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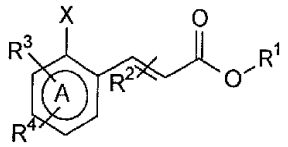
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(56) Related Art
ANNALS OF APPLIED BIOLOGY, VOL.55, 1965, PP 359-371
J. OF AGRIC. FOOD CHEM., VOL.42, 1994, PP 2589-2595
PHYTOCHEMISTRY, VOL.20, 1981, PP 2359-2366

Aryl-acrylic Acid Esters

Abstract

The acrylic acid esters of formula I



wherein A is a benzene or naphthalene ring, R^1 is a saturated or unsaturated, straight or branched, alicyclic or aromatic C_{10}-C_{30} hydrocarbon residue which can contain heteroatoms and can be substituted by an ionic substituent, R_2 in 2- or 3-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue, R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6alkyl or C_1-C_6alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1$-C_6alkyl$)_2$, -N(hydroxyalkyl)$_2$, $-NHCO_2CH_3$ or -NH (heterocycle) R^2, R^3 and R^4 may be the same or different, X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue, and the acrylic double bond is of the E configuration are useful for the delivery of organoleptic compounds, especially for flavours, fragrances and masking agents and antimicrobial compounds. They can also deliver fluorescent whitening agents.

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FOR A STANDARD PATENT

ORIGINAL

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Invention Title: Aryl-acrylic Acid Esters

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

Aryl-acrylic acid esters

The present invention relates to 3-(2-substituted aryl)-acrylic acid esters, especially 3-(2-hydroxyaryl)-acrylic acid esters and 3-(2-aminoaryl)-acrylic acid esters. These compounds are useful as precursors for organoleptic compounds, especially for flavours, fragrances and masking agents, antimicrobial compounds and for fluorescent whitening agents.

A principal strategy currently employed in imparting odours 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.

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.

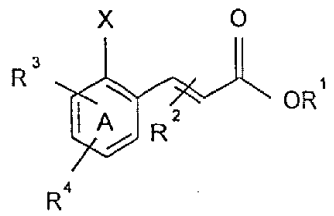
Fragrance precursors for scenting fabrics being washed in the presence of a lipase-containing detergent are described in WO 95/04809. The fragrance precursors

contained in the detergent and/or in the softener are cleaved by the lipase and a single active compound, either an odoriferous alcohol or aldehyde or ketone is yielded. Thereby a prolonged scenting effect on the fabric is obtained. The need for a lipase-containing detergent is limiting. In many parts of the world, detergents do not contain lipase. Other consumers prefer to use 'nonbio' detergents.

Fluorescent whitening agents or brighteners have been added to laundry detergents since the 1950s to help maintain the original brightness of white clothing.

One object of the present invention is to provide new precursors for compounds with different activities and thus impart different activities to a product by the addition of just one compound. A further object of the invention is to provide new compounds which are stable under transport and storage conditions. A further object of the present invention is to provide precursor molecules supplying different active compounds simultaneously or successively.

The present invention relates to 3-(2-substituted aryl)-acrylic acid esters of the formula I



wherein

A is a benzene or naphthalene ring,

R^1 is a saturated or unsaturated, straight, branched, alicyclic or aromatic C_{10}-C_{30} hydrocarbon residue which can contain heteroatoms and can be substituted by an ionic substituent,

R^2 in 2- or 3-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1-C_6$ alkyl$)_2$, $-N$(hydroxyalkyl$)_2$, $-NHCO_2CH_3$ or -NH(heterocycle),

R^2, R^3 and R^4 may be the same or different,

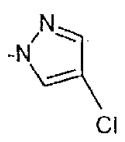
X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{22} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

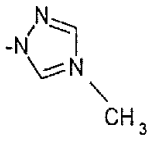
and the acrylic double bond is of the E configuration.

In the above formula I, all possible enantiomers and diastereomers and all mixtures are included within the scope of the invention.

Compounds wherein R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue containing one or more O and/or N atoms and/or C(O) groups and/or alkoxy groups or substituted by an ionic substituent of the formula $NR^5{}_3{}^+$, in which R^5 is the residue of a fatty acid or an alkyl group with 1 to 30 carbon atoms are preferred.

R^2 is preferably a heterocyclic residue of the formula



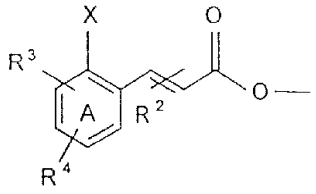


R^3 and/or R^4 are preferably hydrogen, $-N(C_1-C_6$ alkyl$)_2$, $-NH_2$, a five membered heterocyclic residue optionally containing N and/or O atoms, substituted by C_1-C_6 aliphatic and/or aromatic substituents.

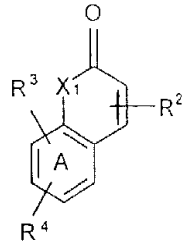
R^1 may be the residue of an olfactory alcohol of the formula R^1OH, the enol form of an olfactory aldehyde of the formula R^1HO or of an olfactory ketone of formula R^1O. R^1 may also be an optionally substituted alkyl, alkenyl or

arylalkyl residue carrying an 1-alkoxy, 1-aryloxy, or 1-arylalkoxy residue.

The compounds of formula I are mostly or nearly odourless at room temperature, atmospheric conditions and about 20 to 100 % relative humidity. However, under activating conditions, they are cleaved. Thereby the residue of formula Ia



yields a coumarin of the formula II



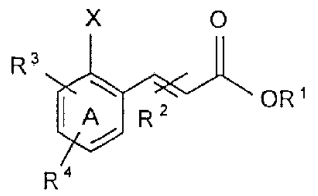
wherein X^1 stands for O or NR^6, R^2, R^3, R^4 have the meaning as defined above. The coumarins of formula II can have organoleptic and/or antimicrobial properties and/or optical brightening activity. Preferred are coumarins with olfactory properties. If R^1 is the residue of an olfactory alcohol or of the enol form of an olfactory aldehyde or

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ketone, upon cleavage two active compounds with the above properties can be obtained. Thus, the compounds of formula I permit the development of useful consumer products with enhanced organoleptic and/or antimicrobial properties and/or optical brightening properties. The organoleptic coumarins and alcohols or aldehydes or ketones obtained are useful as fragrances, flavours, masking agents and antimicrobial agents.

