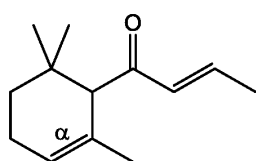


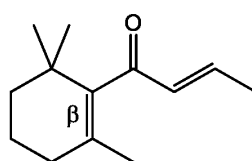
ORGANIC COMPOUNDS

The present invention relates to a particular class of compounds capable of releasing
 fragrant compounds in a controlled manner into the surroundings. The present invention
 5 is also concerned with a process for their production, and consumer products
 comprising them. In particularly the present invention relates to precursors that release
 damascone.

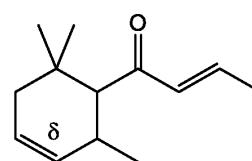
Damascone



DAMASCONA ALPHA



DAMASCONA BETA



DAMASCONA DELTA

10

respectively, 1-(2',6',6'-trimethylcyclohex-2'-en-1'-yl)but-2-en-1-one, 1-(2',6',6'-
 trimethylcyclohex-1'-en-1'-yl)but-2-en-1-one and 1-(2',6',6'-trimethylcyclohex-3'-en-1'-
 yl)but-2-en-1-one is a family of desirable fragrance ingredients that occur in essential
 oils. They are frequently used in perfumery.

15

There is interest in providing a damascone precursor, that is, a compound that is itself,
 basically because of the high molecular weight, essentially odorless, but which, in
 particular circumstances, will decompose to release damascone at a desired time.

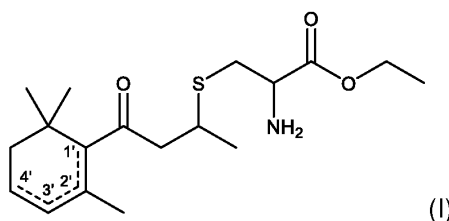
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It has now been found that the compound of formula (I) as herein below described can
 act as precursor for the release, by spontaneous air oxidation, of damascone.

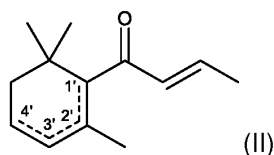
25

Similar compounds are known from International Publication WO 01/35768, in which
 certain carbonyl compounds, including damascone, may be reacted with cysteine to
 provide flavouring products. However, these compounds are not precursors, but integral
 flavouring materials.

Thus, there is provided in one aspect the use of a compound of formula (I)



as precursor for generating, by spontaneous air oxidation, a damascone of formula (II)



wherein one of the dotted lines represents together with the carbon-carbon bond a
 5 double bond and each of the other two dotted lines represent together with the carbon-carbon bond a single bond.

In one preferred embodiment the compound of formula (I) is a compound wherein the
 dotted line between C3' and C4' represents together with the carbon-carbon bond a
 10 double bond (i.e. the compound of formula (I) is ethyl S-(4-oxo-4-(2',6',6'-
 trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate).

The activating conditions, which lead to the cleavage step, comprise the presence of
 molecular oxygen. The concentration of oxygen in the air is sufficient for cleaving the
 15 compound of formula (I) in such a way, that the cleavage products can be detected in
 the ambient air, e.g. by olfaction or GC-MS analysis of headspace samples.

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

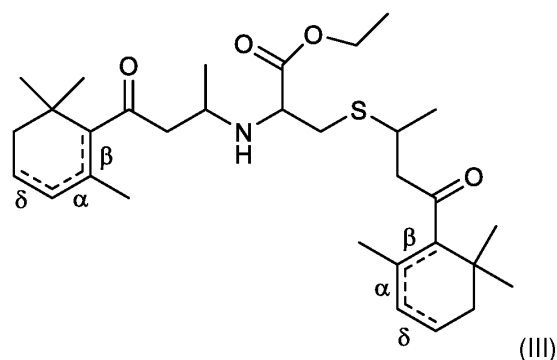
In one specific embodiment the compounds of formula (I) are useful in consumer
 products, such as detergent products, including powder and liquid detergents or

detergents in form of tablets, pouches/single unit doses, soap and laundry bars, fabric conditioner, including tumble dryer sheets, and scent boosters (liquid or solid).

