(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 December 2007 (21.12.2007)

PCT

(10) International Publication Number
WO 2007/143873 A1

(51) International Patent Classification:
C07C 49/12 (2006.01) *C07C 49/213* (2006.01)
C07C 49/175 (2006.01) *C11B 9/00* (2006.01)
C07C 49/203 (2006.01) *C11D 3/50* (2006.01)

(21) International Application Number:
PCT/CH2007/000294

(22) International Filing Date: 13 June 2007 (13.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0611770.9 15 June 2006 (15.06.2006) GB

(71) Applicant *(for all designated States except US)*: **GIVAUDAN SA** [CH/CH]; Chemin de la Parfumerie 5, CH-1214 Vernier (CH).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **FLACHSMANN, Felix** [CH/CH]; Langhagweg 2, CH-8600 Duebendorf (CH).

(74) Agent: **MCSTEA, John, Anthony**; Ueberlandstrasse 138, CH-8600 Duebendorf (CH).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

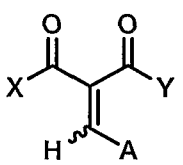
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/143873 A1

(54) Title: FRAGRANCE COMPOUNDS



I

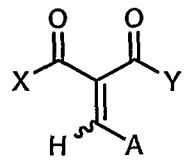
(57) Abstract: A method of providing a fragrant odour to an application, comprising the addition thereto of at least one compound of the formula (I) wherein X and Y are independently selected from the group consisting of $-CR^1R^2R^3$, $-NR^4R^5$ and $-OR^6$, wherein R^1 to R^5 are selected from H and essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom, and R^6 is selected from essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom; and A is an essentially hydrocarbon moiety that optionally comprises at least one oxygen, sulphur, nitrogen or silicon atom, with the proviso that the compound A-CHO is a fragrant aldehyde. The use of these compounds in laundry, household and personal care products confers a long-lasting freshness.

FRAGRANCE COMPOUNDS

This invention relates to the provision of fragrance and to a process and compounds for achieving this.

The provision of fragrance by the addition of inherently fragrant substances to products is well known and widely used. An alternative method of providing fragrance is by the use of a precursor, that is, a substance that is not itself fragrant, but which, in particular circumstances, for example exposure to light, pH change and enzymatic activity, will break down to give at least one fragrant substance.

It has now been discovered that a particular class of substances can act as precursors by providing a source of at least one fragrant aldehyde. The invention therefore provides a method of providing a fragrant odour to an application, comprising the addition thereto of at least one compound of the formula I



I

wherein

X and Y are independently selected from the group consisting of $-CR^1R^2R^3$, $-NR^4R^5$ and $-OR^6$, wherein R^1 to R^5 are selected from H and essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom, and R^6 is selected from essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom; and

A is an essentially hydrocarbon moiety that optionally comprises at least one oxygen, sulphur, nitrogen or silicon atom, with the proviso that the compound A-CHO is a fragrant aldehyde.

The invention additionally provides use of a compound of Formula I as hereinabove defined as a precursor of a fragrance.

By "essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom" (and, in the case of A, also at least one sulphur atom) is meant that the moieties X, Y and A are at least predominantly hydrocarbon in nature, that is, that the moieties will comprise mainly carbon and hydrogen, and that the number of carbon atoms present on a given moiety is greater than that of any oxygen, nitrogen and silicon (and, in the case of A, sulphur) atoms present. Thus, if there is present one oxygen atom, there must be present at least two carbon atoms on the moiety. The oxygen, nitrogen, sulphur and silicon atoms may either form part of the otherwise hydrocarbon chain, or they may be linked to carbon atoms on the chain, either directly (for example, a carbonyl group oxygen or a hydroxyl group) or as part of a substituent (for example, a nitrile group).

The wavy bond to the hydrogen means that the arrangement at the ethylenic double bond may be either in the E- or the Z- configuration. In individual instances, depending on the natures of X and Y, one or other isomer may be preferred, but this is not usually the case. With regard to X and Y, there may be present stereogenic units such as chiral centres or substituted double bonds, which result in there existing several different stereoisomers. In some cases, these can result in odours of different strengths or even characters, and these can be separated by conventional techniques, if desired. However, this adds to the complexity (and therefore the expense), and it is generally preferred to leave the compounds as a mixture of stereoisomers.

A is defined by the requirement that A-CHO is a fragrant aldehyde. Such molecules are well known to the art. Examples of fragrant aldehydes from which the moiety A may be derived include, but are not limited to, the following:

2,6,10-trimethylundec-9-enal,
8,8-dimethyl-1,2,3,4,5,6,7,8-octahydro-naphthalene-2-carbaldehyde,
(4-isopropyl-phenyl)-ethanal,
2,4-dimethyl-cyclohex-3-ene-1-carbaldehyde,
1,3,5-trimethyl-cyclohex-1-ene-4-carbaldehyde,
4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene-1-carbaldehyde,
hex-2-enal,