The activating conditions which lead to cleavage and thereby to the desired active compounds comprise the presence of UV light such as sunlight and elevated temperatures.

The invention relates also to the use of compounds of formula I



wherein

A is a benzene or naphthalene ring,

R^1 is hydrogen, unsaturated or saturated, straight or branched, alicyclic or aromatic C_1-C_{30} hydrocarbon residue which can contain heteroatoms and can be substituted by an ionic substituent,

R^2 in 2- or 3-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue,

R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6 alkyl or C_1-C_6 alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1-C_6$ alkyl$)_2$, $-N$(hydroxyalkyl$)_2$, $-NHCO_2CH_3$ or -NH(heterocycle),

R^2, R^3 and R^4 may be the same or different,

X stands for -OH or NHR^6, wherein R^6 is hydrogen a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue,

and the acrylic double bond is of the E configuration,

as precursors for organoleptic compounds, e.g. flavours, fragrances, odour masking agents and as precursors for antimicrobial agents and as precursors for fluorescent whitening agents.

Preferred substituents are mentioned above.

The esters of formula I can act as fragrance precursors in laundry products. They can also act as precursors for odour masking agents in the same products as the fragrance precursors. They also can act as precursors for antimicrobial agents. In addition, they can also act as

precursors for fluorescent whitening agents. The fragrance precursors and the precursors for odour masking agents as well as the flavour precursors of the invention may be used individually in an amount effective to enhance or to mask the characteristic odour or flavour of a material. More commonly, however, the compounds are mixed with other fragrance or flavour components in an amount sufficient to provide the desired odour or flavour characteristics.

The brightener precursors may be used also individually in an effective amount and mixed with one or more other brightener or colorant substance.

Due to the in situ generation of the active compounds the desired effect is prolonged and the substantivity on different substrates is enhanced. If two active compounds are provided by one ester of the formula I, they can be generated, depending on the precursor and/or the activating conditions, simultaneously or successively. Further, the precursors of the invention provide slow release of the active compounds.

Examples of alcohols R^1OH generated upon cleavage and constituting the residue R^1 in the compounds of formula I are:

amyl alcohol
hexyl alcohol*
2-hexyl alcohol*
heptyl alcohol*
octyl alcohol*

nonyl alcohol*
decyl alcohol*
undecyl alcohol*
lauryl alcohol*
myristic alcohol
3-methyl-but-2-en-1-ol*
3-methyl-1-pentanol
cis-3-hexenol*
cis-4-hexenol*
3,5,5-trimethyl-hexanol
3,4,5,6,6-pentamethylheptan-2-ol*
citronellol*
geraniol*
oct-1-en-3-ol
2,5,7-trimethyl-octan-3-ol
2-cis-3,7-dimethyl-2,6-octadien-1-ol
6-ethyl-3-methyl-5-octen-1-ol*
3,7-dimethyl-oct-3,6-dienol*
3,7-dimethyloctanol*
7-methoxy-3,7-dimethyl-octan-2-ol*
cis-6-nonenol*
5-ethyl-2-nonanol
6,8-dimethyl-2-nonanol*
2,2,8-trimethyl-7(8)-nonene-3-ol
nona-2,6-dien-1-ol
4-methyl-3-decen-5-ol*
dec-9-en-1-ol
benzylalcohol
2-methyl-undecanol
10-undecen-1-ol
1-phenyl-ethanol*

2-phenyl-ethanol*
2-methyl-3-phenyl-3-propenol
2-phenyl-propanol*
3-phenyl-propanol*
4-phenyl-2-butanol
2-methyl-5-phenyl-pentanol*
2-methyl-4-phenyl-pentanol*
3-methyl-5-phenyl-pentanol*
2-(2-methylphenyl)-ethanol*
4-(1-methylethyl)-benzene-methanol
4-(4-hydroxyphenyl)-butan-2-one*
2-phenoxy-ethanol*
4-(1-methylethyl)-2-hydroxy-1-methyl benzene
2-methoxy-4-methyl-phenol
4-methyl-phenol
anisic alcohol*
p-tolyl alcohol*
cinnamic alcohol*
vanillin*
ethyl vanillin*
eugenol*
isoeugenol*
thymol
anethol*
decahydro-2-naphthalenol
borneol*
cedrenol*
farnesol*
fenchyl alcohol*
menthol*
3,7,11-trimethyl-2,6,10-dodecatrien-1-ol

alpha ionol*
tetrahydro ionol*
2-(1,1-dimethylethyl)cyclohexanol*
3-(1,1-dimethylethyl)cyclohexanol*
4-(1,1-dimethylethyl)cyclohexanol*
4-isopropyl-cyclohexanol
6,6-dimethyl-bicyclo[3.3.1]hept-2-ene-2-ethanol
6,6-dimethyl-bicyclo[3.1.1]hept-2-ene-methanol*
p-menth-8-en-3-ol*
3,3,5-trimethyl-cyclohexanol
2,4,6-trimethyl-3-cyclohexenyl-methanol*
4-(1-methylethyl)-cyclohexyl-methanol*
4-(1,1-dimethylethyl)-cyclohexanol
2-(1,1-dimethylethyl)-cyclohexanol
2,2,6-trimethyl-alpha-propyl-cyclohexane propanol*
5-(2,2,3-trimethyl-3-cyclopentenyl)-3-methylpentan-2-ol*
3-methyl-5-(2,2,3-trimethylcyclopentyl-3-enyl)pent-4-en-2-ol*
2-ethyl-4(2,2,3-trimethylcyclopentyl-3-enyl)but-2-en-1-ol*
4-(5,5,6-trimethylbicyclo[2.2.1]hept-2-yl)-cyclohexanol*
2-(2-methylpropyl)-4-hydroxy-4-methyl-tetrahydropyran*
2-cyclohexyl-propanol*
2-(1,1-dimethylethyl)-4-methyl-cyclohexanol*
1-(2-tert-butyl-cyclohexyloxy)-2-butanol*
1-(4-isopropyl-cyclohexyl)-ethanol*
2,6-dimethyl-oct-7-en-2-ol**
2,6-dimethyl-heptan-2-ol**
3,7-dimethyl-octa-1,6-dien-3-ol**

whereby * indicates the preferred alcohols and ** indicate the more preferred alcohols.