- In another specific embodiment the compounds of formula (I) are useful in cosmetic products, which include (a) cosmetic skincare products, especially bath products, skin washing and cleansing products, skincare products, eye makeup, lip care products, nail care products, intimate care products, foot care products;
- (b) cosmetic products with specific effects, especially sunscreens, tanning products, depigmenting products, deodorants, antiperspirants, hair removers, and shaving products;
- (c) cosmetic dental-care products, especially dental and oral care products, tooth care products, cleaners for dental prostheses, adhesives for dental prostheses; and
- (d) cosmetic hair care products, especially hair shampoos, hair care products, hair setting products, hair-shaping products, and hair coloring products.
- Thus, there is provided in a further aspect of the present invention, a consumer product comprising a compound of formula (I) and a product base.

- As used herein, 'consumer product base' means a composition for use as a consumer product to fulfill specific actions, such as cleaning, softening, and caring or the like.
- Examples of such products include fine perfumery, e.g. perfume and eau de toilette; fabric care, household products and personal care products such as cosmetics, laundry care detergents, rinse conditioner, personal cleansing composition, detergent for dishwasher, surface cleaner; laundry products, e.g. softener, bleach, detergent; body-care products, e.g. shampoo, shower gel; air care products (includes products that contain preferably volatile and usually pleasant-smelling compounds which advantageously can even in very small amounts mask unpleasant odors). Air fresheners for living areas contain, in particular, natural and synthetic essential oils such as pine needle oils, citrus oil, eucalyptus oil, lavender oil, and the like.
- In one embodiment the compounds of formula (I) are especially useful as part of fragrances to be used in laundry products, in which they can release damascone upon usage. However, under certain conditions the odor profile is perceived as fruity berry with a slightly plastic off-note. Surprisingly it was found that when combined with a second class of compounds, a combination is obtained which results in an odor profile which is essentially free of the undesirable plastic note.

Thus there is provided in a further aspect of the present invention, a combination of the compound of formula (I) with a compound of formula (III)



- 5 wherein the dotted lines represents a double bond located at one of the alpha-, beta- or delta-positions on each of the cyclohexene rings. These compounds, which are *bis*-adducts, are described in International Publication WO 2008/154765.

It was found that, when a combination of a compound of formula (I) with a compound of
10 formula (III) was used in laundry products, that the deposition rate is enhanced.

It was also found, when a combination of a compound of formula (I) with a compound of
formula (III) was used, that a continuous release of compounds of formula (II) is
noticeable from an early stage to several days (e.g. when used in a detergent product,
15 already on wet fabric).

In one preferred embodiment the compound of formula (III) is a compound wherein the
dotted lines represents a double bond located in delta position on each of the
cyclohexane rings (i.e. the compound of formula (III) is ethyl *N,S*-bis(4-oxo-4-(2',6',6'-
20 trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate))

In another preferred embodiment there is provided a mixture of a compound of formula
(I) and a compound of formula (III) in a ratio of 1: 40 to 40: 1, including a ratio of 1:20 to
1:10, e.g. 1:15 to 1:11.

25

In one particular embodiment there is provided a mixture of ethyl *S*-(4-oxo-4-(2',6',6'-
trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate and ethyl *N,S*-bis(4-oxo-4-(2',6',6'-

trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate), preferably at a ratio of 1:40 to 40:1, including a ratio of 1:20 to 1:10, e.g. 1:15 to 1:11.

The compounds of formula (I), or a mixture of a compound of formula (I) and a compound of formula (III), can be used alone, or in combination with other fragrance ingredients and/or precursors thereof. Such fragrance ingredients are described, for example, in "Perfume and Flavor Chemicals", S. Arctander, Ed., Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 2003 and include fragrance compounds of natural or synthetic origin and essential oils.