3,5,5-trimethyl-hexanal,
heptanal,
2,6-dimethyl-hept-5-enal,
decanal,
dec-9-enal,
dec-4-en-1-al,
2-methyl-decanal,
undec-10-en-1-al,
undecanal,
dodecanal,
2-methyl-undecanal,
tridecanal,
tridec-2-enal,
octanal,
nonanal,
non-2-enal,
undec-9-enal,
2-phenyl-propanal,
2-(4-methyl-phenyl)-ethanal,
3,7-dimethyl-octanal,
dihydrofarnesal,
7-hydroxy-3,7-dimethyl-octanal,
2,6-dimethyl-oct-5-en-1-al,
3-(3-isopropyl-phenyl)-butanal
2-(3,7-dimethyl-oct-6-en-oxy)-ethanal,
4-(4-methyl-pent-3-enyl)-cyclohex-3-ene-1-carbaldehyde,
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,
3-(4-tert-butyl-phenyl)-propanal,
2-(4-isopropyl-phenyl)-propanal,
3-(benzo[1,3]dioxol-5-yl)-2-methyl-propanal,

3,7-dimethyl-oct-6-ene-1-al,
2-methyl-3-(4-isopropylphenyl)-propanal,
4-tert-butyl-cyclohexane-1-carbaldehyde,
4-(octahydro-4,7-methano-5H-inden-5-ylidene)-butanal,
(3,7-dimethyl-oct-6-enyloxy)-ethanal,
(2E,6Z)-nonadienal,
2,4-dimethyl-2,6-heptadienal,
(E)-dec-2-enal,
dodec-2-enal,
3,7-dimethyl-octa-2,6-dienal,
2,4-diethyl-hepta-2,6-dienal,
3,7-dimethyl-nona-2,6-dienal,
3-propyl-hept-2-enal, and
4-isopropenyl-cyclohex-1-ene-1-carbaldehyde.

In particular embodiments, X and Y are independently selected from the following moieties:

(a) C_1-C_{20} alkyl, linear or branched, optionally containing oxygen, nitrogen or silicon atoms, such as methyl, ethyl, propyl, butyl, isobutyl, 2-ethylhexyl, tert.-butyl;

(b) cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl; optionally containing oxygen, nitrogen or silicon atoms, such as tetrahydrofuranyl, pyranyl, piperidinyl, pyrrolidinyl;

(c) C_3-C_{20} alkylcycloalkyl, optionally containing oxygen, nitrogen or silicon atoms, such as methylcyclohexyl, ethylcyclohexyl, methylcyclopentyl;

(d) C_6-C_{20} cycloalkylalkyl optionally containing oxygen, nitrogen or silicon atoms, such as (4-methyl)-cyclohexyl,

(e) C_3-C_{10} alkenyl, linear or branched, optionally containing oxygen, nitrogen or silicon atoms, such as propenyl, isopropenyl, isobutenyl;

(f) C_6-C_{10} aryl with optional substituents, such as phenyl, *o*- or *p*-methoxyphenyl;

(g) C_7-C_{10} alkylaryl with optional substituents and containing optionally oxygen, nitrogen or silicon atoms, such as benzyl, methoxybenzyl;

(g) C_5-C_{10} heteroaryl, such as pyridinyl, furanyl, pyrryl, imidazolyl;

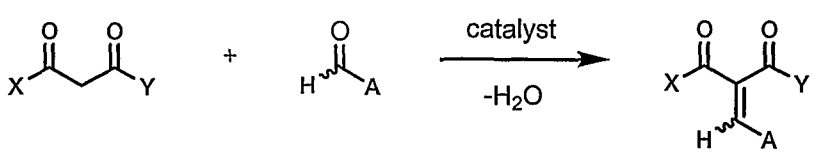
(h) $-OR^6$, wherein R^6 is C_1-C_{20} alkyl, linear or branched, optionally containing oxygen, nitrogen or silicium atoms, such as methyl, ethyl, propyl, butyl, isobutyl, 2-ethylhexyl, tert.-butyl; or cyclopentyl, cyclohexyl; or C_3-C_{10} alkenyl, linear or branched, such as propenyl, isopropenyl, isobutenyl; or C_6-C_8 aryl, such as phenyl or naphtyl; and

(i) $-NR^4R^5$, wherein R^4 and R^5 are, independently of each other, H; C_1-C_{20} alkyl, linear or branched, such as methyl, ethyl, propyl, butyl, isobutyl, 2-ethylhexyl, optionally containing oxygen or nitrogen atoms; or cyclopentyl, cyclohexyl; alternatively NR^4R^5 form together a 3-, 5- or 6-membered ring.

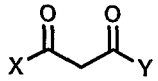
and

A is selected from the group consisting of C_7-C_{17} linear or branched alkyl, cycloalkyl, alkylcycloalkyl or cycloalkylalkyl, C_7-C_{15} linear or branched alkenyl, and C_6-C_{10} aryl.