Examples of aldehydes R^1HO generated upon cleavage and constituting the residue R^1 in the compounds of formula I are

2,6,10-trimethylundec-9-enal*
1,2,3,4,5,6,7,8,-octahydro-8,8-dimethyl-2-napthalenecarboxaldehyde
tridecanal
2-[4-(1-methylethyl)phenyl]-ethanal
2,4-dimethyl-cyclohex-3-ene-1-carbox-aldehyde*
4-carboxaldehyde-1,3,5-trimethyl-cyclohex-1-ene*
1-carboxaldehyde-2,4-dimethyl-cyclohex-3-ene*
1-carboxaldehyde-4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene*
3,5,5-trimethyl-hexanal
heptanal*
2,6-dimethyl-hept-5-enal*
decanal**
dec-9-enal
dec-4-enal
2-methyldecanal*
undec-10-enal**
undecanal*
dodecanal**
2-methyl-undecanal**
tridecanal
octanal**
nonanal*
3,5,5-trimethylhexanal
undec-9-enal**
2-phenyl-propanal*

4-methyl-phenyl-acetaldehyde*
3,7-dimethyl-octanal*
dihydrofarnesal**
7-hydroxy-3,7-dimethyl-octanal*
2,6-dimethyl-oct-5-enal
2-[4-(1-methylethyl)phenyl]-ethanal*
3-(3-isopropyl-phenyl)-butanal**
2-(3,7-dimethyoct-6-enoxy)-ethanal
1-carboxaldehyde-4-(4-methyl-3-pentenyl)-cyclohex-3-ene*
2,3,5,5,-tetramethyl-hexanal
longifolic aldehyde
2-methyl-4-(2,6,6-trimethylcyclohex-2-en-1-yl)-butanal*
2-methyl-3-(4-tert-butylphenyl)-propanal**
4-(1,1-dimethyl-ethyl)-benzene-propanal*
2-[4-(1-methyl-ethyl)-phenyl]-propanal
alpha-methyl-1,3-benzodioxole-5-propanal*
3,7-dimethyl-oct-6-enal*
2-methyl-3-(4-isopropylphenyl)-propionaldehyde*
4-(4-hydroxy-4-methyl-pentyl)-cyclohex-3-en-1-carboxaldehyde**
alpha-methyl-1,3-benzodioxole-5-propanal*
1-carboxaldehyde-4-(1,1-dimethylethyl)-cyclohexane
4-(octahydro-4,7-methano-5H-inden-5-ylidene)-butanal
[(3,7-dimethyl-6-octenyl)-oxy]-acetaldehyde**

whereby * indicates the preferred aldehydes and ** indicate the more preferred aldehydes.

Examples of ketones R^1O:

2-heptyl-cyclopentanone
2,2,6,10-tetrametyltricyclo-[5.4.0.0(6,10)]-undecan-4-one
benzylacetone*
carvone*
1,2,3,5,6,7-hexahydro-1,1,2,3,3,-pentamentyl-4H-inden-4-one*
methyl heptenone*
dimethyl octenone*
2-(butan-2-yl)-cyclohexanone*
2-hexyl-cyclopent-2-en-1-one*
2-(1-methylethyl)-5-methyl-cyclohexanone*
2-(2-methylethyl)-5-methyl-cyclohexanone*
3-methyl-cyclopentadecanone
4-tert-pentyl-cyclohexanone*
3-oxo-2-pentyl-cyclopentane-acetic acid methyl ester**
1-(1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-naphthalenyl)-ethanone*
3-methyl-5-propyl-cyclohex-2-en-1-one*

whereby * indicates the preferred ketones and ** indicate the more preferred ketone.

Examples of fluorescent whitening coumarins of formula II generated upon cleavage and constituting the respective residue in the compounds of formula I are:

7-(3-methyl-1H-pyrazol-1-yl)-3-phenyl-2H-1-benzopyran-2-one
7-(4-methyl-5-phenyl-2H-1,2,3-triazol-2-yl)-3-phenyl-2H-1-

benzopyran-2-one
7-(2H-naphtho[1,2-d]triazol-2-yl)-3-phenyl-2H-1-benzopyran-2-one
3-(1H-pyrazol-1-yl)-7-(2H-1,2,3-triazol-2-yl)-2H-1-benzopyran-2-one
7-(dimethylamino)-1-methyl-3-phenyl-2(1H)-quinolinone
7-(diethylamino)-1-ethyl-3-phenyl-2(1H)-quinolinone
7-amino-4-methyl-2H-1-benzopyran-2-one
7-(dimethylamino)-4-methyl-2H-1-benzopyran-2-one
7-(diethylamino)-4-methyl-2H-1-benzopyran-2-one
7-hydroxy-4-methyl-2H-1-benzopyran-2-one
6,7-dihydroxy-2H-1-benzopyran-2-one

Examples for coumarins of formula II with olfactory properties generated upon cleavage and constituting the respective residue in the compounds of formula I are:

2H-1-benzopyran
3-methyl-benzopyran-2-one
8-(1,1-dimethylethyl)-6-methyl-benzopyrone
4-methyl-7-ethoxy-coumarin
6-methyl-2H-1-benzopyran

It is a matter of course, that it is not possible to give a complete list of the active coumarins, alcohols, aldehydes and ketones which are generated as a result of the desired cleavage of the acrylic acid esters of formula I by UV-light and/or by elevated temperatures. The skilled person is, however, quite aware of those alcohols, aldehydes, ketones and coumarins which provide the desired

organoleptic, e.g. fragrance, flavour and odour masking, antimicrobial and/or brightening effects.