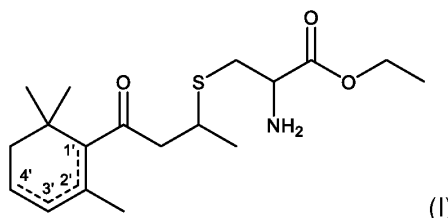
The following list comprises examples of known fragrance ingredients, which may be combined with the compounds of formula (I):

- essential oils and extracts, e.g. castoreum, costus root oil, oak moss absolute, geranium oil, tree moss absolute, basil oil, fruit oils, such as bergamot oil and mandarine oil, myrtle oil, palmarose oil, patchouli oil, petitgrain oil, jasmine oil, rose oil, sandalwood oil, wormwood oil, lavender oil and/ or ylang-ylang oil;
- alcohols, e.g. cinnamic alcohol ((*E*)-3-phenylprop-2-en-1-ol); cis-3-hexenol ((*Z*)-hex-3-en-1-ol); citronellol (3,7-dimethyloct-6-en-1-ol); dihydro myrcenol (2,6-dimethyloct-7-en-2-ol); EbanolTM ((*E*)-3-methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pent-4-en-2-ol); eugenol (4-allyl-2-methoxyphenol); ethyl linalool ((*E*)-3,7-dimethylnona-1,6-dien-3-ol); farnesol ((2*E*,6*Z*)-3,7,11-trimethyldodeca-2,6,10-trien-1-ol); geraniol ((*E*)-3,7-dimethylocta-2,6-dien-1-ol); Super MuguetTM ((*E*)-6-ethyl-3-methyloct-6-en-1-ol); linalool (3,7-dimethylocta-1,6-dien-3-ol); menthol (2-isopropyl-5-methylcyclohexanol); Nerol (3,7-dimethyl-2,6-octadien-1-ol); phenyl ethyl alcohol (2-phenylethanol); RhodinolTM (3,7-dimethyloct-6-en-1-ol); SandaloreTM (3-methyl-5-(2,2,3-trimethylcyclopent-3-en-1-yl)pentan-2-ol); terpineol (2-(4-methylcyclohex-3-en-1-yl)propan-2-ol); or TimberolTM (1-(2,2,6-trimethylcyclohexyl)hexan-3-ol); 2,4,7-trimethylocta-2,6-dien-1-ol, and/or [1-methyl-2(5-methylhex-4-en-2-yl)cyclopropyl]-methanol;
- aldehydes and ketones, e.g. anisaldehyde (4-methoxybenzaldehyde); alpha amyl cinnamic aldehyde (2-benzylideneheptanal); delta Damascone ((2*E*)-1-(2,6,6-trimethylcyclohex-2-en-1-yl)but-2-en-1-one); GeorgywoodTM (1-(1,2,8,8-

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

In one particular embodiment the compound of formula (I), or the mixture of a
 compound of formula (I) and a compound of formula (III), may be used in combination
 30 with other fragrance precursors, including 1-butoxy-3-((1*E*,4*Z*)-hepta-1,4-dien-1-
 yl)benzene, (4-(dodecylthio)-4-methylpentan-2-one, 2-ethoxy-4-((1*E*,4*Z*)-hepta-1,4-
 dien-1-yl)phenol, and ethyl 2-acetyl-4-methyltridec-2-enoate.

- The amounts in which the compounds of formula (I), or the mixture of a compound of formula (I) and the compound of formula (III), may be incorporated in the various consumer products vary within a wide range. The amounts depend on the nature of the product to which the compounds of formula (I), or the mixture of a compound of formula (I) and the compound of formula (III), are added and the desired olfactory effect. The amounts used also depend on the co-ingredients in a given composition when the compounds of formula (I), or the mixture of a compound of formula (I) and the compound of formula (III), are used in admixture with perfuming co-ingredients, solvents or adjuvants. Typical concentrations are from 0.0001 to 5 weight percent of the article. In one embodiment, compounds of the present invention may be employed in a fabric softener in an amount of from 0.0001 to 2 weight percent. In another embodiment, compounds of the present invention may be employed in a detergent in an amount of from 0.0001 to 4 weight percent. In another embodiment, compounds of the present invention may be used in fine perfumery in amounts from 0.001 to 10 weight percent (e.g. up to about 5 weight percent), more preferably between 0.02 and 4 weight percent. However, these values are given only by way of example, since the experienced perfumer may also achieve effects or may create novel accords with lower or higher concentrations.
- The compounds of formula (I) are novel in its own right. Thus there is provided in a further aspect of the invention a compound of formula (I)