One way of preparing the compounds is via a Knoevenagel condensation, in which a fragrant aldehyde is reacted with a suitable 1,3-dicarbonyl compound in the presence of a suitable catalyst, such as secondary amines, for example, piperidine, pyrrolidine, dimethylamine, diethylamine, or ammonium salts, for example, ammonium acetate and ethylene diamine diacetate. Many other catalysts do promote this reaction and are known to the person skilled in the art of organic synthesis. The reaction is depicted schematically below:

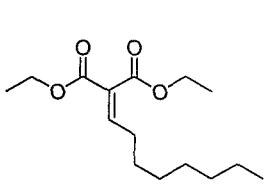


As the groups X and Y of the 1,3-dicarbonyl compound

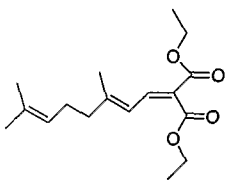


play no part in the reaction, the compound may be chosen from a very wide variety of such materials. Specific examples of 1,3-dicarbonyl compounds include ethyl 3-oxobutanoate, ethyl 3-oxo-3-phenylpropanoate, benzyl 3-oxobutanoate, diethyl malonate, dimethyl malonate, diisopropyl malonate, dibenzyl malonate, 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione (Parsol™ 1789) and ethyl 1-(3,3-dimethylcyclohexyl)ethyl malonate (Musk Nouvelle™, (IFF)).

Specific examples of compounds include the following:



(i)



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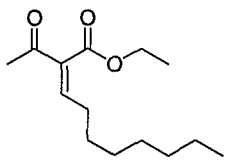

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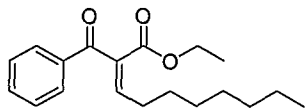

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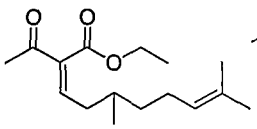

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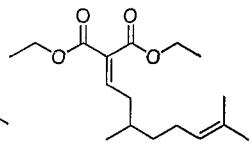

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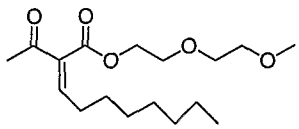

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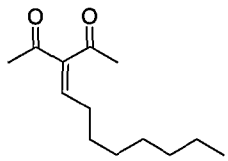

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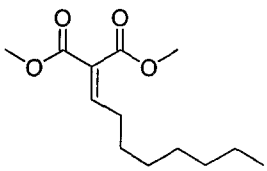

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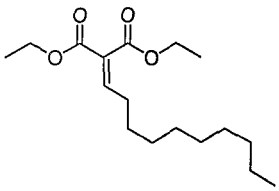

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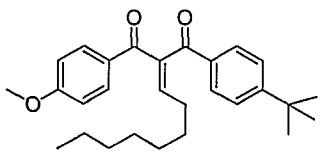

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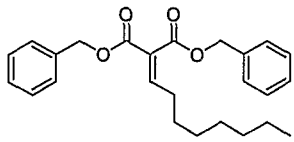

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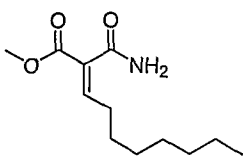

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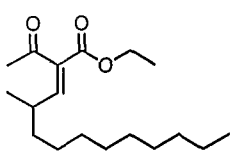

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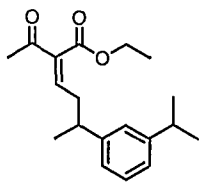

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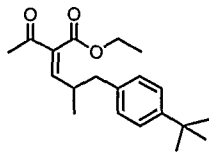

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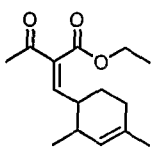

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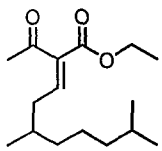

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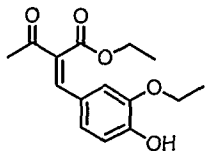

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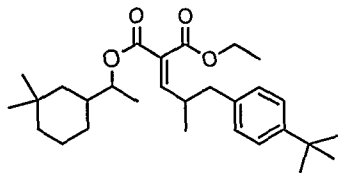
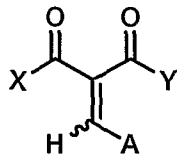


(xx)

While some of these compounds are known (but not for this particular purpose), others are novel. For example, in the formulae depicted above, Nos. (iv), (v), (vii), (xi)-(xxvii) and (xx) are novel. The invention therefore also provides a compound of the formula I



I

wherein

i) X and Y are the same and are selected from

a) $-OR^6$, wherein R^6 is selected from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, benzyl; or

b) phenyl, methyl, ethyl, propyl, isopropyl, butyl, isobutyl ;

or

ii) X and Y are different, and are selected according to the following table:

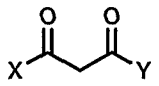
X	Y
Me	OMe, OEt, O-*t*Bu, O-*i*Pr, OBn, O-cis-3-hexenyl
Me	Et, Pr, Bu, Pent
Ph	OMe, OEt
2-(1-(3,3-dimethyl-cyclohexyl)ethoxy	OEt

and;

A is selected from branched or linear C_7-C_{15} alkyl and C_7-C_{15} alkenyl moieties, these optionally comprising oxygen atoms present as ether, hydroxyl, carbonyl or ester moieties.

All of the compounds of formula I hereinabove described have in common the fact that, on exposure to moisture, either liquid water applied to the compounds or to a support on which they have been deposited, or water vapour in the atmosphere, they release a fragrant aldehyde.