The compounds of formula I may preferably be used as sustained release odorants and flavours but also as sustained agents to mask or attenuate undesirable odours or to provide additional odours not initially present in consumer products, i.e. laundry detergents, fabric softeners, fabric softener sheets, toiletries and cosmetics such as sunscreens. Further applications are sustained brighteners and antimicrobial agents in the same products. The brighteners are especially useful for wool, rayon and polyamides. These compounds are also useful for flavouring and aromatizing tobacco products, e.g. cigarettes.

The amount required to produce the desired, overall effect varies depending upon the particular compounds of formula I chosen, the product in which it will be used, and the particular effect desired.

For example, depending upon the selection and concentration of the compound chosen, when a compound of the formula I is added either singly or as a mixture, e.g. to a laundry product composition at levels ranging from about 0.001 to about 10 % by weight, a coumarin and if desired an odoriferous alcohol or aldehyde or ketone in an organoleptically effective amount is released when the product is used. These newly formed odorant(s) serve to enhance the odour of the fragrance. Depending on the

compound of formula I an antimicrobial agent or a brightener can be released.

Depending upon the selection and concentration, addition of the compounds I, either singly or as a mixture, to cigarette tobacco at levels ranging from about 5 ppm to about 50'000 ppm tends to enhance the smoking flavour and/or mask undesirable smoking odours. An important property of these compounds I is that the flavourant or odorant is covalently bound as a non-volatile compound and the flavourant or odorant is released only when the tobacco product is ignited and burns.

Addition of the compounds of formula I either separately or as a mixture at levels suitably ranging from about 5 ppm to about 50'000 ppm by weight onto the media enclosing the tobacco serves to incorporate the odorant/flavourant in the side-stream smoke of the tobacco. Air borne flavourants and/or odorants are thus introduced. This newly formed odorant or flavourant serves to enhance or mask the smoking odours depending upon selection and use levels of the compounds I.

As is evident from the above compilation of alcohols, aldehydes, ketones and coumarins, a broad range of known odorants or flavours or mixtures can be generated from precursors of the invention. While manufacturing compositions the precursors of the invention may be used according to methods known to the perfumer, such as e.g. from W.A. Poucher, Perfumes, Cosmetics, Soaps, 2, 7th Edition, Chapman and Hall, London 1974. The fluorescent whitening agents may be added in the same manner.

The compounds of formula I can be prepared by using standard methods known to the skilled chemist. Convenient methods are outlined in the Examples without limiting the invention thereto.

Example 1

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid ethyl ester

To a solution of 75.0 g (carbethoxyethylidene)triphenyl phosphorane in 350 ml of toluene, 23.2 g of salicylaldehyde was dropped in at 20°C while cooling in an ice-bath. After stirring at room temperature for 90 min., the reaction mixture was diluted with toluene and washed to neutrality with water. The organic phase was dried, filtered and evaporated to dryness. The resulting yellow oil was purified by chromatography to yield 35.5 g of a colourless solid.

NMR ($CDCl_3$) δ 7.82 (s, 1H), 7.30-6.85 (m, 4H), 6.6 (s, OH), 4.35-4.17 (q, 2H), 2.04 (s, 3H), 1.40-1.28 (t, 3H)

Example 2

(E)-3-(2-Hydroxy-phenyl)-acrylic acid methyl ester

According to the procedure of Example 1, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid methyl ester was prepared from methyl(triphenyl-phosphoranylidene)acetate and salicylaldehyde.

Example 3

(E)-3-(2-Hydroxy-phenyl)-acrylic acid ethyl ester

According to the procedure of Example 1, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid methyl ester was prepared from ethyl(triphenyl-phosphoranylidene)acetate and salicylaldehyde.

Example 4

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid

To a solution of 35.5 g of (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid ethyl ester in 600 ml of ethanol, a solution of 10.66 g of potassium hydroxide in 500 ml of water was dropped in. After refluxing for 5 hours, another 5.0 g of potassium hydroxide was put in and the mixture was refluxed for another 19 hours. Then the reaction mixture was cooled down, diluted with ether and washed to pH 4 with HCl 2N and water. The organic phase was dried, filtered and evaporated to dryness. The resulting colourless crystals were not further purified.

NMR ($CDCl_3$) δ 7.90 (s, 1H), 7.31-6.83 (m, 4H), 2.07 (s, 3H)

Example 5

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid 3,7 dimethyl-oct-6-enyl ester

A solution of 6.0 g of (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid, 5.3 g of citronellol and 1 g of p-toluene-sulfonic acid in 150 ml of cyclohexane was refluxed for 6.5 hours using a water separator. Then the reaction mixture was cooled down, diluted with hexane and washed to neutrality with saturated sodium bicarbonate and water. The organic phase was dried, filtered and evaporated to dryness. The resulting yellow oil was purified by chromatography to yield 6.45 g of a colourless oil.

NMR ($CDCl_3$) δ 7.80 (s, 1H), 7.38-6.83 (m, 4H), 6.4 (s, OH), 5.09 (t, 1H) 4.25 (t, 2H), 2.10-1.90 (m, 5H), 1.88-1.08 (m, 11H), 0.93 (d, 3H)

Example 6

(E)-3-(2-Hydroxy-phenyl)-2-methyl-acrylic acid phenethyl ester

According to the same procedure of Example 3, (E)-3-(2-hydroxy-phenyl)-2-methyl-acrylic acid phenethyl ester was prepared from 3-(2-hydroxy-phenyl)-2-methyl-acrylic acid, phenyl ethyl alcohol and p-toluenesulfonic acid.

