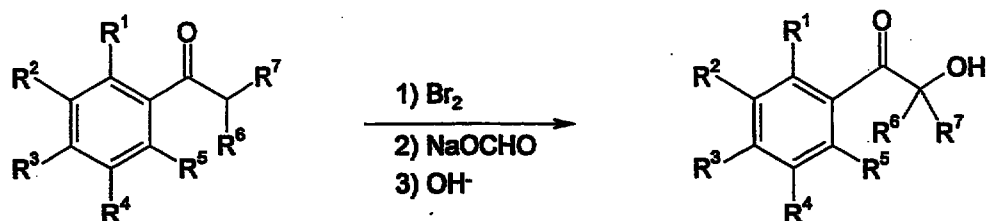
Today's consumers select a certain product not only based on performance but also based on the odor. From the foregoing it is evident that products for introducing a
20 variety of fragrance accords to products having alkaline pH are desirable. The fragrance precursors of the present invention have the advantage that they are not or only slightly volatile and chemically stable in consumer products having alkaline and neutral pH. A precursor of
25 formula I added to a powder detergent, is stable in the detergent powder throughout storage. During the washing cycle (alkaline pH) and the rinsing cycle (neutral pH) the precursor is deposited on the fabric surface. It is only upon exposure of the fabric to light, for example during
30 line drying in the sun, that the release of the fragrant ketone of formula II and the fragrant ester of formula III is started.

It has been mentioned above that esters of formula III, and especially the aliphatic ones, are rather volatile compounds. Furthermore, they are water soluble and are, therefore, lost to some extent during the washing/rinsing cycle if introduced directly into detergents.

The fragrance precursors of formula I have the advantage that they have good substantivity on different substrates, especially on fabrics. Furthermore, the precursors are not or only slightly volatile, thus no loss occurs during storage. With the precursors of the present invention highly volatile esters of formula III with low substantivity are successfully applied to achieve a long lasting pleasant odor. The volatile esters are produced in situ after application of the precursors of formula I onto a fabric during the washing cycle.

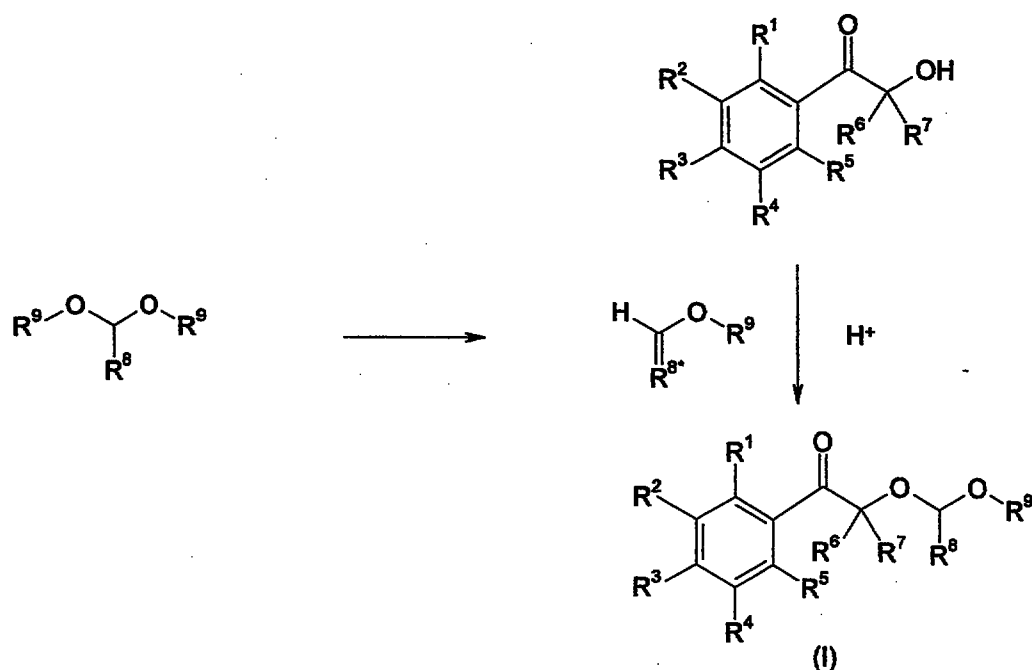
In the precursors of the invention the moiety derived from a fragrant ketone of formula II brings three advantages: it introduces stability as well as substantivity to the precursors of formula I and upon activation by light exhibits fragrant properties.

The fragrance precursors of the present invention are advantageously prepared via two methods. Both methods use an α -hydroxy-ketone as starting material. The latter is prepared by bromination of the corresponding fragrant ketone followed by sodium formate treatment and subsequent hydrolysis shown in scheme I:



Scheme I

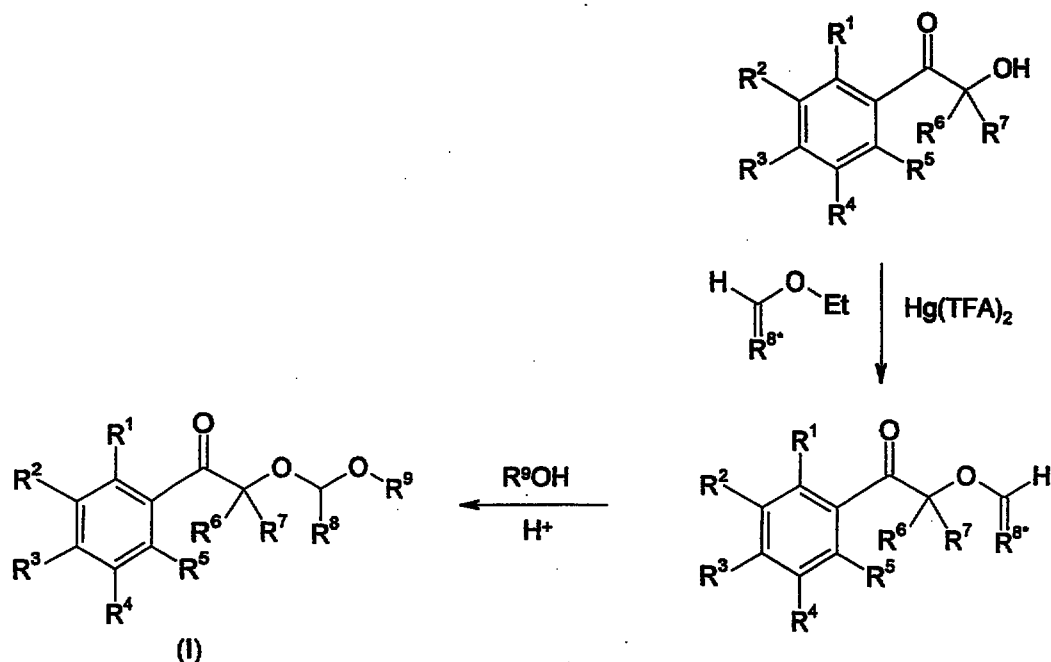
Then according to the first method the α -hydroxy-ketone intermediate is reacted under acid conditions with a vinyl ether to the desired precursor of formula I. The vinyl ether is obtained via the acetal of an aldehyde R^8CHO and an alcohol R^9OH . The synthesis is illustrated in scheme II:



10 Scheme II

According to the second method the α -hydroxy-ketone is transformed to the corresponding vinyl ether using a Hg catalyst. The vinyl ether is then coupled with the alcohol R^9OH from which the fragrant ester of formula III is derived. This method allows for the use of a great variety of alcohols, i.e. residues R^9 especially for allylic

residues. The synthesis via this route is illustrated in scheme III:



5

Scheme III

Preferred precursors of the present invention are compounds releasing an aliphatic ester of formula III wherein R^8 is the residue of an aliphatic acid having 1 to 4 carbon atoms and R^9 is the residue of an aliphatic alcohol having 2 to 20 carbon atoms. Most preferred precursors are those releasing an ester derived from acetic acid, i.e. wherein R^8 is $-CH_3$.