- wherein one of the dotted lines represents together with the carbon-carbon bond a double bond and each of the other two dotted lines represent together with the carbon-carbon bond a single bond.

- The compounds of formula (I) may be prepared by a 1,4 addition of cysteine-ethyl ester to damascone in a suitable solvent such as tetrahydrofuran, dimethyl formamide, ethanol or water and in the presence of an organic or inorganic base, such as N-ethyldiisopropylamine, triethylamine, potassium or sodium carbonate or hydroxide.

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

5 The mixture of a compound of formula (I) and a compound of formula (III) may be either prepared by admixing the two compounds in the desired ratio after each of them was prepared independently of each other. Alternatively, the mixture can be prepared in situ, e.g., by following the process as described in the Examples.

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

Example 1: Ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl) cysteinate

15 In a 250 mL two-neck round-bottom flask were placed (*E*)-1-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)but-2-en-1-one (10 g, 52.0 mmol) and L-cysteine ethyl ester hydrochloride (15 g, 81 mmol) in water (100 ml). Under stirring at room temperature, potassium carbonate (8 g, 57.9 mmol) was added in one portion and the resulting mixture was stirred overnight at room temperature. MTBE (50 ml) was added to the mixture which
20 was then stirred for an additional hour. The mixture was transferred to a separatory funnel, the phases were separated and the aq. phase was extracted with MTBE (2x 50 ml). The org. phases were combined and washed with water (3x 50 ml), water/brine (20 ml/30 ml) and brine (50 ml), dried over MgSO₄, filtered and the solvent was evaporated to give ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)-L-cysteinate
25 (16.91 g, 49.5 mmol, 95% yield) as a mixture of four isomers and as a light yellow oil.

Odor description (dry-down of a 10% DPG solution after 24 hours on a smelling strip): fruity berry, reminiscent of stewed apple, slightly plastic, chemical.

30 ¹H NMR (CDCl₃, 400 MHz): δ = 5.57-5.51 (m, 1H), 5.44 (br d, *J* = 10 Hz, 1H), 4.20 (br q, *J* = 7.1 Hz, 2H), 3.71-3.63 (m, 1H), 3.38-3.30 (m, 1H), 3.00-2.88 (m, 1.5H), 2.83-2.77 (m, 1H), 2.73-2.71 (m, 1H), 2.56-2.48 (m, 1.5H), 2.22 (d, *J* = 10.5 Hz, 0.5 H), 2.21 (d, *J* = 10.6 Hz, 0.5 H), 1.97 (br d, *J* = 17.6 Hz, 1H), 1.8 (br s, 2H), 1.70 (br d, *J* = 17.6 Hz, 1H), 1.32-1.30 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.01-0.87 (m, 9H) ppm.

35

¹³C-NMR (CDCl₃, 100 MHz): δ = 211.91, 211.80, 173.76, 131.59, 131.57, 131.51, 131.48, 124.04, 123.92, 123.9, 62.67, 62.64, 62.59, 61.00, 60.97, 55.03, 54.91, 54.89, 54.82, 54.32, 54.30, 54.06, 41.53, 41.50, 36.07, 36.03, 35.93, 35.86, 34.71, 34.67, 34.41, 32.97, 32.94, 32.92, 32.87, 31.57, 31.52, 31.43, 31.38, 29.65, 29.61, 29.58, 21.76, 21.74, 21.56, 21.50, 20.55, 20.53, 19.73, 19.68 ppm.

