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(54) Title: ALPHA, BETA, UNSATURATED NITRILES AS FRAGRANCES

(57) Abstract: The use of short chain α,β-unsaturated nitriles as flavour and fragrance ingredient and flavour and fragrance applications comprising them.

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ORGANIC COMPOUNDS

The present invention refers to the use of short chain alk-2-enenitriles as perfuming ingredients and to flavour and fragrance compositions comprising them.

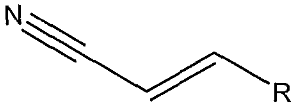
In the fragrance industry there is a constant demand for new compounds that enhance or improve on odour notes.

Short chain alk-2-enenitriles are known from the prior art. However, to the best of our knowledge, the prior art is completely silent with regard to their organoleptic properties or any use of this class of compounds in the field of perfumery.

The only short chain nitriles suitable in the field of perfumery described in literature are 3-butenenitrile and 4-pentenenitrile possessing onion-like and pungent mustard-like odour notes respectively (6th Int. Congr. Essent. Oils 1974, 73, W. S. Brud et al.).

Surprisingly, inventors found that certain short chain alk-2-enenitriles possess very interesting green, fruity odour notes.

Accordingly, the present invention refers in one of its aspects to the use as fragrance or flavour ingredient of a compound of formula (I)



(I)

wherein R is selected from linear, branched C_{3-4} alkyl and C_{3-4} cycloalkyl, such as propyl, prop-2-yl, butyl, 1-methylprop-1-yl, 2-methylprop-1-yl and cyclopropyl; and the double bond is in E or Z configuration; or a mixture thereof.

Whereas the (Z)- and (E)-isomers show similar olfactory profiles, the odour threshold of the (Z)-isomer compared to its corresponding (E)-isomer is higher. Accordingly, the use of the pure (E)-isomer is preferred. However, a mixture of both isomers, preferably enriched in the (E)-isomer, which is readily available synthetically, can also be used.

The term "enriched" is used herein to describe the compounds of the present invention having an isomeric purity greater than 1:1 in favour of the (E)-isomer. Particularly preferred are compounds having an isomeric purity of 1.5:1 (E:Z), more preferably 2:1 (E:Z) or 3:1 (E:Z), and most preferably 5:1 (E:Z) or greater.

The compounds according to the present invention may contain one stereocenter, and as such exist as mixtures of stereoisomers. They can be used as stereoisomeric mixtures, or may be resolved in diastereomerically and/or enantiomerically pure form. Resolving stereoisomers adds to the complexity of manufacture and purification of these compounds, and so it is preferred to use the compounds as mixtures of their stereoisomers simply for economic reasons. However, if it is desired to prepare individual stereoisomers, this may be achieved according to methodology known in the art, e. g. preparative HPLC and GC or by stereoselective syntheses.

In particular embodiments are the use as flavour or fragrance ingredient of compounds of formula (I) selected from the list consisting of hex-2-enenitrile, hept-2-enenitrile, 4-methylhex-2-enenitrile, 5-methylhex-2-enenitrile, 4-methylpent-2-enenitrile and 3-cyclopropylacrylonitrile, preferably enriched in favour of its (E)-isomer.

The compounds of formula (I) may be used alone, as mixtures thereof, or in combination with a base material. As used herein, the "base material" includes all known odorant molecules selected from the extensive range of natural products and synthetic molecules currently available, such as essential oils, alcohols, aldehydes and ketones, ethers and acetals, esters and lactones, macrocycles and heterocycles, and/or in admixture with one or more ingredients or excipients conventionally used in conjunction with odorants in fragrance compositions, for example, carrier materials, and other auxiliary agents commonly used in the art, e.g. solvents such as dipropylene glycol (DPG), isopropyl myristate (IPM), and thriethyl citrate (TEC).