Example 7

3-(4-Diethylamino-2-hydroxy-phenyl)-but-2-enoic acid ethyl ester

To a suspension of 5.27 g ethoxycarbonylmethylene-triphenylphosphorane in 10 ml of toluene, a solution of 2.02 g 1-(4-diethylamino-2-hydroxy-phenyl)-ethanone (DE 28 44 606) was dropped in at room temperature. Then the reaction mixture was heated to reflux. After refluxing for 31 hours the mixture was cooled down and evaporated to dryness. The resulting dark oil was purified by chromatography to yield a colourless oil.

NMR ($CDCl_3$) δ 7.22-7.09 (m, 1H), 6.57-6.42 (m, 1H), 6.32-6.20 (m, 2H), 5.01 (s, 1H), 4.18-4.01 (q, 2H), 3.42-3.24 (q, 4H), 2.49 (s, 3H), 1.31-1.08 (m, 9H).

The compounds of Examples 1-4 yield upon cleavage organoleptic coumarins, Examples 5 and 6 organoleptic coumarins and organoleptic alcohols and Example 7 a brightener coumarin.

Example 8

(E)-3-(2-Hydroxy-5-methyl-phenyl)-acrylic acid ethyl ester

A solution of 193.7 g 3-[5-methyl-2-(tetrahydro-pyran-2-yloxy)-phenyl]-acrylic acid ethyl ester (Bunce, R., Moore, J., Org. Prep. Proc., 29(3), 293 (1997)) and 2 g p-toluenesulfonic acid in 2.5 l of ethanol was stirred at

room temperature for 24 hours. Then the reaction mixture was concentrated and the residue was diluted with ether, washed with saturated sodium bicarbonate and brine, dried and evaporated to dryness. The resulting yellow solid was recrystallized to yield 97.7 g of colourless crystals.

NMR ($CDCl_3$) δ 8.10-7.93 (d, 1H), 7.27 (s, 1H), 7.10-6.98 (d, 1H), 6.82-6.70 (d, 1H), 6.69-6.55 (d, 1H), 4.38-4.20 (q, 2H), 2.27 (s, 3H), 1.42-1.28 (t, 3H) ppm.

(E)-3-(2-Hydroxy-phenyl)-acrylic acid

To a solution of 100.0 g 3-(2-hydroxy-phenyl)-acrylic acid ethyl ester in 500 ml of ethanol, a solution of 50.9 g potassium hydroxide in 500 ml of water was dropped in at room temperature. After stirring at reflux for 28 hours, the reaction mixture was concentrated. The residue was diluted with 500 ml HCl 2N and extracted with ether. The organic phase was washed with 2N HCl and water, dried and evaporated to dryness. The resulting solid was recrystallized to yield 44.3 g of colourless crystals.

NMR (DMSO) δ 12.2 (br s, 1H), 10.2 (br s, 1H), 7.95-7.75 (d, 1H), 7.65-7.50 (d, 1H), 7.32-7.15 (m, 1H), 6.99-6.76 (m, 2H), 6.62-6.45 (d, 1H) ppm.

(E)-3-(2-Hydroxy-phenyl)-acrylic acid dec-9-enyl ester

A mixture of 5.0 g 3-(2-hydroxy-phenyl)-acrylic acid ethyl ester, 6.1 g dec-9-en-1-ol and 1.0 g tetraisopropyl-ortho-titanate was heated to 150°C removing the ethanol formed. After stirring for 2.5 hours at this temperature, the reaction mixture was cooled, diluted with ether and washed with brine. The organic phase was dried and evaporated to dryness. The resulting oil was Kugelrohr-distilled, crystallized and recrystallized to yield 1.69 g of colourless crystals.

NMR ($CDCl_3$) δ 8.11-7.96 (d, 1H), 7.55-7.40 (d, 1H), 7.32-7.15 (m, 1H), 6.99-6.72 (m, 2H), 6.71-6.57 (d, 1H), 5.93-5.69 (m, 1H), 5.07-4.88 (m, 2H), 4.31-4.15 (t, 2H), 2.12-1.93 (m, 2H), 1.85-1.55 (m, 2H), 1.54-1.15 (m, 10H) ppm.

(E)-3-(2-Hydroxy-phenyl)-acrylic acid 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-but-2-enyl ester

According to the same procedure, 3-(2-hydroxy-phenyl)-acrylic acid 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-but-2-enyl ester was prepared from 3-(2-hydroxy-phenyl)-acrylic acid ethyl ester, 2-ethyl-4(2,2,3-trimethyl cyclopentyl-3-en-1-yl)-but-2-en-1-ol and tetraisopropyl-o-titanate.

(E)-3-(2-Hydroxy-5-methyl-phenyl)-acrylic acid 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-but-2-enyl ester

According to the same procedure, 3-(2-hydroxy-5-methyl-phenyl)-acrylic acid 2-ethyl-4-(2,2,3-trimethyl-cyclopent-3-enyl)-but-2-enyl ester was prepared from 3-(2-hydroxy-5-methyl-phenyl)-acrylic acid ethyl ester, 2-ethyl-4(2,2,3-trimethyl cyclopentyl-3-en-1-yl)-but-2-en-1-ol and tetraisopropyl-o-titanate.

(E)-3-(2-Hydroxy-5-methyl-phenyl)-acrylic acid 3-methyl-5-phenyl-pentyl ester

According to the same procedure, 3-(2-hydroxy-5-methyl-phenyl)-acrylic acid 3-methyl-5-phenyl-pentyl ester was prepared from 3-(2-hydroxy-5-methyl-phenyl)-acrylic acid ethyl ester, 3-methyl-5-phenyl-pentanol and tetraisopropyl-o-titanate.