As previously mentioned, the groups X and Y of the 1,3-dicarbonyl compound



play no part in the reaction, and they may be chosen from a very wide variety of such materials. However, in a further aspect of the invention, they can be chosen such that the compound, once separated from the fragrant aldehyde, performs a desired function. For example, the compound itself may have fragrant characteristics, either as a fragrant material in its own right, or as a modifier for the fragrant aldehyde, or other fragrant material also present in a composition in which the compound useful in the invention is used. Another possibility is that it may enhance substantivity or stability in a given application. A third possibility is that it perform an entirely independent function in a composition. For example, it may act as a sunscreen, thus, for example, supplying a cosmetic composition simultaneously with a fragrance and a protective function. The skilled person will readily comprehend that there are many other possible uses, and will be able to tailor the 1,3-dicarbonyl compound appropriately to perform any such function.

The invention is useful for providing a fragrant odour to an application where release of the odour is desired at some particular time point and is caused by the presence of moisture. "Application" in the context of this invention means any use in which such an effect is desired. Examples include laundry use (release in a wash liquor, in a dryer or on laundry post-drying), use in hard surface cleaners, cosmetics, protective creams, personal care products, such as hair care products, skin creams and lotions, fine fragrances and air-care products, such as air fresheners.

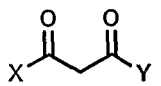
In use, the compounds may be combined with any other suitable free fragrance material. For example, they may be combined with free fragrance aldehydes, so that the free fragrance delivers an immediate impact and the compounds of the invention provide a lasting fragrance. By using the compounds of the present invention, the strong floral-fresh

impact of many fragrant aldehydes, which by themselves are not substantive, can be prolonged in many applications where such long-lasting freshness is desired, without having to overdose the aldehydes in the perfume. This opens new possibilities for fragrance creation.

The compounds for use in this invention may be incorporated into commercial products in conventional proportions and by art-recognised methods. Commercial products include washing and laundry detergents, fabric softeners and conditioners, personal care products, such as hair and skin care preparations, soaps and lotions. They may be incorporated directly into such compositions, or they may be added in conjunction with a carrier, such as microcapsules, adsorbed on to suitable particulate matter or spray-dried.

One of the particular features of this invention is that, if the Knoevenagel synthesis hereinabove described is used, the compounds need not be made in a manufacturing plant and shipped to the user, but they may be made *in situ*. They can thus be made simply and easily on site and then added directly to the composition in which their presence is desired. This confers a considerable versatility, in that it allows a user to make a desired compound on the spot, without waiting for a delivery. The invention therefore also provides a process of manufacturing a fragranced composition, in which the fragrance is gradually released on exposure to moisture, comprising the steps of

(a) blending a compound of the formula II



II

wherein X and Y are as hereinabove defined, with a fragrant aldehyde in the presence of a base under such conditions that a Knoevenagel condensation takes place; and
(b) adding the product of (a) to the composition.

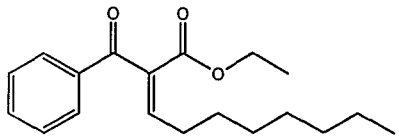
Conditions allowing a Knoevenagel condensation to take place *in situ*, i.e. step a) in the above-described process, include also thermal dehydration methods such as spray-drying. Therein, the mixture of a compound of formula II, together with one or several fragrant aldehydes and a base are formulated into an aqueous emulsion, containing optional carrier

materials and surfactants. This emulsion is then spray-dried, thereby producing solid particles containing products of formula I.

The invention is now further described with reference to the following non-limiting examples, which describe preferred embodiments.

Example 1:

Preparation of 2-benzoyl-dec-2-enoic acid ethyl ester, a compound according to the formula



Piperidine (0.10 ml, 0.5 mol%) is added to a mixture of octanal (25.6 g, 0.20 mol) and ethyl benzoylacetate (38.4 g, 0.20 mol) at 5°C. The resulting solution is warmed to room temperature and stirred for 24 h, during which a fine emulsion is formed. The mixture is diluted with methyl *t*-butyl ether and the organic layer washed with 2 N aq. HCl-solution, water and brine, then dried over $MgSO_4$.

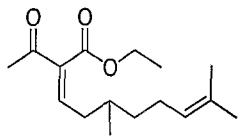
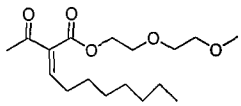
The solvent is removed *in vacuo* and the residue distilled to yield 18.0 g (38%) of product as an *E/Z*-mixture, boiling at 129-135°C / 0.1 mbar.

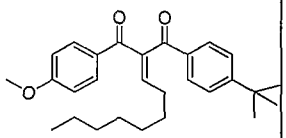
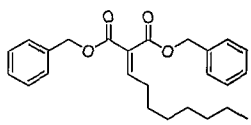
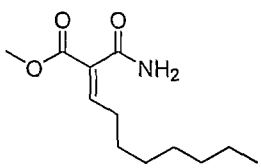
^{13}C-NMR ($CHCl_3$, 100 MHz; main isomer): 194.5 (s), 164.6 (s), 148.6 (d), 137.2 (s), 133.7 (d), 133.6 (s), 129.0 (d), 128.8 (d), 61.0 (t), 31.6 (t), 29.5 (t), 29.1 (t), 28.8 (t), 28.3 (t), 22.5 (t), 14. (q), 13.9 (q).