MS (EI, 70 eV): 341 ([M]⁺, 2), 123 (67), 117 (69), 102 (65), 81 (51), 76 (49), 75 (80), 69 (100), 43 (60), 41 (58), 29 (56).

10 Example 2: Ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)
cysteinate (GR-87-1182-2) and Ethyl N,S-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-
1'-yl)butan-2-yl)cysteinate)

In a 1500 mL sulfonation flask were placed (*E*)-1-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)but-2-en-1-one (200 g, 1.04 mol) and L-cysteine ethyl ester hydrochloride (98.1 g, 0.53 mol) in water (520 ml). Under stirring at room temperature, potassium carbonate (72.16 g, 0.52 mol) was added in one portion. The reaction mixture was then stirred overnight at room temperature. The solution was transferred into a separatory funnel, MTBE (100 ml) was added, the phases were separated and the aq. phase was extracted with MTBE (100 ml). The org. phases were combined and washed with brine (250 ml), dried over MgSO₄, filtered and the solvent was evaporated to give a clear yellow oil containing a mixture of isomers of S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)-L-cysteinate and isomers of ethyl N,S-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)-L-cysteinate in a ratio of 1:14 (255.39 g, 0.48 mol, 92% yield)

25 Odor description of the obtained mixture (dry-down of a 10% DPG solution after 24 hours on a smelling strip): fruity, damascone like, stewed apple, clean, pleasant

30 The activating conditions to release compounds of formula II comprise a combination of change of pH, elevated temperature and exposure to air. The combination of trigger conditions has the advantage of continuous release of odoriferous compounds of formula II from an early stage (e.g. on wet fabric in detergent application) to several days.

Example 3: Ethyl *N*-(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)but-2-en-2-yl)-*S*-(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)butan-2-yl)cysteinate)

Step 1: In a 250 ml sulfonation flask surmounted by a dean-stark, 3-hydroxy-1-(2,6,6-trimethylcyclohex-3-en-1-yl)but-2-en-1-one diketone (5.1 g, 24.5 mmol) and L-cysteine ethyl ester hydrochloride (4.46 g, 24 mmol) were suspended in toluene (50 ml). Acetic acid (10 ml, 175 mmol) was added and the mixture was heated to reflux ($T_{\text{bath}}=130\text{ }^{\circ}\text{C}$) overnight. The mixture was transferred into a separatory funnel and a mixture of water/brine (20 ml/30 ml) was added. The phases were separated and the aq. phase was washed with MTBE (30 ml). The org. phases were combined, washed with sat. aq. Na_2CO_3 (50 ml), brine/water (20 ml/10 ml) and brine (30 ml), dried over MgSO_4 , filtered and the solvent was evaporated to give ethyl-(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)but-2-en-2-yl)cysteinate (8.3 g, 24.5, quant. yield) as a yellow oil.

MS (EI, 70 eV): 339 ($[\text{M}]^{+}$, 4), 216 (94), 174 (100), 142 (65), 116 (42), 107 (27), 84 (41), 67 (36), 58 (39), 41 (33), 29 (67).

Step 2: Ethyl-(4-oxo-4-(2,6,6-trimethylcyclohex-3-en-1-yl)but-2-en-2-yl)cysteinate (3 g, 8.8 mmol) was placed in a 100 ml two-neck round-bottom flask together with (*E*)-1-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)but-2-en-1-one (1.7 g, 8.8 mmol). Water (50 ml), THF (10 ml) and potassium carbonate (1.2 g, 8.7 mmol) were added and the mixture was stirred at room temperature for three days. The orange mixture was transferred into a separatory funnel, the phases were separated and the aq. phase was washed with MTBE (2x 30 ml). The org. phases were combined and washed with water/brine (2x 20ml/10ml) and brine (20 ml), dried over MgSO_4 , filtered and the solvent was evaporated to give a yellow oil which was further purified by chromatography (eluent: heptane/MTBE, 8/2) to give ethyl-*N*-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)but-2-en-2-yl)-*S*-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate (1.54 g, 29 mmol, 32.8 % yield) as a mixture of isomers and a light yellow oil.