15

Other preferred precursors include compounds wherein R^8 is the residue of an aliphatic acid having 5 to 20 carbon atoms and R^9 is the residue of an aliphatic alcohol having 1 to 5 carbon atoms. Most preferred compounds are those releasing an ester derived from ethanol, i.e. wherein R^9 is $-CH_2CH_3$.

20

Other preferred precursors include compounds wherein R⁸ is the residue of an aliphatic acid having 1 to 4 carbon atoms and R⁹ is the residue of a terpene alcohol having 10 to 20 carbon atoms. Most preferred compounds are those wherein the alcohol is a monoterpene alcohol.

Other preferred precursors include compounds wherein R⁸ is the residue of a cycloaliphatic acid having 5 to 20 carbon atoms and R⁹ is the residue of an aliphatic alcohol having 1 to 5 carbon atoms. Most preferred compounds are those wherein the alcohol is ethanol.

Other preferred precursors include compounds wherein R⁸ is the residue of an aliphatic acid having 1 to 4 carbon atoms and R⁹ is the residue of an araliphatic alcohol having more than 5 carbon atoms. Most preferred precursors are those releasing an ester derived from acetic acid, wherein R⁸ is -CH₃.

Other preferred precursors include compounds wherein at least one of the residues R⁶ or R⁷ = H. Most preferred are compounds wherein R⁶ and R⁷ = H. Upon cleavage of these precursors a fragrant ketone of formula II is released wherein said ketone is an aryl methyl ketone.

Other preferred precursors include compounds wherein R⁶ and R⁷ = H and R¹ to R⁵ represent independently hydrogen, -NO₂, linear or branched C₁-C₆ alkyl, alkenyl, alkynyl, and C₁-C₄ alkoxy. Most preferred compounds are those releasing a fragrant ketone of formula II wherein the fragrant ketone is selected from 1-phenyl-ethanone, 2,4-dimethylphenyl-ethanone, 1-[4-(1,1-dimethylethyl)-2,6-dimethylphenyl]-

ethanone, 1-(4-tert-butyl-3,5-dinitro-2,6-dimethyl)-ethanone and 1-(4-methoxyphenyl)-ethanone.

Other preferred precursor include compounds wherein R¹ and R², R² and R³, R³ and R⁴, R⁴ and R⁵ form together an
5 aliphatic or aromatic ring, wherein this ring may optionally contain substituted or unsubstituted C₁-C₄ alkyl, alkenyl, alkynyl residues and may comprise one or more oxygen atoms. Most preferred compounds are those releasing a fragrant ketone of formula II wherein the
10 fragrant ketone is selected from 1-(2-naphtalenyl)-ethanone, 4-acetyl-6-tert-butyl-1,1-dimethyl-indan, 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3',5',5',8',8'-penta-
15 methyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3'-ethyl-5',5',8',8'-tetramethyl-2-naphthalenyl)-ethanone, 1-(2,3-dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl)-ethanone, 1-[2,3-dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl-1H-inden-5-yl)-ethanone, 5-acetyl-1,1,2,3,3-pentamethyl-indane, 1-(5,6,7,8-tetrahydro-2-naphthalenyl)-
20 ethanone.

Since the compounds of formula I, upon exposure to light are cleaved and provide a fragrant ketone of formula II and a fragrant ester of formula III, they permit the
25 development of useful consumer products with enhanced fragrant properties, especially having long lasting pleasant odor. Therefore, the present invention also relates to the use of all compounds of formula I as precursors for fragrant compounds.

30

The fragrance precursors of the present invention can be used in any product in which a prolonged and defined release of the above mentioned fragrant compounds is

desired. Therefore, these precursors are especially useful in functional perfumery, in products which are exposed to sunlight, during or after application.

5 The compounds of the present invention can act as fragrance precursors in functional and fine perfumery i.e. in fine fragrances, industrial, institutional, home and personal care products. Industrial, institutional and home cleaning products to which the fragrance precursors can be
10 added are all kinds of detergents, window cleaners, hard surface cleaners, all purpose cleaners and furniture polishes. The products can be liquids or solids, such as powders or tablets. Fabrics and surfaces treated with a product comprising a fragrance precursor of the present
15 invention will diffuse a fresh and clean odor upon exposure to light much longer than when cleaned with a conventional cleaner. Fabrics or cloths washed with such detergents will release the fragrant compounds even after having been stored for weeks in a dark place, e.g. a
20 wardrobe.

The precursors of the present invention are also useful for application in all kinds of body care products. Especially interesting products are hair care products,
25 for example shampoos, conditioners and hairsprays and skin care products such as cosmetic products and especially sun protection products.

The above mentioned examples are of course only
30 illustrative and non-limiting. Many other products to which the precursors of the present invention may be added include soaps, bath and shower gels, deodorants and even perfumes and colognes.

The fragrance precursors of the present invention can be used alone or in combination with other fragrance ingredients, solvents or adjuvants known to those skilled
5 in the art. Such ingredients are described, for example, in "Perfume and Flavor Chemicals", S. Arctander, Ed., Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 1994 and include fragrance compounds of natural or synthetic origin and essential oils of natural products.

10

The amounts in which the precursors of formula I are incorporated in the various above-mentioned products vary within a wide range. The amounts depend on the nature of the fragrant compounds to be released, the nature of the
15 product to which the precursors are added and the desired olfactory effect. The amounts used also depend on the co-ingredients in a given composition when the precursors of the present invention are used in admixture with perfuming co-ingredients, solvents or adjuvants. Typical
20 concentrations are in the order of 0.01% to 5% by weight of the products.

The following non-limiting examples further illustrate the embodiments of the invention.

25

The following chemicals were obtained from commercial sources: bromo-acetonaphtone, bromo-acetanisole, sodium formate, trifluoroacetic acid, ethyl vinyl ether, mercury trifluoroacetate, 2-phenyl-ethanol, cis-3-hexenol, 3,5,5-
30 trimethyl-hexanol, hexanol, 3-phenyl-propanol, citronellol, 3,7-dimethyl-3-octanol, 4-tert-butyl-cyclohexanol, β -methoxy-styrene.

α -Bromo-Fixolide was prepared from Fixolide[®] according to R.M. Cowper, L.H. Davidson, *Org. Synth. Coll. Vol. II*, 1943, 480-481.

5 NMR: values of coupling constants J are given in Hertz (Hz).

Example 1

Preparation of Phenacyl acetals

10

1. General procedure for the preparation of hydroxy-acetophenones

A suspension of the corresponding bromo-acetophenone (0.05 mmol) and sodium formate (17 g, 0.25 mol, 5 eq.) in aqueous ethanol (85%, 150 ml) was heated at reflux until completion of the reaction (TLC). Most of the ethanol was evaporated and the mixture partitioned between MTBE (80 ml) and water (70 ml). The organic phase was separated and washed with aq. NaHCO_3 (sat.) and brine. Removal of the solvent in vacuo, after drying over MgSO_4 , afforded a crude product as a solid which was recrystallised from ethanol.

2-Hydroxy-1-(4-methoxy-phenyl)-ethanone

25 Obtained according to the general procedure.

mp 104-105 °C.

¹H-NMR (400 MHz, CDCl_3): 3.48 (t, 1H, J 4); 4.82 (d, 2H, J 4); 6.95-7.0 (m, 2H); 7.85-7.95 (m, 2H).

IR (ν_{max} , cm^{-1} , neat): 3415m, 2929w, 1672s, 1603s.

30 MS [m/z (EI)]: 166 (M^+ , 4), 155 (100), 77 (28).

1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-2-hydroxy-ethanone

Obtained according to the general procedure.

mp 81-82 °C.