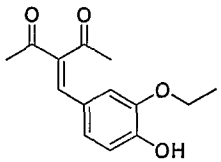
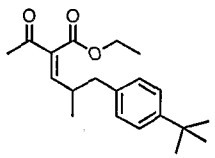
MS (EI, 70 eV): 302 (<1, M^+), 257 (2), 217 (10), 199 (15), 186 (15), 171 (4), 157 (13), 105 (100).

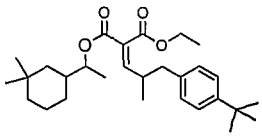
Examples 2-12

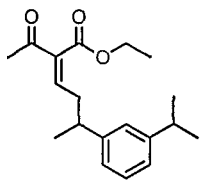
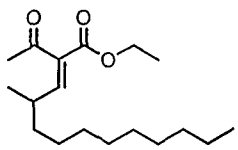
The following compounds are made by a method according to claim 1, using the appropriate fragrant aldehyde and 1,3-dicarbonyl compound:

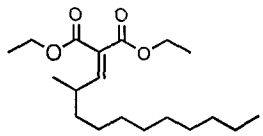
N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
2		127 / 0.07	194.9 (s), 166.5 (s), 147.5 (d), 139.8 (s), 131.6 (s), 124.2 (d), 59.4 (t), 39.5 (t), 35.3 (t), 32.3 (d), 27.4 (t), 25.7 (q), 22.4 (q), 19.6	266 (29, M^+), 221 (27), 205 (26), 177 (29), 149 (20), 43
3	 (*)	168-171°C / 0.08	195.0 (s), 168.8 (s), 149.3 (d), 136.6 (s), 71.8 (t), 70.4 (t), 68.9 (t), 63.5 (t), 58.9 (q), 32.5 (t), 30.0 (t), 29.2 (t), 29.0 (t), 27.0 (t), 22.5 (t), 27.0 (q), 14.0 (q).	272 (<1), 239 (7), 195 (17), 137 (45), 124 (27), 59 (94), 45 (100).

N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
4		(purified by chromato-graphy)	194.1 (s), 192.8 (s), 163.9 (s), 156.2 (s), 147.9 (d), 141.9 (s), 133.3(s), 131.7 (d), 130.3 (s), 129.5 (d), 125.4 (d), 13.7 (d), 55.5 (q), 35.1 (s), 31.6 (t), 31.1 (q), 31.0 (t), 31.0 (t), 29.2 (t), 28.9 (t), 22.5 (t), 14.0 (q).	420 (24, M^+), 363 (95), 335 (39), 279 (36), 255 (35), 161 (91), 150 (97), 135 (100).
5		(purified by chro-mato-graphy)	165.3 (s), 163.8 (s), 151.1 (d), 135.6 (s), 135.4 (s), 128.5 (d), 128.4(d), 128.3 (d), 128.2 (d), 128.0 (d), 128.0 (d), 67.0 (t), 66.9 (t), 31.7 (t), 29.9 (t), 29.2 (t), 28.9 (t), 28.3 (t), 22.6 (t), 14.1 (q).	394 (5, M^+), 200 (16), 197 (20), 179 (77), 123 (15), 109 (12), 91 (100).
6		(purified by chro-mato-graphy)	166.8 (s), 166.2 (s), 155.3 (d), 127.3 (s), 52.3 (q), 31.6 (t), 30.4 (t), 30.0 (t), 29.2 (t), 28.9 (t), 22.6 (t), 14.0 (q).	227 (3, M^+), 210 (19), 178 (39), 168 (37), 153 (62), 139 (65), 113 (92), 81 (93), 41 (100).

N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
7		(purified by chromato-graphy) m.p. 126-128°C	206.4 (s), 196.4 (s), 148.4 (s), 146.0 (s), 140.6 (s), 140.1 (d), 125.0 (s), 125.0 (d), 114.9 (d), 112.2 (d), 64.6 (t), 31.7 (q), 26.3 (q), 14.7 (q).	248 (30, M^+), 233 (8), 219 (4), 205 (11), 191 (11), 177 (11), 163 (25), 145 (11), 43 (100).
8		(purified by chromato-graphy, only Z-isomer described)	201.2 (s), 164.4 (s), 152.3 (d), 149.2 (s), 136.3 (s), 134.9 (s), 128.9 (d), 125.2 (d), 61.1 (t), 42.4 (t), 36.5 (d), 34.4 (s), 31.3 (q), 30.5 (q), 19.9 (q), 14.1 (q).	316 (<1, M^+), 298 (3), 270 (8), 147 (100).