(E)-3-(4-Diethylamino-2-hydroxy-phenyl)-but-2-enoic acid dec-9-enyl ester

According to the same procedure, 3-(4-diethylamino-2-hydroxy-phenyl)-but-2-enoic acid dec-9-enyl ester was prepared from 3-(4-diethylamino-2-hydroxy-phenyl)-but-2-enoic acid ethyl ester, dec-9-en-1-ol and tetraisopropyl-o-titanate.

(E)-3-(4-Diethylamino-2-hydroxy-phenyl)-but-2-enoic acid 3-methyl-5-phenyl-pentyl ester

According to the same procedure, 3-(4-diethylamino-2-hydroxy-phenyl)-but-2-enoic acid 3-methyl-5-phenyl-pentyl ester was prepared from 3-(4-diethylamino-2-hydroxy-

phenyl)-but-2-enoic acid ethyl ester, 3-methyl-5-phenyl-pentanol and tetraisopropyl-o-titanate.

Example 9

3-[2-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid tert-butyl-dimethyl-silyl ester

To a solution of 5.0 g of (E)-3-(2-hydroxy-phenyl)-acrylic acid and 4.6 g of imidazole in 100 ml of DMF was added at room temperature a solution of 10.1 g of TBDMS-Cl. The reaction mixture was stirred overnight, poured onto 200 ml of cold water and extracted 3x with 150 ml of MTBE. The combined organic phases were dried ($MgSO_4$) and evaporated to dryness. The resulting oil was dried at 0.08 Torr/120-170°C to remove excess of TBDMS-Cl to yield 11.4 g of 3-[2-(tert-butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid tert-butyl-dimethyl-silyl ester as a yellowish oil.

NMR ($CDCl_3$) δ 7.96 (d, 1H), 7.52 (dd, 1H), 7.23 (m, 1H), 6.94 (m, 1H), 6.82 (dd, 1H), 6.37 (d, 1H), 1.00 (s, 9H), 0.97 (s, 9H), 0.32 (s, 6H), 0.22 (s, 6H)

Example 10

3-[2-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-acryloyl chloride

To a 0°C cold solution of 6.3 g of 3-[2-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid tert-butyl-

dimethyl-silyl ester and 8 drops of DMF in 15 ml of CH_2Cl_2 was added dropwise 2.0 ml of oxalyl chloride. After complete addition the reaction mixture was allowed to warm to room temperature and stirring was continued for 60 h. The reaction mixture was filtered, evaporated to dryness and taken up in MTBE. The solution was cooled in the refrigerator overnight, filtered and evaporated to yield 4.4 g of 3-[2-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-acryloyl chloride.

NMR ($CDCl_3$) δ 8.28 (d, 1H), 7.55 (dd, 1H), 7.35 (m, 1H), 7.01 (m, 1H), 6.87 (dd, 1H), 6.63 (d, 1H), 1.04 (s, 9H), 0.26 (s, 6H)

Example 11

3-(2-Hydroxy-phenyl)-acrylic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester

To a suspension of 0.72 g of NaH (55% in oil), previously washed with hexane, in 22.5 ml of THF was added 1.67 ml of *tert*-butanol over a period of 12 min. The reaction mixture was stirred at room temperature for 1.25 h, was then cooled to -15°C and 2.85 g of 3-(3-isopropyl-phenyl)-butanal (Florhydral) was slowly added. Stirring was continued for 45 min. and then this cold enolate solution was added via Teflon canula to a -5°C cold solution of 4.44 g of 3-[2-(*tert*-butyl-dimethyl-silanyloxy)-phenyl]-acryloyl chloride in 7.5 ml of THF. After complete addition stirring at -5°C was continued for 1 h, the reaction mixture was quenched with 80 ml of water / 40 ml

of brine and was extracted with MTBE. The combined organic phases were washed with water/brine 2:1, dried ($MgSO_4$) and evaporated to dryness to yield 6.65 g of crude 3-[2-(tert-Butyl-dimethyl-silanyloxy)-phenyl]-acrylic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester as a yellowish, viscous oil.

To a 0°C cold solution of 6.2 g of this oil in 70 ml of THF was added slowly 13.7 ml of a 1M TBAF/THF solution. The reaction mixture was stirred at 0°C for 1.5 h, poured onto 200 ml of H_2O and extracted 3x with 150 ml of MTBE. The combined organic phases were washed with brine, dried ($MgSO_4$) and evaporated to dryness. The resulting oil was purified by chromatography to yield 2.64 g of 3-(2-Hydroxy-phenyl)-acrylic acid 3-(3-isopropyl-phenyl)-but-1-enyl ester in form of a yellowish oil.

NMR ($CDCl_3$) δ 8.12 and 8.01 (d, 1H), 7.50-6.80 (m, 10H), 6.66 and 6.56 (d, 1H), 5.75 and 5.13 (m, 1H), 4.13 (m, CH), 3.53 (m, CH), 2.89 (m, CH), 1.42 (d, 3H), 1.25 (d, 6H)

Example 12

(E)-3-[2-(tert-Butyl-dimethyl-silanoxy)-phenyl]-acrylic acid

To a solution of 8.2 g of (E)-3-(2-hydroxy-phenyl)-acrylic acid and 15.2 g of TBDMS-Cl in 10 ml of DMF was added 11.9 g of imidazole and the mixture was stirred at room temperature for 24 h. After aqueous work-up, the *bis*-

silylated product was saponified with 2.1 g of LiOH in THF-H_2O for 0.5 h at 0°C. The mixture was concentrated *in vacuo* and TBDMS-OH removed by extraction with hexane. The aqueous layer was acidified to pH 4 with $KHSO_4$ and extracted with EtOAc. The organic phases were washed with brine, dried (Na_2SO_4) and evaporated to dryness. The semi-solid residue was suspended in hexane, filtered and the filtrate evaporated to dryness to yield 7.5 g of a pale yellow oil, which solidified upon standing.