5 **¹H-NMR** (400 MHz, CDCl₃): 1.0 (d, 3H, *J* 6.8); 1.08 (s, 3H); 1.26 (s, 3H); 1.31 (s, 3H); 1.33 (s, 3H); 1.41 (dd, 1H, *J* 13.2, 2.4); 1.63 (dd, 1H, *J* 13.2, 13.2); 1.8-1.95 (m, 1H); 2.54 (s, 3H); 4.76 (s, 2H); 7.26 (s, 1H); 7.57 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 3447w, 2963m, 2911m, 1675s, 1607w.

10 **MS** [*m/z* (EI)]: 274 (M⁺, 3), 243 (100).

2-Hydroxy-1-naphthalen-2-yl-ethanone

Obtained according to the general procedure.

mp 114-115 °C.

15 **¹H-NMR** (400 MHz, CDCl₃): 3.59 (t, 1H, *J* 4.4); 5.02 (d, 2H, *J* 4.4); 7.55-7.7 (m, 2H); 7.85-8.0 (m, 4H); 8.43 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 3428m, 3391m, 3051w, 2931w, 1680s, 1627m.

20 **MS** [*m/z* (EI)]: 186 (M⁺, 12), 155 (75), 127 (100), 40 (26), 28 (41).

2. General procedure for the preparation of alkyl vinyl ethers

25 A solution of the alcohol (0.1 mol) and mercury(II) trifluoroacetate (4 mmol, 0.04 eq.) in ethyl vinyl ether (50 ml, 1 mol, 5 eq.) was heated at reflux until completion of the reaction (TLC, GC). The ethyl vinyl ether was evaporated and the residue diluted with MTBE and
30 poured into aq. NaHCO₃ (sat.). The separated aqueous phase was extracted with MTBE and the combined organic layers were washed with brine and dried over MgSO₄. After

concentration, the crude oil was distilled under reduced pressure to afford the desired product as a colorless oil.

Hexyloxy-ethene

5 Obtained according to the general procedure.

bp_{170mbar} 89 °C.

¹H-NMR (400 MHz, CDCl₃): 0.9 (t, 3H, J 6.8); 1.25-1.42 (m, 6H); 1.6-1.7 (m, 2H); 3.67 (t, 2H, J 6.8); 3.96 (dd, 1H, J 6.8, 2); 4.16 (dd, 1H, J 14.4, 2); 6.46 (dd, 1H, J 14.4, 6.8).

IR (ν_{max}, cm⁻¹, neat): 3119w, 2957s, 2932s, 2861m, 1740w, 1636m, 1611s.

MS [m/z (EI)]: 128 (M⁺, 1), 56 (34), 55 (23), 43 (100), 41 (39).

(2-Vinyloxy-ethyl)-benzene

Obtained according to the general procedure.

¹H-NMR (400 MHz, CDCl₃): 2.96 (t, 2H, J 7.2); 3.88 (t, 2H, J 7.2); 3.99 (dd, 1H, J 6.8, 2); 4.18 (dd, 1H, J 14.4, 2); 6.46 (dd, 1H, J 14.4, 6.8); 7.19-7.32 (m, 5H).

IR (ν_{max}, cm⁻¹, neat): 3028m, 2947m, 2872m, 1636m, 1615s.

MS [m/z (EI)]: 148 (M⁺, 1), 105 (100), 104 (36), 79 (21), 77 (21).

(3,5,5-Trimethyl-hexyloxy)-ethene

Obtained according to the general procedure.

bp_{45mbar} 95 °C.

¹H-NMR (400 MHz, CDCl₃): 0.9 (s, 9H); 0.95 (d, 3H, J 6.4); 1.05-1.27 (m, 2H); 1.42-1.52 (m, 1H); 1.6-1.7 (m, 2H); 3.68 (t, 2H, J 6.4); 3.96 (dd, 1H, J 7, 2); 4.16 (dd, 1H, J 15, 2); 6.46 (dd, 1H, J 15, 7).

IR (ν_{max}, cm⁻¹, neat): 2955s, 2870m, 1649m, 1635m, 1610m.

MS [m/z (EI)]: 170 (M^+ , 1), 71 (23), 70 (24), 69 (21), 57 (100), 41 (22).

1-Vinyloxy-hex-3(Z)-ene

5 Obtained according to the general procedure.

bp_{140mbar} 86 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.97 (t, 3H, J 7.2); 2.0-2.1 (m, 2H); 2.37-2.45 (m, 2H); 3.68 (t, 2H, J 7.2); 3.98 (dd, 1H, J 6.8, 2); 4.18 (dd, 1H, J 14.4, 2); 5.3-5.4 (m, 1H);
10 5.47-5.55 (m, 1H); 6.46 (dd, 1H, J 14.4, 6.8).

IR (ν_{max} , cm^{-1} , neat): 3011w, 2965m, 2934m, 2874m, 1740w, 1636m, 1613m.

MS [m/z (EI)]: 126 (M^+ , 1), 83 (21), 70 (45), 67 (34), 55 (100), 41 (45).

15

(1-Ethyl-1,5-dimethyl-hexyloxy)-ethene

Obtained according to the general procedure.

bp_{15mbar} 88-90°C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.85-0.9 (m, 9H); 1.12-1.6 (m, 9H); 1.18 (s, 3H); 4.01 (d, 1H, J 6.4); 4.40 (dd, 1H, J 13.6, 0.4); 6.41 (dd, 1H, J 13.6, 6.4).
20

IR (ν_{max} , cm^{-1} , neat): 3010w, 2940s, 2860m, 1625s.

MS [m/z (EI)]: 184 (M^+ , 1), 85 (51), 71 (59), 69 (20), 57 (100), 55 (31), 43 (83), 41 (32), 29 (23).

25

2,6-Dimethyl-8-vinyloxy-oct-2-ene

Obtained according to the general procedure.

bp_{15mbar} 98 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.82 (d, 3H, J 8); 1.05-1.7 (m, 5H); 1.51 (s, 3H); 1.59 (s, 3H); 1.8-2.0 (m, 2H); 3.57-3.65 (s, 2H); 3.87 (dd, 1H, J 8, 4); 4.07 (dd, 1H, J 16, 4); 4.97-5.05 (m, 1H); 6.37 (dd, 1H, J 16, 8).
30

IR ($\nu_{\max}$, cm^{-1} , neat): 2960m, 2927w, 1636w, 1610m.

MS [m/z (**EI**)]: 182 (M^+ , 1), 181 (1), 123 (22), 95 (36), 82(28), 81(37), 69 (100), 68 (22), 67 (33), 55 (47), 41 (64).

5

(3-Vinyloxy-propyl)-benzene

Obtained according to the general procedure, after chromatography (SiO_2 , EtOAc/Hexane) of the crude.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 1.9-2.05 (m, 2H); 2.72 (t, 2H, J 7.6); 3.68 (t, 2H, J 6.4); 3.98 (dd, 1H, J 6.8, 2); 4.16 (dd, 1H, J 14.4, 2); 6.48 (dd, 1H, J 14.4, 6.8); 7.15-7.35 (m, 5H).

IR ($\nu_{\max}$, cm^{-1} , neat): 3027w, 2946w, 2870w, 1636m, 1613s.

MS [m/z (**EI**)]: 162 (M^+ , 1), 118 (52), 117 (30), 91 (100).

15

1-*t*-Butyl-4-vinyloxy-cyclohexane

Obtained according to the general procedure.

bp_{15mbar} 95 °C.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.8-0.9 (m, 9H); 0.95-1.1 (m, 2H); 1.1-1.45 (m, 4H); 1.5-1.6 (m, 1H); 1.75-1.85 (m, 1H); 1.9-2.13 (m, 2H); 3.57-3.67 (m, 0.6H); 3.95-4.05 (m, 1.4H); 4.28 (dd, 1H, J 14, 1.2); 6.27-6.37 (m, 1H).

IR ($\nu_{\max}$, cm^{-1} , neat): 2943s, 2865m, 1633m, 1607w.