N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
9		(purified by chromato-graphy)	165.4 (s), 164.1 (s), 152.9 (d), 152.6 (d), 148.9 (s), 135.8 (s), 135.6 (s), 129.0 (d), 128.8 (d), 128.7 (d), 128.6 (d), 128.2 (d), 127.8 (d), 127.7 (d), 125.2 (d), 76.2 (d), 61.1 (t), 41.6 (t), 41.6 (t), 41.2 (s, 1 C), 41.1 (t), 39.1 (t), 39.0 (t), 38.3 (d), 38.2 (d), 38.2 (d), 36.1 (d), 35.8 (d), 34.3 (s), 33.5 (q), 33.4 (q), 31.3 (q), 30.5 (s), 30.5 (s), 30.4 (s), 28.3 (t), 28.3 (t), 24.5 (q), 21.9 (t), 21.9 (t), 19.1 (q), 18.9 (q), 17.1 (q), 17.0 (q), 14.1 (q)	456 (2, M^+), 318 (7), 300 (11), 147 (100).

N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
10		(purified by chromato-graphy)	(only *E*-isomer described) 195.0 (s), 166.3 (s), 149.1 (s), 146.8 (d), 145.3 (s), 137.6 (s), 128.5 (d), 125.1 (d), 124.5 (d), 123.9 (d), 61.1 (t), 39.5 (d), 38.3 (t), 34.1 (d), 26.8 (q), 24.0 (q), 21.6 (q), 14.1 (q).	302 (<1, M^+), 256 (9), 228 (5), 213 (5), 172 (9), 147 (100), 105 (20), 91 (14).
11		(purified by chromato-graphy)	(mixture of *E* and Z-isomers) 201.2 (s), 195.1 (s), 166.6 (s), 164.5 (s), 153.6 (d), 153.4 (d), 135.8 (s), 134.4 (s), 61.1 (t), 61.1 (s), 36.5 (t), 36.5 (t), 34.9 (d), 34.0 (d), 31.8 (t), 31.3 (t), 29.6 (t), 29.5 (t), 29.4 (t), 29.2 (t), 27.4 (t), 27.3 (t), 26.8 (q), 22.6 (t), 20.1 (q), 19.8 (q), 14.1 (q), 14.1 (q), 14.0 (q).	296 (<1, M^+), 281 (2), 250 (71), 151 (42), 143 (26), 137 (50), 124 (18), 43 (100).

N°	Structure	b.p. (if distilled) [°C / mbar]	^{13}C-NMR $CDCl_3$, 100 MHz (only main isomer)	MS EI, 70 eV
12		(purified by chromato-graphy)	165.7 (s), 164.0 (s), 154.2 (d), 127.3 (s), 61.1 (t), 61.1 (t), 36.4 (t), 34.7 (d), 31.8 (t), 29.5 (t), 29.5 (t), 29.2 (t), 27.3 (t), 22.6 (t), 19.8 (q), 14.1 (q), 14.0 (q).	326 (<1, M^+), 311 (<1), 297 (<1), 281 (23), 253 (4), 234 (100), 199 (9), 173 (59), 160 (62), 141 (41), 122 (85), 108 (86).

(*) The product contains ca. 15% of 2-(1-hydroxy-ethylidene)-dec-3-enoic acid 2-(2-methoxy-ethoxy)-ethyl ester. The starting material, 3-oxo-butyric acid 2-(2-methoxy-ethoxy)-ethyl ester, is prepared as follows:

Ethyl acetoacetate (39.0 g, 0.30 mol) and diethyleneglycol monomethyl ether (36.0 g, 0.30 mol) are heated to 110°C (oil bath temperature) and tetraisopropyl orthotitanate (0.60 ml, 2.0 mmol, 0.7 mol%) is added. The temperature is further increased to 150°C. After 30 min methanol (5 g) is distilling off and collected. The temperature is maintained for further 8 h while lowering the pressure in the apparatus to 800 mbar. After cooling to room temperature, the residue is distilled at 65-120°C / 0.06 mbar to isolate 30.5 g of product containing ca. 10% of diethyleneglycol monomethyl ether (yield 44%).

^{13}C-NMR ($CHCl_3$, 100 MHz): 200.4 (s), 167.0 (s), 89.9 (d), 71.8 (t), 70.4 (t), 68.8 (t), 64.2 (t), 59.0 (q), 50.0 (t), 30.0 (q).

MS (EI, 70 eV): 302 (<1, M^+), 257 (2), 217 (10), 199 (15), 186 (15), 171 (4), 157 (13), 105 (100).

Example 13

Application in fabric softener

To each of two samples of a standard unperfumed fabric softener base of the ester quat type is added one of the following:

1) 0.20 % wt/wt of 2-methylundecenal
2) 0.32 % wt/wt of ethyl 2-acetyl-4-methyltridec-2-enoate (Example 11), equivalent to 0.20 % wt/wt of 2-methylundecanal.

These bases are then added to the rinse cycle of a washing machine loaded with cotton terry towels. After centrifugation, the towels are evaluated olfactorily by a panel of trained evaluators. Odour scores are attributed to each towel at the given time, which are as follows: 0 (odourless), 1 (very weak), 2 (weak), 3 (medium), 4 (strong) and 5 (very strong). The arithmetic means of the scores from all evaluators are reported in the following table.