Odor description (dry-down of a 10% DPG solution after 24 hours on a smelling strip): licorice, sweet, damascone.

^{13}C -NMR (CDCl_3 , 100 MHz): δ = 211.98, 211.95, 211.93, 211.90, 211.89, 211.84, 200.41, 200.37, 200.35, 170.32, 170.30, 170.28, 170.18, 170.15, 159.97, 159.86,

- 159.78, 159.72, 159.64, 132.55, 132.51, 131.71, 131.61, 124.17, 124.02, 123.89, 123.85, 100.21, 100.14, 62.81, 62.78, 62.73, 62.72, 62.56, 61.65, 61.63, 56.92, 56.82, 56.76, 56.69, 56.66, 55.28, 55.20, 55.13, 55.09, 55.07, 55.05, 55.01, 42.12, 41.67, 41.65, 41.62, 35.33, 35.26, 35.20, 35.12, 34.35, 34.27, 34.16, 33.97, 33.87, 33.82, 33.74, 33.06, 33.04, 32.69, 31.80, 31.67, 31.65, 31.56, 31.53, 31.05, 31.02, 30.04, 30.01, 29.74, 29.69, 28.94, 22.62, 21.98, 21.95, 21.82, 21.77, 21.75, 21.72, 21.59, 21.53, 21.19, 20.66, 20.63, 20.08, 20.04, 19.85, 19.80, 19.34, 19.31, 19.29, 19.27, 14.05, 14.04 ppm.
- 10 MS (EI, 70 eV): 408 ($[C_{22}H_{34}NO_4S]^+$, 2), 123 (100), 110 (36), 107 (32), 84 (44), 83 (34), 81 (95), 69 (54), 67 (43), 55 (27), 41 (26).

Example 4: Odor assessment

	Wet	Dry-down after 24 hours	Dry-down after 3 days
Compound A	Nice, fruity, damascone with a slight plastic note	fruity berry, reminiscent of stewed apple, slightly plastic, chemical	Damascone, fresh
Compound B	fruity, damascone, sweet	Fruity, clean, damascone	Fruity, sweet, damascone
Compound A + compound B (ratio 1: 14)	Damascone, stewed apple, strawberry	fruity, damascone like, stewed apple, clean, pleasant	damascone

Compound A: Ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl) cysteinate

Compound B: Ethyl N,S-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate)

As can be seen from the odor description above, when combining the compound of formula (I) with a compound of formula (III) the plastic note disappeared.

Example 5: Fragrance comprising a compound of formula (I)

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

STEMONE ((Z)-5-methylheptan-3-one oxime)	1
TETRAHYDRO LINALOL	50
UNDECAVERTOL	10
Dipropylen glycol (DPG)	165
5	Total: 1000

The fragrance composition above is a fresh floral green accord, reminiscent of fresh green muguet. This fragrance can be applied, e.g. in high density liquid detergent (HDLD, at 0.1 – 1.5 wt% (e.g. 0.6 wt%).

By replacing 45 parts of DPG of the accord above by a mixture of ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl) cysteinate and ethyl *N,S*-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate (ration about 1 : 14), the overall character is now softer, fruitier, reminiscent of stewed apple on dry fabric. The fresh fruitiness is clearly enhanced over time, and last for several days.

By replacing 55 parts of DPG of the accord above by a mixture comprising ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl) cysteinate (2.7 parts), ethyl *N,S*-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate (37.3 parts), and one additional precursor (4-(dodecylthio)-4-methylpentan-2-one (15 parts)), a very unusual and pleasant effect is the overall lift and radiance of the perfume on the dry fabric ; with this combination the fresh fruitiness is not only enhanced and prolonged, but it furthermore has an enhanced volume and lift.