MS [m/z (**EI**)]: 182 (M^+ , 4), 83 (46), 69 (23), 57 (100), 55 (23), 41 (25).

25

3. General procedure for the preparation of phenacyl acetals (I, fragrance precursors)

30 To a suspension of the α -hydroxy-acetophenone (20 mmol) in toluene (10 ml) was added the alkyl vinyl ether (2 eq.), followed by trifluoroacetic acid (2 or 3 drops, ~ 0.01

eq.). The mixture was heated at 50°C. When the reaction was finished (TLC), it was diluted with MTBE and poured into aq. NaHCO₃ (sat.). The aqueous phase was separated and extracted with MTBE, and the combined organic layers were washed with brine and dried over MgSO₄.

The crude, obtained after evaporation of the solvents, was purified by chromatography (SiO₂, EtOAc/Hexane) to afford the desired product as a colorless to pale yellow oil.

10 **2-(1-Ethoxy-ethoxy)-1-(4-methoxy-phenyl)-ethanone (1)**

Obtained according to the general procedure without the use of solvent. No purification was required.

¹H-NMR (400 MHz, CDCl₃): 1.19 (t, 3H, *J* 7.2); 1.4 (d, 3H, *J* 5.2); 3.5-3.7 (m, 2H); 3.87 (s, 3H); 4.77 (m, 2H); 4.91 (q, 1H, *J* 5.6); 6.9-7.0 (m, 2H); 7.9-8.0 (m, 2H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2977w, 1693m, 1601s, 1576m, 1512.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 219 (11796), 273 (17127).

MS [*m/z* (EI)]: 237 (M⁺), 135 (100), 77 (26).

20 **1-(4-Methoxy-phenyl)-2-(1-phenethyloxy-ethoxy)-ethanone (2)**

Obtained according to the general procedure without the use of solvent.

¹H-NMR (200 MHz, CDCl₃): 1.37 (d, 3H, *J* 5); 2.8-2.9 (m, 2H); 3.65-3.9 (m, 2H); 3.87 (s, 3H); 4.42-4.62 (m, 2H); 4.89 (q, 1H, *J* 5); 6.87-6.95 (m, 2H); 7.1-7.3 (m, 5H); 7.75-7.85 (m, 2H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2987m, 2936m, 2840m, 1693s, 1601s, 1575m, 1512m.

30 UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 276 (15042).

MS [*m/z* (EI)]: 314 (M⁺), 150 (44), 135 (86), 105 (100), 77 (29).

**2-(1-Hex-3(Z)-enyloxy-ethoxy)-1-(4-methoxy-phenyl)-
ethanone (3)**

Obtained according to the general procedure without the
5 use of solvent.

¹H-NMR (200 MHz, CDCl₃): 0.95 (t, 3H, *J* 7.5); 1.4 (d, 3H, *J* 6); 1.95-2.15 (m, 2H); 2.25-2.4 (m, 2H); 3.4- 3.7 (m, 2H); 3.87 (s, 3H); 4.8 (m, 2H); 4.92 (q, 1H, *J* 6); 5.25-5.55 (m, 2H); 6.9-7.0 (m, 2H); 7.9-8.0 (m, 2H).

10 **IR** ($\nu_{\max}$, cm⁻¹, neat): 2963m, 2934m, 2874m, 1695m, 1602s, 1576m, 1512m.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 219 (11211), 273 (16231).

MS [*m/z* (EI)]: 292 (M⁺, 1), 150 (27), 135 (100), 83 (75), 55 (57).

15

**1-(4-Methoxy-phenyl)-2-[1-(3,5,5-trimethyl-hexyloxy)-
ethoxy]-ethanone (4)**

Obtained according to the general procedure without the
use of solvent.

20 **¹H-NMR** (200 MHz, CDCl₃): 0.8-0.95 (m, 3H); 0.86 (s, 9H); 1.0-1.35 (m, 3H); 1.41 (d, 3H, *J* 5); 1.45-1.7 (m, 2H); 3.4-3.7 (m, 2H); 3.89 (s, 3H); 4.65-4.7 (m, 2H); 4.9 (q, 1H, *J* 5); 5.05-5.1 (m, 1H); 6.9-7.0 (m, 2H); 7.9-8.0 (m, 2H).

25 **IR** ($\nu_{\max}$, cm⁻¹, neat): 2954s, 1695m, 1602s, 1576m, 1512m.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 219 (10941), 273 (15481).

MS [*m/z* (EI)]: 336 (M⁺), 135 (73), 71 (24), 70 (22), 69 (21), 57 (100), 41 (22).

30 **2-(1-Hexyloxy-ethoxy)-1-(4-methoxy-phenyl)-ethanone (5)**

Obtained according to the general procedure, but using
Montmorillonite[®] in refluxing toluene instead of TFA.

¹H-NMR (200 MHz, CDCl₃): 0.8-1.0 (m, 3H); 1.1-1.7 (m, 11H); 3.4-3.7 (m, 2H); 3.89 (s, 3H); 4.7-4.8 (m, 2H); 4.91 (q, 1H, *J* 6.2); 6.9-7.0 (m, 2H); 7.9-8.0 (m, 2H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2932s, 2859m, 1694m, 1601s, 1576m, 1512s.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 219 (10656), 276 (15203).

MS [*m/z* (EI)]: 294 (M⁺), 135 (93), 85 (21), 56 (35), 55 (24), 43 (100), 41 (36).

10 **1-(4-Methoxy-phenyl)-2-[1-(3-phenyl-propoxy)-ethoxy]-ethanone (6)**

Obtained according to the general procedure without the use of solvent.

15 **¹H-NMR** (400 MHz, CDCl₃): 1.4 (d, 3H, *J* 5.2); 1.85-1.9 (m, 2H); 2.65-2.7 (m, 2H); 3.45-3.65 (m, 2H); 3.86 (s, 3H); 4.76 (m, 2H); 4.9 (q, 1H, *J* 5.2); 6.9-7.0 (m, 2H); 7.1-7.3 (m, 5H); 7.9-8.0 (m, 2H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2936w, 1693m, 1600s, 1575m, 1511m.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 217 (18180), 273 (18826).

20 **MS** [*m/z* (EI)]: 328 (M⁺), 135 (51), 118 (45), 117 (29), 92 (20), 91 (100), 77 (22).

2-[1-(3,7-Dimethyl-oct-6-enyloxy)-ethoxy]-1-(4-methoxy-phenyl)-ethanone (7)

25 Obtained according to the general procedure.

¹H-NMR (400 MHz, CDCl₃): 0.8-0.95 (m, 3H); 1.1-1.2 (m, 1H); 1.25-1.45 (m, 5H); 1.5-1.7 (m, 8H); 1.9-2.05 (m, 2H); 3.45-3.7 (m, 2H); 3.87 (s, 3H); 4.7-4.82 (m, 2H); 4.9 (q, 1H, *J* 5.6); 5.05-5.1 (m, 1H); 6.9-7.0 (m, 2H); 7.9-8.0 (m, 30 2H).

IR ($\nu_{\max}$, cm⁻¹, neat): 3534w, 2914m, 1694m, 1601s, 1576m, 1511m.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 218 (13546), 273 (18063).

MS [m/z (EI)]: 348 (M⁺), 193 (42), 135 (100), 121 (31), 83 (29), 81 (24), 69 (60), 41 (22).

5 **1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-2-(1-hexyloxy-ethoxy)-ethanone (8)**

Obtained according to the general procedure without the use of solvent.

¹H-NMR (400 MHz, CDCl₃): 0.87 (t, 3H, *J* 7.2); 0.99 (d, 3H, *J* 6.9); 1.06 (s, 3H); 1.15-1.45 (m, 20H); 1.5-1.7 (m, 2H); 1.8-1.95 (m, 1H); 2.48 (s, 3H); 3.4-3.65 (m, 2H); 4.68 (m, 2H); 4.89 (q, 1H, *J* 5.2); 7.21 (s, 1H); 7.55 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2960m, 2929m, 2871m, 1681m, 1607w, 1544w.