The following list comprises examples of known odorant molecules, which may be combined with the compounds of the present invention:

- essential oils and extracts, e.g. 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 or ylang-ylang oil;

- alcohols, e.g. cinnamic alcohol, cis-3-hexenol, citronellol, Ebanol®, eugenol, farnesol, geraniol, Super Muguet™, linalool, menthol, nerol, phenylethyl alcohol, rhodinol, Sandalore®, terpineol or Timberol®;

- aldehydes and ketones, e.g. anisaldehyde, α-amylcinnamaldehyde, Georgywood™, hydroxycitronellal, Iso E® Super, Isoraldeine®, Hedione®, Lilial®, maltol, Methyl cedryl ketone, methylionone, verbenone or vanillin;

- ethers and acetals, e.g. Ambrox®, geranyl methyl ether, rose oxide or Spirambrene;

- esters and lactones, e.g. benzyl acetate, Cedryl acetate, γ-decalactone, Helvetolide®, γ-undecalactone or Vetivenyl acetate;

- macrocycles, e.g. Ambrettolide, Ethylene brassylate or Exaltolide®;

- heterocycles, e.g. isobutylquinoline.

The compounds according to formula (I) may be used in a broad range of fragrance applications, e.g. in any field of fine and functional perfumery, such as perfumes, household products, laundry products, body care products and cosmetics. The compounds can be employed in widely varying amounts, depending upon the specific application and on the nature and quantity of other odorant ingredients. The proportion is typically from 0.001 to 20 weight percent of the application. In one embodiment, compounds of the present invention may be employed in a fabric softener in an amount of from 0.001 to 0.05 weight percent. In another embodiment, compounds of the present invention may be used in fine perfumery in amounts of from 0.1 to 20 weight percent, more preferably between 0.1 and 5 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 as described hereinabove may be employed into the fragrance application simply by directly mixing the fragrance composition with the fragrance application, or they may, in an earlier step, be entrapped with an entrapment material, for example, polymers, capsules, microcapsules and nanocapsules, liposomes, film formers, absorbents such as carbon or zeolites, cyclic oligosaccharides and mixtures thereof, or they may be chemically bonded to substrates, which are adapted to release the fragrance molecule upon application of an external stimulus such as light, enzyme, or the like, and then mixed with the application.

Thus, the invention additionally provides a method of manufacturing a fragrance application, comprising the incorporation of a compound of the present invention, as a fragrance ingredient, either by directly admixing the compound to the application or by admixing a fragrance composition comprising a compound of formula (I), which may then be mixed to a fragrance application, using conventional techniques and methods.

As used herein, "fragrance application" means any product, such as fine perfumery, e.g. perfume and eau de toilette; household products, e.g. detergent for dishwasher, surface cleaner; laundry products, e.g. softener, bleach, detergent; body care products, e.g. shampoo, shower gel; and cosmetics, e.g. deodorant, vanishing creme, comprising an odorant. This list of products is given by way of illustration and is not to be regarded as being in any way limiting.

The α,β-unsaturated nitriles according to formula (I) may be conveniently prepared by Wittig reaction of saturated aldehydes with (triphenylphosphoranilydene)acetonitrile under conditions known to the skilled person.

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: Hex-2-enenitrile

A mixture of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol), distilled butyraldehyde (1.2 g, 16.6 mmol), and distilled dibenzyl ether (15 ml) was heated 4 h at 80 °C. The reaction mixture (E/Z 70:30) was then cooled down and distilled using a Kugelrohr apparatus (ball-to-ball rotary distillation apparatus) at 40 mbar till 220 °C. The main fraction (1.59 g) was then microdistilled in the presence of 1.6 g paraffin (15 mbar, oil bath temperature: 120 °C) giving a 63:37 mixture of (E/Z)-hex-2-enenitrile (0.6 g, 38%) having a boiling point of 79 °C at 15 mbar.

Odour description (E/Z)-hex-2-enenitrile: fruity, green, citrus.