Example 6: Precursor deposition studies on cotton in heavy duty liquid detergent application

A liquid detergent composition (4.0 mg) was prepared with unperfumed heavy duty liquid detergent (HDLD) base containing 0.2% wt/wt of a mixture of Example 2. This liquid detergent composition was dissolved in 1 L of cold tap water to produce a wash liquor containing precursor. The wash liquor (100 mL) was placed in a 150 mL conical flask together with 2 cotton pads (10x10 cm², each weighing 2.5 g). The flask was closed with a screwcap and shaken on a thermostated shaking table at 200 rpm and 40 °C for 1 h. The liquids were discarded and the cotton pads wrung out (wet weight 4.5

- g) and put back in the conical flasks. After adding 75 mL of cold tap water, rinsing was effected by shaking for 30 min at RT. The cotton pads were wrung out and extracted with an accelerated solvent extractor (CH₃CN, 60 °C, 1500 psi), and the extracts (15-20 ml, precisely determined) were submitted to quantitative analysis by HPLC. The above process was repeated, with the difference that the towels were extracted after a period of 24 h line dry in ambient air.

The above two processes were repeated with liquid detergent composition containing 0.2% of δ -Damascone instead of the mixture of Example 2.

- 10 The quantification of δ -Damascone as such and the precursors thereof in the cotton pad extracts was effected by HPLC-UV with external calibration (0.3-20 ppm) of the reference materials in CH₃CN. The results are shown in the Table below.

HDL	Mixture of Example 2 (δ -Damascone precursor + released δ -Damascone)	δ -Damascone (comparison)
wet	(9+2)%	6%
24 h line dry	(6+1)%	0.7%

- 15 The results show that the mixture of Example 2, which contains a mixture of bis- and mono adduct, leads to the release of a perceivable amount of δ -Damascone already on the wet stage. After 24 h line drying, the amount of δ -Damascone delivered from the precursor has exceeded the amount when using free δ -Damascone. In addition, a large reservoir of precursor is available for continued long lasting release of the odorant.
- 20 Overall, the amount of bound and free δ -Damascone delivered from the precursor on dry fabric is over 5 times bigger than when using free δ -Damascone. The results suggest also that a combination of free δ -Damascone and precursor may produce advantageous effects.

- 25 Example 7: Precursor deposition studies on cotton in heavy duty liquid detergent application

Example 6 was repeated replacing the unperfumed heavy duty liquid detergent base with an unperfumed fabric conditioner base. The application involved a single cycle of

shaking at 200 rpm at room temperature for 20 min, following by wringing out the cotton pads and ASE (accelerated solvent extractor) extraction.

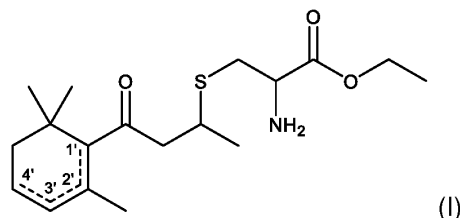
- 5 The quantification of δ -Damascone as such and the precursors thereof in the cotton pad extracts was effected by HPLC-UV with external calibration (0.3-20 ppm) of the reference materials in CH₃CN. The results are shown in the Table below.

Fabric conditioner	Mixture of Example 2 (δ -Damascone precursor + released δ -Damascone)	δ -Damascone (comparison)
wet	(43+7)%	14%
24 h line dry	(34+1.3)%	1.1%

- 10 The results show that the mixture of Example 2, which contains a mixture of bis- and mono adduct, leads to the release of a perceivable amount of δ -Damascone already on wet stage. After 24 h line drying, the amount of δ -Damascone delivered from the precursor had slightly exceeded the amount when using free δ -Damascone. Overall, the amount of bound and free δ -Damascone delivered from the precursor on wet fabric was 2.6 times higher than when using free δ -Damascone and over 25 times bigger on dry
- 15 fabric. The results suggest also that a combination of free δ -Damascone and precursor may produce advantageous effects.