15 **UV** [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 217 (20110), 257 (11478).

MS [m/z (EI)]: 402 (M⁺), 243 (100), 85 (22), 43 (24).

1-(3,5,5,6,8,8-Hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-2-(1-hex-3(Z)-enyloxy-ethoxy)-ethanone (9)

20 Obtained according to the general procedure without the use of solvent. No purification was required.

¹H-NMR (400 MHz, CDCl₃): 0.95 (t, 3H, *J* 6.8); 0.99 (d, 3H, *J* 6.8); 1.07 (s, 3H); 1.15-1.45 (m, 12H); 1.6-1.7 (m, 2H); 1.8-1.95 (m, 1H); 2.0-2.1 (m, 2H); 2.25-2.35 (m, 2H); 2.48 (s, 3H); 3.4-3.7 (m, 2H); 4.69 (m, 2H); 4.91 (q, 1H, *J* 5.2); 5.3-5.5 (m, 2H); 7.21 (s, 1H); 7.54 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2963s, 2931m, 1681m, 1608w, 1544w.

UV [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 216 (21722), 258 (12495), 295 (2228).

30 **MS** [m/z (EI)]: 400 (M⁺, 1), 243 (100), 83 (28), 55 (24).

2-(1-Ethoxy-ethoxy)-1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydro-naphthalen-2-yl)-ethanone (10)

Obtained according to the general procedure without the use of solvent.

- 5 **¹H-NMR** (400 MHz, CDCl₃): 0.94 (d, 3H, *J* 6.8); 1.0 (s, 3H); 1.15-1.45 (m, 15H); 1.55-1.7 (m, 2H); 1.8-1.95 (m, 1H); 2.47 (s, 3H); 3.5-3.75 (m, 2H); 4.68 (m, 2H); 4.89 (q, 1H, *J* 5.6); 7.21(s, 1H); 7.55 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2964s, 2929m, 1681m, 1607w, 1544w.

- 10 **UV** [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 217 (20799), 257 (11635).

MS [*m/z* (EI)]: 346 (M⁺), 243 (100).

2-(1-Hexyloxy-ethoxy)-1-naphthalen-2-yl-ethanone (11)

Obtained according to the general procedure.

- 15 **¹H-NMR** (400 MHz, CDCl₃): 0.86 (t, 3H); 1.2-1.4 (m, 6H); 1.43 (d, 3H, *J* 5.2); 1.5-1.6 (m, 2H); 3.45-3.7 (m, 2H); 4.9-5.02 (m, 3H); 7.52-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.47 (s, 1H).

IR ($\nu_{\max}$, cm⁻¹, neat): 2930m, 2858w, 1697m, 1628w.

- 20 **UV** [$\lambda(\epsilon)$, nm, CH₂Cl₂]: 250 (51217), 285 (9882).

MS [*m/z* (EI)]: 314 (M⁺), 155 (100), 127 (87), 56 (22), 43 (67), 41 (23).

2-[1-(3,7-Dimethyl-oct-6-enyloxy)-ethoxy]-1-naphthalen-2-yl-ethanone (12)

Obtained according to the general procedure.

- 25 **¹H-NMR** (400 MHz, CDCl₃): 0.8-0.95 (m, 3H); 1.1-1.2 (m, 1H); 1.25-1.5 (m, 2H); 1.43 (d, 3H, *J* 5.6); 1.5-1.7 (m, 8H); 1.57 (s, 3H); 1.66 (s, 3H); 1.85-2.05 (m, 2H); 3.45-3.75 (m, 2H); 4.9-5.0 (m, 3H); 5.02-5.1 (m, 1H); 7.52-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.47 (s, 1H).
- 30

IR ($\nu_{\max}$, cm^{-1} , neat): 2914m, 1698m, 1623w, 1597w.

UV [$\lambda(\epsilon)$, nm, CH_2Cl_2]: 250 (51252), 285 (9760).

MS [m/z (**EI**)]: 368 (M^+), 213 (26), 155 (83), 142 (26), 127 (26), 83 (54), 81 (31), 69 (100), 57 (28), 55 (24), 41 (35).

2-[1-(1-Ethyl-1,5-dimethyl-hexyloxy)-ethoxy]-1-naphtalen-2-yl-ethanone (13)

Obtained according to the general procedure.

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.8-0.9 (m, 9H); 1.1-1.65 (m, 15H); 4.9-5.02 (m, 2H); 5.27 (m, 1H); 7.55-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.49 (s, 1H).

IR ($\nu_{\max}$, cm^{-1} , neat): 3520w, 2951m, 1699s, 1628m, 1597w.

UV [$\lambda(\epsilon)$, nm, CH_2Cl_2]: 250 (54132), 284 (10278).

MS [m/z (**EI**)]: 370 (M^+ , 2), 213 (32), 156 (21), 155 (100), 141 (55), 127 (65), 85 (53), 71 (60), 69 (23), 57 (74), 55 (32), 43 (74), 41 (34).

2-[1-(4-*t*-Butyl-cyclohexyloxy)-ethoxy]-1-naphtalen-2-yl-ethanone (14)

Obtained according to the general procedure. The two diastereoisomers could be separated by chromatography.

trans-isomer :

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.82 (s, 9H); 0.9-1.05 (m, 3H); 1.15-1.35 (m, 2H); 1.42 (d, 3H, J 2.1); 1.7-1.8 (m, 2H); 1.95-2.1 (m, 2H); 3.75-3.6 (m, 1H); 4.95 (m, 2H); 5.1 (q, 1H); 7.5-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.5 (s, 1H).

cis-isomer :

$^1\text{H-NMR}$ (400 MHz, CDCl_3): 0.84 (s, 9H); 0.95-1.05 (m, 2H); 1.25-1.55 (m, 6H); 1.75-2.05 (m, 4H); 3.9-3.95 (m, 1H); 4.95 (m, 2H); 5.02 (q, 1H); 7.5-7.65 (m, 2H); 7.85-8.05 (m, 4H); 8.5 (s, 1H).

IR ($\nu_{\max}$, cm^{-1} , neat): 2939m, 2865m, 1698m, 1628w.

UV [$\lambda(\epsilon)$, nm, CH_2Cl_2]: 251 (43232), 287 (8289).

MS [m/z (**EI**)]: 368 (M^+), 170 (28), 155 (39), 139 (38), 127 (31), 83 (53), 57 (100), 41 (27).

5

**1-(4-Methoxy-phenyl)-2-(1-methoxy-2-phenyl-ethoxy)-
ethanone (15)**

Obtained according to the general procedure without the use of solvent.

10 **$^1\text{H-NMR}$** (400 MHz, CDCl_3): 3.0-3.05 (m, 2H); 3.35 (s, 3H); 3.88 (s, 3H); 4.76 (m, 2H); 4.8-4.85 (m, 1H); 6.9-6.95 (m, 2H); 7.15-7.25 (m, 5H); 7.9-7.95 (m, 2H).

IR ($\nu_{\max}$, cm^{-1} , neat): 2933 m, 2838m, 1692m, 1600s, 1575m, 1511s.

15 **UV** [$\lambda(\epsilon)$, nm, CH_2Cl_2]: 218 (17292), 277 (13404).

MS [m/z (**EI**)]: 300 (M^+), 209 (26), 149 (34), 135 (100), 134 (21), 121 (46), 91 (43), 77 (24).

Example 2

20

Photolysis of phenacyl acetals (I) in solutions

Photorelease assays were conducted on solutions (typical concentrations of precursors (I): 0.05% to 0.1% g/v) in organic solvents (preferably ethanol) or on cotton towels
25 after deposition of the phenacyl acetals (I), as described below in the example 3.