Data of (E)-hex-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.72 (*dt*, J = 6.9, 16.4, H-C(3)), 5.33 (*dt*, J = 1.7, 16.4, H-C(2)), 2.21 (*qd*, J = 1.7, 7.2, H-C(4)), 1.49 (*sext.*, J = 7.3, H-C(5)), 0.94 (*t*, J = 7.3, *Me*CH_2).
^{13}C-NMR (100MHz, $CDCl_3$): δ155.91 (*d*, C(3)), 117.55 (*s*, CN), 99.78 (*d*, C(2)), 35.22 (*t*, C(4)), 20.90 (*t*, C(5)), 13.41 (*q*, C(6)).
MS (EI): 95 (3), 94 (1), 80 (3), 68 (4), 67 (22), 66 (7), 65 (3), 64 (5), 63 (3), 62 (1), 55 (14), 54 (100), 53 (12), 52 (9), 51 (7), 50 (4), 43 (3), 42 (8), 41 (28), 40 (9), 39 (23), 38 (6), 29 (15), 28 (3), 27 (15).
IR: ν_{max} 2964, 2935, 2876, 2223, 1633, 1461, 1437, 1382, 1341, 1309, 1053, 967, 795 cm^{-1}.
Data of (Z)-hex-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.49 (*dt*, J = 7.7, 10.9, H-C(3)), 5.32 (*dt*, J = 1.4, 10.9, H-C(2)), 2.41 (*qd*, J = 1.3, 7.4, H-C(4)), 1.50 (*sext.*, J = 7.3, H-C(5)), 0.97 (*t*, J = 7.3, *Me*CH_2).
^{13}C-NMR (100MHz, $CDCl_3$): δ154.97 (*d*, C(3)), 115.97 (*s*, CN), 99.63 (*d*, C(2)), 33.72 (*t*, C(4)), 21.52 (*t*, C(5)), 13.46 (*q*, C(6)).
MS (EI): 95 (2), 94 (2), 80 (4), 68 (4), 67 (33), 66 (5), 65 (3), 64 (4), 63 (2), 62 (1), 55 (11), 54 (100), 53 (13), 52 (9), 51 (7), 50 (4), 43 (2), 42 (7), 41 (35), 40 (9), 39 (23), 38 (6), 29 (12), 28 (3), 27 (14).
IR: ν_{max} 2964, 2935, 2875, 2220, 1621, 1461, 1381, 1338, 1241, 1210, 1075, 1044, 1003, 970, 916, 874, 852, 735 cm^{-1}.

Example 2: Hept-2-enenitrile

Distilled valeraldehyde (1.43 g, 16.6 mmol) was added dropwise to a suspension of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol) in distilled pentane (15 ml). After refluxing for 8 h, the reaction mixture was cooled down, filtered, and concentrated (rotary evaporator at 50 °C without vacuum). The residue (E:Z 70:30) was then distilled using a Kugelrohr apparatus (ball-to-ball rotary distillation apparatus) at 10 mbar and 81 °C giving two fractions of (E/Z)-hept-2-enenitrile (first fraction: 1.04 g, 58%, E:Z 64:36; second fraction: 0.45 g, E:Z 84:16, 25%) having a boiling point of 81 °C at 10 mbar.

Odour description: green, fruity, citrus, fatty.

Data of (E)-hept-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.73 (*dt*, J = 7.0, 16.3, H-C(3)), 5.33 (*dt*, J = 1.8, 16.3, H-C(2)), 2.23 (*qd*, J = 1.6, 7.2, H-C(4)), 1.51-1.29 (*m*, 4H), 0.92 (*t*, J = 7.3, *Me*CH_2).
^{13}C-NMR (100MHz, $CDCl_3$): δ156.14 (*d*, C(3)), 117.57 (*s*, CN), 99.59 (*d*, C(2)), 32.97 (*t*, C(4)), 29.66 (*t*, C(5)), 22.02 (*t*, C(5)), 13.67 (*q*, C(7)).
MS (EI): 109 (1), 108 (2), 94 (5), 81 (4), 80 (5), 69 (10), 68 (11), 67 (32), 66 (7), 65 (3), 64 (4), 57 (4), 56 (100), 55 (10), 54 (54), 53 (14), 52 (10), 51 (8), 50 (4), 43 (41), 42 (10), 41 (73), 40 (7), 39 (28), 38 (4), 29 (5), 28 (5), 27 (20).
Data of (Z)-hept-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.49 (*dt*, J = 7.8, 10.9, H-C(3)), 5.31 (*dt*, J = 1.3, 10.9, H-C(2)), 2.43 (*qd*, J = 1.3, 7.3, H-C(4)), 1.51-1.29 (*m*, 4H), 0.93 (*t*, J = 6.8, *Me*CH_2).
^{13}C-NMR (100MHz, $CDCl_3$): δ155.23 (*d*, C(3)), 116.96 (*s*, CN), 99.40 (*d*, C(2)), 31.55 (*t*, C(4)), 30.26 (*t*, C(5)), 22.09 (*t*, C(5)), 13.70 (*q*, C(7)).
MS (EI): 109 (1), 108 (3), 94 (7), 81 (6), 80 (7), 69 (12), 68 (13), 67 (76), 66 (6), 65 (4), 64 (4), 57 (4), 56 (100), 55 (9), 54 (55), 53 (18), 52 (13), 51 (10), 50 (5), 43 (49), 42 (12), 41 (82), 40 (8), 39 (30), 38 (5), 29 (6), 28 (6), 27 (23).