NMR ($CDCl_3$) δ 8.08 (d, 1H), 7.46 (dd, 1H), 7.18 (dt, 1H), 6.87 (t, 1H), 6.75 (dd, 1H), 6.31 (d, 1H), 0.93 (s, 9H), 0.13 (s, 6H)

Example 13

(E)-3-(2-Hydroxy-phenyl)-acrylic acid 1-ethoxy-3-(3-isopropyl-phenyl)-butyl ester

A solution of 6.5 g of (E)-3-[2-(tert-Butyl-dimethyl-silanoxy)-phenyl]-acrylic acid and 5.5 g of 1-(3-ethoxy-1-methyl-allyl)-3-isopropyl-benzene, accessible from 3-(3-isopropyl-phenyl)-butyraldehyde *via* a two step procedure according to P.D. Bartlett and A.A. Frimer, Heterocycles 11, 419-435, (1978), in 25 ml of toluene was heated to reflux and stirred for 16 h. After concentration, the reaction mixture was purified by flash chromatography to yield 7.5 g of the intermediate (E)-3-[2-(tert-Butyl-dimethyl-silanoxy)-phenyl]-acrylic acid 1-ethoxy-3-(3-isopropyl-phenyl)-butyl ester as a pale yellow oil. This was dissolved in 50 ml THF and treated at 0°C with 4.7 g

of TBAF•$3H_2O$. After 20 min., the mixture was concentrated and purification by flash chromatography yielded 2.2 g of the title ester (a mixture of diastereoisomers) as a pale yellow oil.

NMR ($CDCl_3$) δ 8.12 and 8.08 (d, 1H), 7.47 (dt, 1H), 7.35 (br s, 1H), 7.31-7.18 (m, 2H), 7.12-6.98 (m, 3H), 6.92 (dt, 1H), 6.83 (dd, 1H), 6.68 and 6.61 (d, 1H), 5.96 and 5.77 (dd, 1H), 3.82-3.65 (m, 1H), 3.63-3.40 (m, 1H), 3.05-2.77 (m, 2H), 2.22-1.95 (m, 2H) and 1.38-1.12 (m, 12H)

Example 14

(E)-3-(2-Hydroxy-phenyl)-acrylic acid 3-(4-tert-butyl-phenyl)-1-ethoxy-propyl ester

A solution of 3.1 g of (E)-3-[2-(tert-Butyl-dimethyl-silanoxy)-phenyl]-acrylic acid, 3.0 g of 1-tert-butyl-4-(3-ethoxy-2-methyl-allyl)-benzene, accessible from 3-(4-tert-butyl-phenyl)-2-methyl-propionaldehyde via a two step procedure according to P.D. Bartlett and A.A. Frimer, Heterocycles 11, 419-435, (1978), and 20 mg of *p*-TSA in 25 ml of toluene was stirred at 0 °C for 4 h and at room temperature for 14 h. The reaction mixture was partitioned between saturated sodium carbonate and hexane and the organic layer was washed with brine, dried over (Na_2SO_4) and evaporated to dryness to yield 5.3 g of the crude intermediate (E)-3-[2-(tert-Butyl-dimethyl-silanoxy)-phenyl]-acrylic acid 3-(4-tert-butyl-phenyl)-1-ethoxy-

propyl ester as a pale yellow oil. This was dissolved in 20 ml of THF and treated at 0 °C with 3.2 g of solid TBAF•$3H_2O$. After 30 min., the mixture was concentrated and purification by repeated flash chromatography yielded 1.2 g of the title ester (a mixture of diastereoisomers) as a pale yellow oil.

NMR ($CDCl_3$) δ 8.17 and 8.13 (d, 1H), 7.50 (ddd, 1H), 7.36-7.18 (m, 4H), 7.11 (br dd, 2H), 6.98-6.83 (m, 2H), 6.73 and 6.69 (d, 1H), 5.94 (t, 1H), 3.92-3.70 (m, 1H), 3.71-3.54 (m, 1H), 3.05-2.81 (m, 1H), 2.52-2.34 (m, 1H), 2.30-2.12 (m, 1H) and 1.31 (s, 9H), 1.33-1.20 (m, 3H), 0.97 and 0.90 (t, 3H)

Example 15

Test cloth was washed with detergent to which one or more of the precursors of Examples 1-14 had been added. The cloth was then line dried. The cloth dried in sunlight had a distinct fragrance note, as determined by a trained panel. In contrast, the cloth dried without sunlight was olfactively neutral.

Example 16

Test cloth was washed with a detergent and then a fabric softener, containing one ore more of the precursors of Examples 1-14, was added to the rinse cycle. The cloth was then line dried. The cloth dried in sunlight had a distinct fragrance note, as determined by a trained panel.

In contrast, the cloth dried without sunlight was olfactively neutral.

Example 17

A 1% solution of one or more of the products of Examples 1-14 in ethanol was applied to cigarette papers to produce levels of 5-50'000 ppm of each flavourant. The paper was incorporated in cigarettes and, upon burning, released a fragrant odour.

Example 18

A broad spectrum (UV-A and UV-B) oil/water sunscreen lotion was prepared with 0,5%.

Part A

Recipe:%	Compound	Chemical Name
2 %	PARSOL MCX	Octyl methoxycinnamate
3 %	PARSOL 1789	4-4-Butyl-4'methoxy-dibenzoyl methane
12 %	Cétiol LC	Coco-caprylate/caprate
4 %	Dermol 185	Isostearyl neopentanoate
0,25 %	Diethyl-eneglycol monostearate	PEG-2-stearate
1 %	Cetylalcohol	Cetylalcohol
0,25 %	MPOB/PPOB	Methyl-propylparabene
0,1 %	EDTA BD	EDTA-sodium salt

1 %	Amphisol DEA (Giv.)	Diethanolamine cetyl-phosphate

Part B

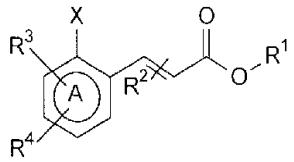
20 %	Permulene TR-1 (+%)	Acrylate C10-C30 Alkyl-acrylate
50,1 %	water deion	water deion
5 %	Propyleneglycol	1,2-Propanediol
0,8 %	KOH (10%)	Potassium hydroxide

Part A was heated in a reactor to 85°C.