The solutions were irradiated with a mercury lamp (150 W) in a borosilicate glass apparatus (Pyrex[®]) so as to limit the irradiation window to mainly the UVA and UVB spectrum
30 of sun light. The alcoholic solution was irradiated for one hour and samples taken every 15 min to analyze the extent of the photolysis.

Analysis

The presence of the aryl ketone (II) and ester (III) after photolysis in solutions was determined by using GC retention times. Samples (0.2 μ l) were injected (on column injection) without further dilution. Gas chromatography-flame ionisation detection (GC-FID) was carried out with a Fisons-GC 8000series apparatus, using a J&W Scientific DB-5 capillary column (30m, 0.32mm id, 0.25 μ m film, He carrier gas, 85 kPa). The results are summarized in table 1.

Whereas precursors derived from Oranger Crystals[®] cleaved fairly slowly (Figure 1), those derived from acetanisol cleaved fast and Fixolide[®] precursors even faster. The estimated half lives under the said conditions were inferred from the curves given in Figure 1. * The rates are calculated from the GC analysis (corresponding peak area). Representative UV spectra are shown in Figure 2.

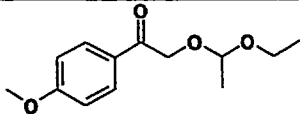
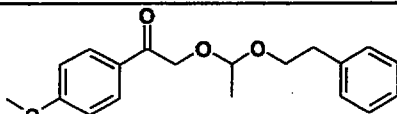
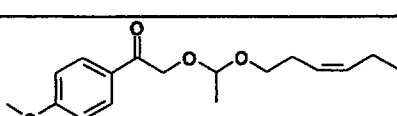
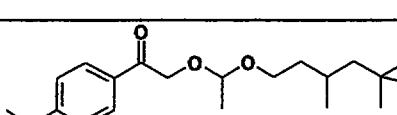
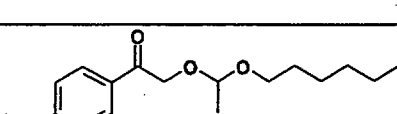
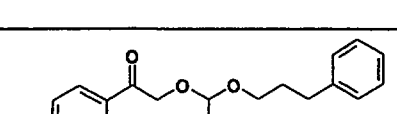
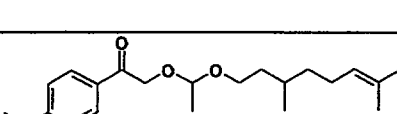
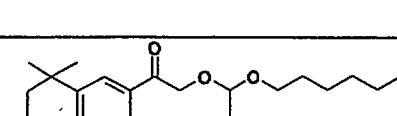
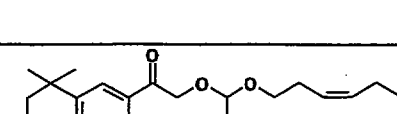
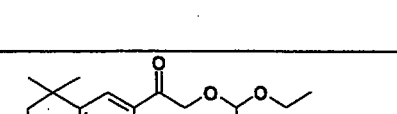
$t_{1/2}$ (Fixolide[®]) = 15 min

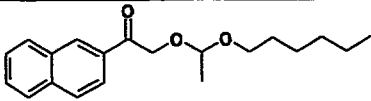
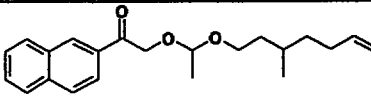
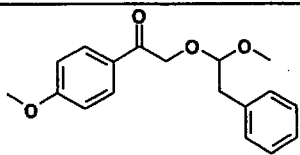
$t_{1/2}$ (Acetanisol) = 20-30 min

$t_{1/2}$ (Oranger Crystals[®]) = 50-60 min

Table 1 : Release of aryl ketones (II) and esters (III) from phenacyl acetals (I) in solution upon irradiation with a mercury lamp

	STRUCTURE (I)	Fragrance Target		UV-test*
		aryl ketone (II)	ester (III)	

1		acetanisol	(ethyl acetate)	++
2		acetanisol	phenethyl acetate	++
3		acetanisol	cis-3-hexenyl acetate	++
4		acetanisol	nonanyl acetate	++
5		acetanisol	hexyl acetate	++
6		acetanisol	phenylpropyl acetate	++
7		acetanisol	citronellyl acetate	++
8		Fixolide®	hexyl acetate	+++
9		Fixolide®	cis-3-hexenyl acetate	+++
10		Fixolide®	(ethyl acetate)	+++

11		Oranger Crystals®	hexyl acetate	+
12		Oranger Crystals®	citronellyl acetate	+
15		acetanisole	methyl phenyl- acetate	++

* 0 : no cleavage, + : slow cleavage, ++ : medium cleavage, +++ : fast cleavage

Example 3

5

Spray tests

1 g of an approximately 0.2% phenacyl acetal (I) solution in ethanol was evenly sprayed on a Terry towel (white cotton towel, 25cm x 25cm, 45 g), corresponding to 45-75

10 µg/g cotton. The sprayed towels were allowed to dry in a dark and odorless place. When dry, the towels were irradiated for a few seconds up to a few minutes with a tanning lamp (Osram Ultra-Vitalux®, 300 W; at a distance of 50 cm, the light has approximately six to seven times the

15 effect of the natural sunlight at noon on a sea-side mid-summer day). The evaluation was done by a trained panel of perfumers before and after irradiation. Before irradiation, the towels were judged to be odorless. The results after irradiation are summarized in table 2.

20

Table 2 : Release of aryl ketones (II) and esters (III) from phenacyl acetals (I) on fabrics upon irradiation with a tanning lamp

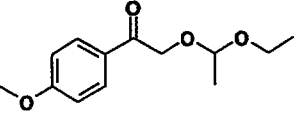
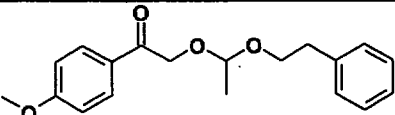
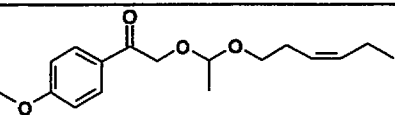
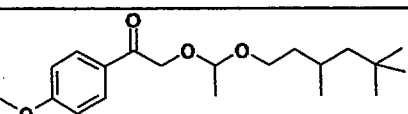
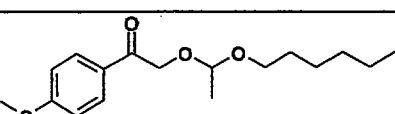
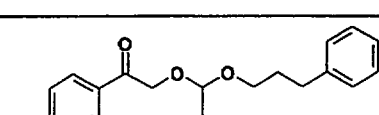
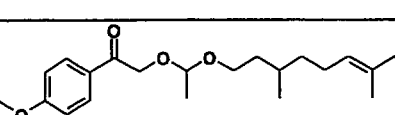
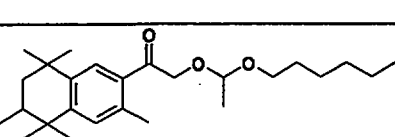
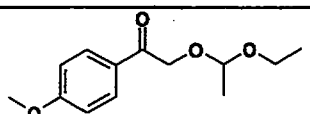
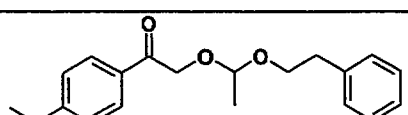
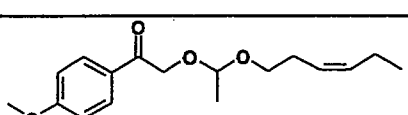
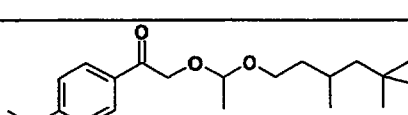
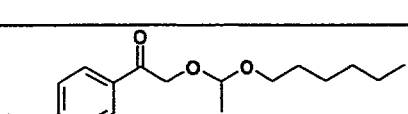
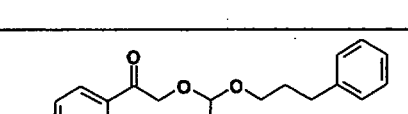
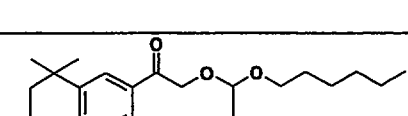
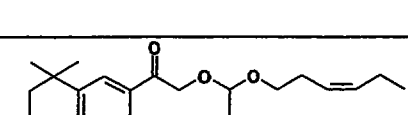
	STRUCTURE (I)	Fragrance Target (perception)*		Global appreci- ation*
		aryl ketone (II)	ester (III)	
1		acetanisoie (++)	ethyl acetate (0)	+
2		acetanisoie (++)	phenethyl acetate (+++)	+++
3		acetanisoie (++)	cis-3-hexenyl acetate (++)	++
4		acetanisoie (++)	nonanyl acetate (+)	+
5		acetanisoie (++)	hexyl acetate (++)	++
6		acetanisoie (++)	phenylpropyl acetate (++)	++
7		acetanisoie (++)	citronellyl acetate (+)	++
8		Fixolide® (++)	hexyl acetate (+++)	+++