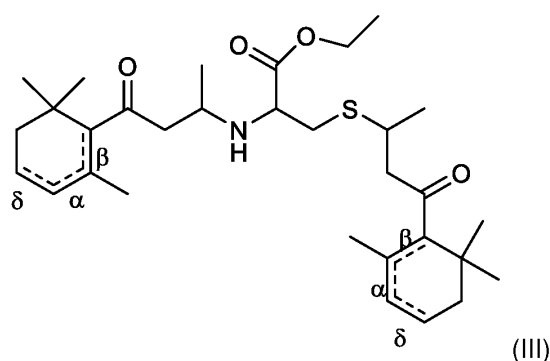
Claims

1. A compound of formula (I)



in which one of the dotted lines represents together with the carbon-carbon bond a double bond and each of the other two dotted lines represent together with the carbon-carbon bond a single bond.

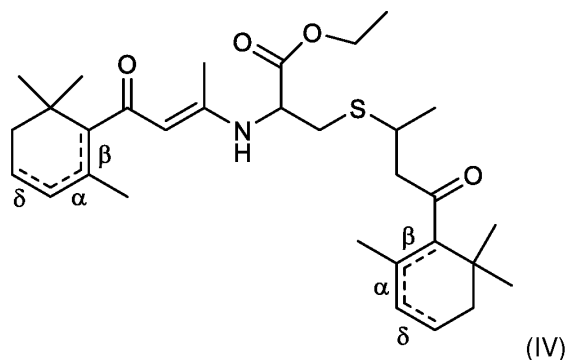
2. A mixture comprising a compound of formula (I) as defined in claim 1 and a compound of formula (III)



wherein the dotted lines represents a double bond located at one of the alpha-, beta- or delta-positions on each of the cyclohexene rings.

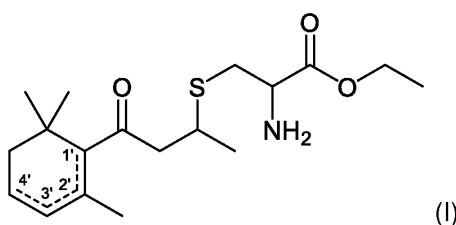
3. A mixture according to claim 2 characterised in that the mixture comprises a compound of formula (I) and a compound of formula (II) in an ratio of 1 : 40 to 40 : 1.
4. A mixture according to claim 3 wherein the compound of formula (I) is ethyl S-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl) cysteinate and the compound of formula (III) is ethyl N,S-bis(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate.

5. A mixture according to any of the claims 2 to 4 further comprising a compound of formula (IV)

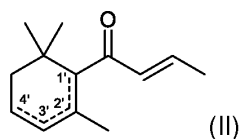


wherein the dotted lines represent a double bond located at one of the alpha-, beta- or delta-positions on each of the cyclohexene rings.

6. A mixture according to claim 5 wherein the compound of formula (IV) is ethyl *N*-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)but-2-en-2-yl)-*S*-(4-oxo-4-(2',6',6'-trimethylcyclohex-3'-en-1'-yl)butan-2-yl)cysteinate.
7. The use of a compound of formula (I)



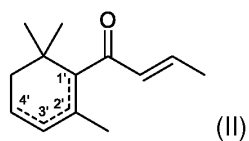
as precursor for generating, by spontaneous air oxidation, a damascone of formula (II)



wherein one of the dotted lines represents together with the carbon-carbon bond a double bond and each of the other two dotted lines represent together with the carbon-carbon bond a single bond.

8. A method of generating a compound of formula (II)

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characterized in that the compound of formula (I) as defined in claim 1 is exposed to oxygen.

9. A consumer product comprising a compound of formula (I) as defined by claim 1 or a mixture as defined in one of the claims 2 to 6 and a consumer product base.
10. A product according to claim 9 wherein the consumer product is not a food product, oral care product, tobacco product, confectionery or pharmaceutical.
11. A product according to claim 10 wherein the consumer product is a detergent or fabric conditioner.