	2-methylundecanal	**ethyl 2-acetyl-4-methyltridec-2-enoate**
wet	5	2.1
1 d	0.3	3.6
2d	0.9	4
6d	0.3	3.8

From day 1 to day 6, the towel washed with the fabric softener base containing a compound according to the invention exhibits a strong 2-methylundecanal note, whereas the towels washed with base containing the free aldehyde are almost odourless.

Example 14

Application in liquid detergent

To each of four samples of a standard unperfumed heavy duty liquid detergent base samples is added one of the following:

1) 0.20 % wt/wt of 2-methylundecenal

2) 0.32 % wt/wt of ethyl 2-acetyl-4-methyltridec-2-enoate (Example 11), equivalent to 0.20 % wt/wt of 2-methylundecanal.

3) 0.20 % wt/wt of 3-(3-isopropylphenyl)butanal

4) 0.32 % wt/wt of ethyl 2-acetyl-5-(3-isopropylphenyl)hex-2-enoate (Example 10), equivalent to 0.20 % wt/wt of 3-(3-isopropylphenyl)butanal)

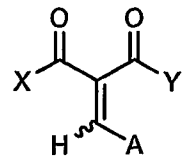
Four individual 40°C wash cycles are performed with the above samples, each with a load of cotton terry towels. Odour scores are attributed to the individual towels after time intervals by a panel of trained evaluators as described in example 3. The results are shown in the following table:

	2-methylundecanal ("Aldehyde C12MNA")	**ethyl 2-acetyl-4-methyltridec-2-enoate**	**3-(3-isopropylphenyl)-butanal ("Florhydral")**	**2-acetyl-5-(3-isopropylphenyl)-hex-2-enoate**
wet	3.6	1.5	2.3	3.5
1 d	0	2.3	1.0	2.8
2d	0	2.3	n.d.	n.d.
3d	0	2.4	n.d.	n.d.

From wet to day 3, the towels washed with the liquid detergent base comprising a compound according to the invention exhibit a strong 2-methylundecanal note, whereas the towels washed with base containing the free aldehyde are almost weak to odourless. Likewise, the towels washed with 2-acetyl-5-(3-isopropylphenyl)hex-2-enoate exhibit a strong Florhydral note after 1 day on the dry towel, whereas the towel washed with free Florhydral has only a very weak smell.

Claims:

1. A method of providing a fragrant odour to an application, comprising the addition thereto of at least one compound of the formula I



I

wherein

X and Y are independently selected from the group consisting of $-CR^1R^2R^3$, $-NR^4R^5$ and $-OR^6$, wherein R^1 to R^5 are selected from H and essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom, and R^6 is selected from essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom; and

A is an essentially hydrocarbon moiety that optionally comprises at least one oxygen, sulphur, nitrogen or silicon atom, with the proviso that the compound A-CHO is a fragrant aldehyde.

2. Use of a compound of Formula I as described in claim 1 as a precursor of a fragrance.

3. Method according to claim 1, in which the fragrant aldehyde from which the moiety A is selected from the group consisting of: 2,6,10-trimethylundec-9-enal, 8,8-dimethyl-1,2,3,4,5,6,7,8-octahydro-naphthalene-2-carbaldehyde, (4-isopropyl-phenyl)-ethanal, 2,4-dimethyl-cyclohex-3-ene-1-carbaldehyde, 1,3,5-trimethyl-cyclohex-1-ene-4-carbaldehyde, 4-(4-hydroxy-4-methylpentyl)-cyclohex-3-ene-1-carbaldehyde, hex-2-enal, 3,5,5-trimethyl-hexanal, heptanal, 2,6-dimethyl-hept-5-enal, decanal, dec-9-enal, dec-4-en-1-al, 2-methyl-decanal, undec-10-en-1-al, undecanal, dodecanal, 2-methyl-undecanal, tridecanal, tridec-2-enal, octanal, nonanal, non-2-enal, undec-9-enal, 2-phenyl-propanal, 2-(4-methyl-phenyl)-ethanal, 3,7-dimethyl-octanal, dihydrofarnesal, 7-hydroxy-3,7-

dimethyl-octanal, 2,6-dimethyl-oct-5-en-1-al, 3-(3-isopropyl-phenyl)-butanal, 2-(3,7-dimethyl-oct-6-en-oxy)-ethanal, 4-(4-methyl-pent-3-enyl)-cyclohex-3-ene-1-carbaldehyde, 2,3,5,5,-tetramethyl-hexanal, longifolic aldehyde, 2-methyl-4-(2,6,6-rimethylcyclohex-2-en-1-yl)-butanal, 2-methyl-3-(4-tert-butylphenyl)-propanal, 3-(4-tert-butyl-phenyl)-propanal, 2-(4-isopropyl-phenyl)-propanal, 3-(benzo[1,3]dioxol-5-yl)-2-methyl-propanal, 3,7-dimethyl-oct-6-ene-1-al, 2-methyl-3-(4-isopropylphenyl)-propanal, 4-tert-butyl-cyclohexane-1-carbaldehyde, 4-(octahydro-4,7-methano-5H-inden-5-ylidene)-butanal, (3,7-dimethyl-oct-6-enyloxy)-ethanal, (2E,6Z)-nonadienal, 2,4-dimethyl-2,6-heptadienal, (E)-dec-2-enal, dodec-2-enal, 3,7-dimethyl-octa-2,6-dienal, 2,4-diethyl-hepta-2,6-dienal, 3,7-dimethyl-nona-2,6-dienal, 3-propyl-hept-2-enal, and 4-isopropenyl-cyclohex-1-ene-1-carbaldehyde.