Table 3 : Stability of phenacyl acetals (III) under different pH

	STRUCTURE (I)	pH 2.5	pH 7	pH 9.5	pH 11*
1		unstable	stable	stable	not tested
2		unstable	stable	stable	stable
3		unstable	stable	stable	stable
4		unstable	stable	stable	stable
5		unstable	stable	stable	stable
6		unstable	stable	stable	stable
8		stable	stable	stable	stable
9		stable	stable	stable	stable

* The results at pH 11 were determined under washing conditions as described in the example 5 below.

Example 5

Hand washing tests

Washing tests were performed according to the following
5 hand washing test procedure' with OMO Progress® base which
contains the following ingredients:

LAS	22.0 %
STP	13.3 %
CP5 (as 100%)	1.5 %
SCMC (as 100%)	0.34 %
Fluorescer (E1/1)	1.41
Savinase	1.15 %
Lipolase	0.15 %
Amlase	0.30 %
Perborate	8.0 %
TAED	2.4 %
Alkalinity (pH)	14.4

- 1- The washing powder (2.1 g) comprising the phenacyl
acetal (I, about 21 mg, 1%) was dissolved in water (500
10 ml) at room temperature.
- 2- The towels (35 g) were added to the liquor and mixed
with a glass stick.
- 3- Towels were soaked for 45 min with stirring every 15
min.
- 15 4- The wringed towels were rinsed three times with fresh
water (250 ml) with intermediate wringing.
- 5- Towels were allowed to dry in a dark and odorless place
before analysis or evaluation.

Analysis

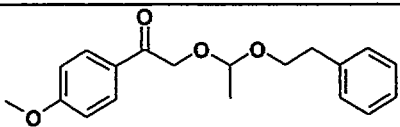
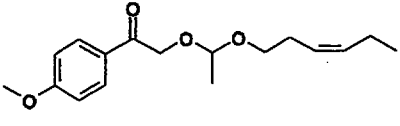
The towels were extracted with an organic solvent (preferably *t*-butyl methyl ether) using a Dionex ASE200 Accelerated Solvent Extractor and the extracts were
 5 analyzed by HPLC (Hewlett Packard Series 1100, column: Zorbax Eclipse XDB-C18, dimensions 15 cm x 4.6 mm x 5 μ m). The washing liquor was extracted with an organic solvent (preferably *t*-butyl methyl ether, 250 ml) and analyzed by HPLC as above.

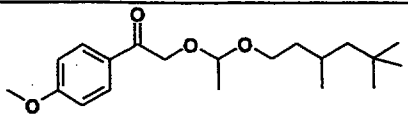
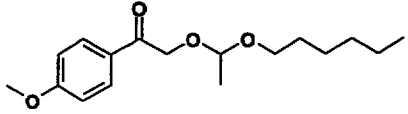
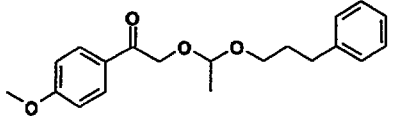
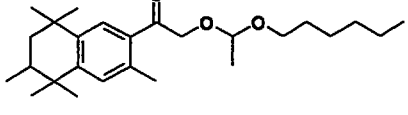
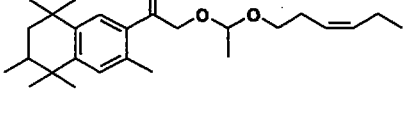
10

Stability in washing liquor :

The washing liquor (2.1 g washing powder containing 1% phenacyl acetal (I) in 500 ml water), according to 1 in the above described washing procedure, was stirred during
 15 one hour at room temperature. Extraction with an organic solvent (preferably *t*-butyl methyl ether) to recover organic compounds and analysis with HPLC gave the amounts of recovered phenacyl acetal (I), table 4.

20 Table 4: Stability of phenacyl acetals (I) under washing conditions

	STRUCTURE	Amount incorporated (mg)	Amount recovered (mg)	Recovered (mg)
2		22.3	18.5	83 (± 10)
3		21	22.3	100 (± 10)

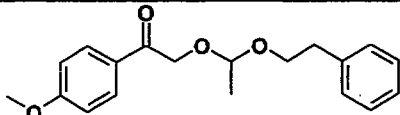
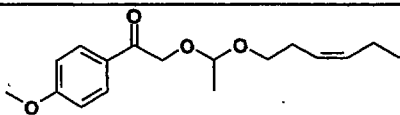
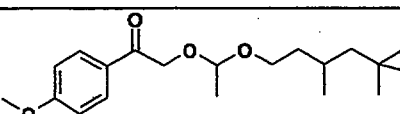
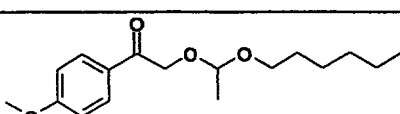
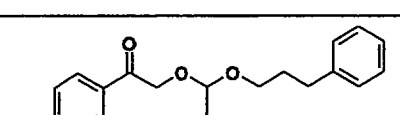
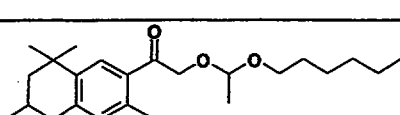
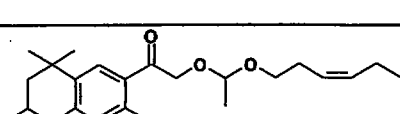
4		21.9	23.5	100 (±10)
5		24.4	25.7	100 (±10)
6		22.2	20.8	94 (±10)
8		22.5	22.2	99 (±10)
9		20.8	20.0	96 (±10)

Washing :

The dried towels, taken from the described hand washing
 5 procedure, were either irradiated with the previously
 mentioned tanning lamp and olfactively evaluated or
 analyzed by HPLC.

The aqueous liquors were extracted with an organic solvent
 (preferably *t*-butyl methyl ether) and analytical HPLC gave
 10 the results in table 5, which are related to partition
 between water and fabric.