Part B was slowly added within 10 min., followed by addition of KOH and 0.5% of the product of Example 5. The emulsion was then cooled and degassed.

The claims defining the invention are as follows:

1. Use of compounds of formula I

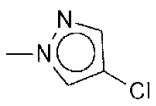


wherein A is a benzene or naphthalene ring, R^1 is a saturated or unsaturated, straight or branched, alicyclic or aromatic C_{10}-C_{30} hydrocarbon residue which can contain heteroatoms and can be substituted by an ionic substituent, R_2 in 2- or 3-position is hydrogen, a straight or branched C_1-C_6 residue; an optionally substituted aromatic or optionally substituted heterocyclic residue, R^3 and R^4 stand for hydrogen, a straight or branched C_1-C_6alkyl or C_1-C_6alkoxy residue, a substituted or condensed heterocyclic residue, -OH, $-NO_2$, $-NH_2$, $-N(C_1-C_6alkyl)_2$, -N(hydroxyalkyl)$_2$, $-NHCO_2CH_3$ or -NH (heterocycle) R^2, R^3 and R^4 may be the same or different, X stands for -OH or NHR^6, wherein R^6 is hydrogen, a saturated or unsaturated, straight or branched C_1-C_{20} hydrocarbon or an optionally substituted aromatic or heterocyclic residue, and the acrylic double bond is of the E configuration, as precursors for organoleptic, antimicrobial compounds and/or fluorescent whitening agents.

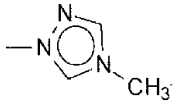
2. Use according to claim 1 wherein R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue containing one or more O and/or N atoms and/or C(O) groups and/or alkoxy groups.

3. Use according to claim 1 wherein R^1 is a saturated or unsaturated, straight or branched C_{10}-C_{30} hydrocarbon residue substituted by an ionic substituent of the formula $NR^5_3^+$, in which R^5 is the residue of a fatty acid or an alky group with 1 to 30 carbon atoms.

4. Use according to claim 1 wherein R^2 is a heterocyclic residue of the formula



or



5. Use according to claim 1 wherein R^3 and/or R^4 are five membered heterocyclic residues containing N and/or O atoms.

6. Use according to claim 1 wherein R^3 and/or R^4 is hydrogen, $-N(C_1-C_6$ alkyl)$_2$, $-NH_2$, a five membered heterocyclic residue, substituted by C_1-C_6 aliphatic and/or aromatic substituents.

7. Use according to claim 1 wherein R^2 is hydrogen or methyl.

8. Use according to claim 1 wherein R^1 is the residue of an olfactory alcohol, of the formula R^1OH.

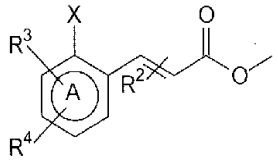
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9. Use according to claim 1 wherein R^1 is the residue of the enol form of an olfactory aldehyde of formula R^1HO.

10. Use according to claim 1 wherein R^1 is the residue of the enol form of an olfactory ketone of formula R^1O.

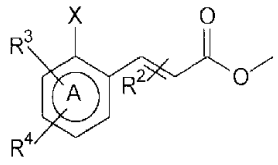
11. Use according to claim 1 wherein R^1 is an optionally substituted alkyl, alkenyl, arylalkyl residue carrying a 1-alkoxy, 1-aryloxy or 1-arylalkoxy residue.

12. Use according to claim 1 wherein the residue of formula Ia



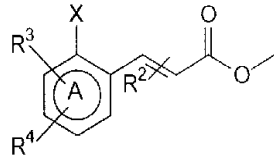
is the precursor for fragrant coumarins.

13. Use according to claim 1 wherein the residue of formula Ia



is the precursor for fluorescent whitening coumarins.

14. Use according to claim 1 wherein R^1 is the residue of an olfactory alcohol, aldehyde or ketone and the residue of formula Ia



is the precursor for a fragrant coumarin.

15. Use of a compound of Formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 as a precursor for organoleptic, antimicrobial compounds and/or fluorescent whitening agents.

16. Use according to any one of claims 1 to 14 in laundry products.

17. Use according to any one of claims 1 to 14 in tobacco products.

18. Use according to any one of claims 1 to 14 in cosmetics and toiletries.

19. Use of a precursor compound of formula I in a laundry product substantially as hereinbefore described with reference to Example 15 or Example 16.

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20. Use of a precursor compound of formula I in a tobacco product substantially as hereinbefore described with reference to Example 17.

21. Use of a precursor compound of formula I in a cosmetic/toiletry product substantially as hereinbefore described with reference to Example 18.

22. An organoleptic agent containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

23. An antimicrobial agent containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

24. A fluorescent agent containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

25. A whitening agent containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

26. A laundry product containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

27. A tobacco product containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

28. A cosmetic product containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

29. A toiletry containing at least one precursor compound of formula I as defined in any one of claims 1 to 14 and a suitable excipient, adjuvant or carrier.

30. An organoleptic agent containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

31. An antimicrobial agent containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

32. A fluorescent agent containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

33. A whitening agent containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

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34. A laundry product containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

35. A tobacco product containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

36. A cosmetic product containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

37. A toiletry product containing at least one precursor compound of formula I substantially as hereinbefore described with reference to any one of Examples 1 to 14 and a suitable excipient, adjuvant or carrier.

Dated 30 August, 2000
Givaudan Roure (International) S.A.

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