4. Method according to claim 1 in which X and Y are independently selected from the following moieties:

(a) C_1-C_{20} alkyl, linear or branched, optionally containing oxygen, nitrogen or silicon atoms;

(b) cyclopropyl, cyclopentyl, cyclohexyl, cyclooctyl; optionally containing oxygen, nitrogen or silicon atoms;

(c) C_3-C_{20} alkylcycloalkyl, optionally containing oxygen, nitrogen or silicon atoms;

(d) C_6-C_{20} cycloalkylalkyl optionally containing oxygen, nitrogen or silicon atoms;

(e) C_3-C_{10} alkenyl, linear or branched, optionally containing oxygen, nitrogen or silicon atoms;

(f) C_6-C_{10} aryl with optional substituents, such as phenyl, *o*- or *p*-methoxyphenyl;

(g) C_7-C_{10} alkylaryl with optional substituents and containing optionally oxygen, nitrogen or silicon atoms;

(g) C_5-C_{10} heteroaryl;

(h) -OR^6, wherein R^6 is C_1-C_{20} alkyl, linear or branched, optionally containing oxygen, nitrogen or silicon atoms; or C_3-C_{10} alkenyl, linear or branched; or C_6-C_8 aryl; and

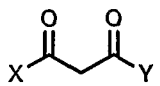
(i) -NR^4R^5, wherein R^4 and R^5 are, independently of each other, H; C_1-C_{20} alkyl, linear or branched, optionally containing oxygen or nitrogen atoms; or cyclopentyl, cyclohexyl; or NR^4R^5 form together a 3-, 5- or 6-membered ring.

and

A is selected from the group consisting of C_7-C_{17} linear or branched alkyl, cycloalkyl, alkylcycloalkyl or cycloalkylalkyl, C_7-C_{15} linear or branched alkenyl, and C_6-C_{10} aryl.

5. A process of manufacturing a fragranced composition, in which the fragrance is gradually released on exposure to moisture, comprising the steps of

(a) blending a compound of the formula II

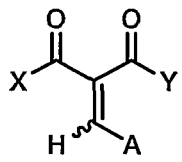


II

in which X and Y are independently selected from the group consisting of -$CR^1R^2R^3$, -NR^4R^5 and -OR^6, wherein R^1 to R^5 are selected from H and essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom, and R^6 is selected from essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom with a fragrant aldehyde in the presence of a base under such conditions that a Knoevenagel condensation takes place; and

(b) adding the product of (a) to the composition.

6. A compound according to Formula I



I

wherein

i) X and Y are the same and are selected from

a) $-OR^6$, wherein R^6 is selcted from the group consisting of methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, benzyl; or

b) phenyl, methyl, ethyl, propyl, isopropyl, butyl, isobutyl ;

or

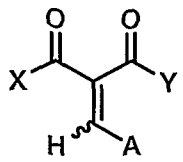
ii) X and Y are different, and are selected according to the following table:

X	Y
Me	OMe, OEt, O-*t*Bu, O-*i*Pr, OBn, O-cis-3-hexenyl
Me	Et, Pr, Bu, Pent
Ph	OMe, OEt
2-(1-(3,3-dimethyl-cyclohexyl)ethoxy	OEt

and;

A is selected from branched or linear C_7-C_{15} alkyl and C_7-C_{15} alkenyl moieties, these optionally comprising oxygen atoms present as ether, hydroxyl, carbonyl or ester moieties.

7. An application comprising known application ingredients and at least one compound of Formula I:



I

wherein

X and Y are independently selected from the group consisting of $-CR^1R^2R^3$, $-NR^4R^5$ and $-OR^6$, wherein R^1 to R^5 are selected from H and essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom, and R^6 is selected from essentially hydrocarbon moieties that optionally comprise at least one oxygen, nitrogen or silicon atom; and

A is an essentially hydrocarbon moiety that optionally comprises at least one oxygen, sulphur, nitrogen or silicon atom, with the proviso that the compound A-CHO is a fragrant aldehyde.

8. Application according to claim 7, selected from laundry products, hard surface cleaners, cosmetics, protective creams, personal care products, cleansing products, skin creams and lotions, fine fragrances and air-care products.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CH2007/000294

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C49/12 C07C49/175 C07C49/203 C07C49/213 C11B9/00
C11D3/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C11B C07C C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	DE 41 01 737 A1 (HOECHST A.-G., GERMANY) 1 August 1991 (1991-08-01) example 26	6
X	DE 23 35 067 A1 (PRINCETON BIOMEDIX INC.) 31 January 1974 (1974-01-31) example 3	6
X	GB 857 163 A (COUNCIL SCIENT IND RES) 29 December 1960 (1960-12-29) page 3, line 14 - line 23	6

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 August 2007	17/09/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Hillebrecht, Dieter

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