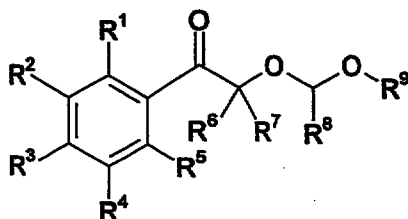
Table 5 : Partition between water and fabric
(substantivity) of phenacyl acetals (I)

	STRUCTURE (I)	Amount incorporated (mg)	Amounts recovered			
			Water		Towel extract	
			mg	% ($\pm 10\%$)	mg	% ($\pm 10\%$)
2		23.9	15	63 %	10.5	44 %
3		22.6	13.3	59 %	14	62 %
4		23.2	17.5	75 %	8.9	38 %
5		25.2	18.4	73 %	11.7	46 %
6		22.2	14.5	65 %	17	47 %
8		20.6	16.3	69 %	8.7	42 %
9		22.8	15.3	67 %	10.3	45 %



Claims

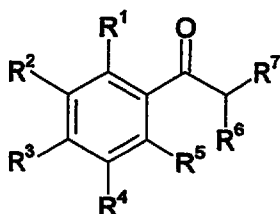
1. Fragrance precursors of formula I



5

(I)

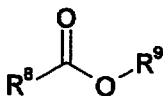
for a fragrant ketone of formula II



(II)

and a fragrant ester of formula III

10



(III)

R^1 to R^5 represent independently H, $-\text{NO}_2$, linear or branched $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_6\text{-alkenyl}$, $\text{C}_1\text{-C}_6\text{-alkinyl}$ or $\text{C}_1\text{-C}_4\text{-alkoxy}$,

15

R^1 and R^2 , R^2 and R^3 , R^3 and R^4 and R^4 and R^5 may form together one or two aliphatic or aromatic rings, these rings may optionally contain linear or branched



C₁-C₄-alkyl, C₁-C₄-alkenyl or C₁-C₄-alkinyl residues, and the above rings and residues may comprise one or more oxygen atoms,

- 5 R⁶ and R⁷ are independently H, linear or branched C₁-C₆-alkyl-, C₁-C₆-alkenyl, C₁-C₆-alkinyl, and R⁶ or R⁷ may form with either R¹ or R⁵ a carbocyclic ring optionally substituted by an aliphatic residue
- 10 R⁸ and R⁹ are the residues of an acid R⁸-COOH and an alcohol R⁹OH respectively forming the fragrant ester of formula III.
- 15 2. Fragrance precursors of formula I, wherein R⁸ is the residue of an aliphatic acid having 1 to 4 carbon atoms and R⁹ is the residue of an aliphatic alcohol having 2 to 20 carbon atoms.
- 20 3. Fragrance precursors of formula I, wherein R⁸ is -CH₃ and R⁹ is the residue of an aliphatic alcohol having 2 to 20 carbon atoms.
- 25 4. Fragrance precursors of formula I, wherein R⁸ is the residue of an aliphatic acid having 5 to 20 carbon atoms and R⁹ is the residue of an aliphatic alcohol having 1 to 5 carbon atoms.
- 30 5. Fragrance precursors of formula I, wherein R⁸ is the residue of an aliphatic acid having 5 to 20 carbon atoms and R⁹ is -CH₂CH₃.
6. Fragrance precursors of formula I, wherein R⁸ is the residue of an aliphatic acid having 1 to 4 carbon



atoms and R^9 is the residue of a terpene alcohol having 10 to 20 carbon atoms.

- 5 7. Fragrance precursors of formula I, wherein R^8 is the residue of an aliphatic acid having 1 to 4 carbon atoms and R^9 is the residue of a monoterpene alcohol.
- 10 8. Fragrance precursors of formula I, wherein R^8 is the residue of a cycloaliphatic acid having 5 to 20 carbon atoms and R^9 is the residue of aliphatic alcohol having 1 to 5 carbon atoms.
- 15 9. Fragrance precursors of formula I, wherein R^8 is the residue of a cycloaliphatic acid having 5 to 20 carbon atoms and R^9 is $-\text{CH}_2\text{CH}_3$.
- 20 10. Fragrance precursors of formula I, wherein R^8 is the residue of an aliphatic acid having 1 to 4 carbon atoms and R^9 is the residue of an araliphatic alcohol having more than 5 carbon atoms.
- 25 11. Fragrance precursors of formula I, wherein R^8 is $-\text{CH}_3$ and R^9 is the residue of an araliphatic alcohol having more than 5 carbon atoms.
12. Fragrance precursors of formula I, wherein at least one of the residues R^6 and R^7 is H.
- 30 13. Fragrance precursors of formula I, wherein the residues R^6 and R^7 are H.
14. Fragrance precursors of formula I, wherein R^6 and R^7 are H and R^1 to R^5 represent independently H, $-\text{NO}_2$,

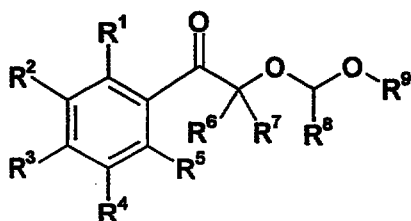


linear or branched C₁-C₆-alkyl, C₁-C₆-alkenyl, C₁-C₆-alkinyl or C₁-C₄ alkoxy.

15. Fragrance precursors of formula I wherein the
5 fragrant ketone of formula II ketone is selected from
1-phenyl-ethanone, 2,4-dimethylphenyl-ethanone, 1-[4-
(1,1-dimethylethyl)-2,6-dimethylphenyl]-ethanone, 1-
(4-tert-butyl-3,5-dinitro-2,6-dimethyl)-ethanone and
1-(4-methoxyphenyl)-ethanone.
- 10 16. Fragrance precursors of formula I, wherein R¹ and R²,
R² and R³, R³ and R⁴, R⁴ and R⁵, form together an
aliphatic or aromatic ring which may optionally
contain substituted or unsubstituted C₁-C₄-alkyl, C₁-
15 C₄-alkenyl, C₁-C₄-alkinyl residues and may comprise
one or more oxygen atoms.
17. Fragrance precursors of formula I wherein the
fragrant ketone of formula II is selected from 1-(2-
20 naphthalenyl)-ethanone, 4-acetyl-6-tert-butyl-1,1-
dimethyl-indan, 1-(5,6,7,8-tetrahydro-3,5,5,6,8,8-
hexamethyl-2-naphthalenyl)-ethanone, 1-(5,6,7,8-
tetrahydro-3',5',5',8',8'-pentamethyl-2-
naphthalenyl)-ethanone, 1-(5,6,7,8-tetrahydro-3'-
25 ethyl-5',5',8',8'-tetramethyl-2-naphthalenyl)-
ethanone, 1-(2,3-dihydro-1,1,2,3,3,6-hexamethyl-1H-
inden-5-yl)-ethanone, 1-[2,3-dihydro-1,1,2,6-
tetramethyl-3-(1-methylethyl-1H-inden-5-yl)-ethanone,
5-acetyl-1,1,2,3,3-pentamethyl-indane, 1-(5,6,7,8-
30 tetrahydro-2-naphthalenyl)-ethanone.



18. Compounds of formula I



(I)

5 wherein

R^1 to R^5 represent independently H, $-\text{NO}_2$, linear or branched $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_6\text{-alkenyl}$, $\text{C}_1\text{-C}_6\text{-alkinyl}$, or $\text{C}_1\text{-C}_4\text{-alkoxy}$,

10

R^1 and R^2 , R^2 and R^3 , R^3 and R^4 and R^4 and R^5 may form together one or two aliphatic or aromatic rings, these rings may optionally contain substituted or unsubstituted $\text{C}_1\text{-C}_4\text{-alkyl}$, $\text{C}_1\text{-C}_4\text{-alkenyl}$ or $\text{C}_1\text{-C}_4\text{-alkinyl}$ residues, and may comprise one or more oxygen atoms,

15

R^6 and R^7 are independently H, linear or branched $\text{C}_1\text{-C}_6\text{-alkyl}$, $\text{C}_1\text{-C}_6\text{-alkenyl}$, $\text{C}_1\text{-C}_6\text{-alkinyl}$, and R^6 or R^7 may form with either R^1 or R^5 a substituted or unsubstituted carbocyclic ring and R^8 and R^9 are the residues of an acid and an alcohol respectively, which together form a fragrant ester.

20

25 19. Use of the precursors of formula I according to one of the claims 1 to 18 in perfumery.