Example 3: 4-Methylhex-2-enenitrile

A mixture of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol), distilled 2-methylbutyraldehyde (1.43 g, 16.6 mmol), and distilled pentane (15 ml) was heated for 18 h at reflux, filtered, and concentrated (rotary evaporator at 50 °C without vacuum). FC (pentane) of the crude product (1.2 g) gave a 85:15 mixture of (E/Z)-4-methylhex-2-enenitrile (0.9 g, 50%) having a boiling point of 50 °C at 10 mbar.

Odour description: green, slightly cucumber, slightly fruity, slightly fatty-oily.

Data of (E)-4-methylhex-2-enenitrile:

^{1}H-NMR (400MHz, CDCl$_3$): δ6.63 (*dd*, J = 7.8, 16.4, H-C(3)), 5.32 (*dd*, J = 1.3, 16.4, H-C(2)), 2.23 (br. *hept.t*, J = 1.1, 6.7, H-C(4)), 1.41 (*quint.*, J = 7.3, 2 H-C(5)), 1.05 (*d*, J = 6.7, MeC(4)), 0.89 (*t*, J = 7.4, MeC(5)).

^{13}C-NMR (100MHz, CDCl$_3$): δ161.03 (*d*, C(3)), 117.64 (*s*, CN), 98.25 (*d*, C(2)), 39.25 (*d*, C(4)), 28.42 (*t*, C(5)), 18.37 (*q*, *Me*C(4)), 11.37 (*q*, C(6)).

MS (EI): 109 (1), 108 (1), 94 (3), 81 (8), 80 (20), 69 (6), 68 (25), 67 (13), 66 (7), 65 (4), 56 (100), 54 (22), 53 (24), 52 (10), 51 (8), 42 (12), 41 (22), 39 (14), 29 (7), 28 (3), 27 (10).

Data of (Z)-4-methylhex-2-enenitrile:

^{1}H-NMR (400MHz, CDCl$_3$): δ6.25 (*t*, J = 10.6, H-C(3)), 5.28 (*dd*, J = 0.6, 10.6, H-C(2)), 2.75-2.62 (*m*, H-C(4)), 1.56-1.30 (*m*, 2 H-C(5)), 1.07 (*d*, J = 6.7, MeC(4)), 0.91 (*t*, J = 7.3, MeC(5)).

^{13}C-NMR (100MHz, CDCl$_3$): δ160.38 (*d*, C(3)), 118.41 (*s*, CN), 98.17 (*d*, C(2)), 38.56 (*d*, C(4)), 29.12 (*t*, C(5)), 19.56 (*q*, *Me*C(4)), 11.55 (*q*, C(6)).

MS (EI): 109 (1), 108 (1), 94 (4), 81 (16), 80 (35), 69 (7), 68 (52), 67 (16), 66 (7), 65 (5), 56 (100), 54 (37), 53 (30), 52 (13), 51 (11), 42 (20), 41 (25), 39 (18), 29 (9), 28 (4), 27 (13).

Example 4: 5-Methylhex-2-enenitrile

A mixture of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol), distilled isovaleraldehyde (1.43 g, 16.6 mmol), and distilled pentane (15 ml) was heated for 6.5 h at reflux, filtered, and concentrated (rotary evaporator at 50 °C without vacuum). FC (pentane) of the crude product (2.1 g) gave a 66:34 mixture of (E/Z)-5-methylhex-2-enenitrile (1.0 g, 56%) having a boiling point of 64 °C at 10 mbar.

Odour description: green-fruity, fatty (isovalerianic).

Data of (E)-5-methylhex-2-enenitrile:

^{1}H-NMR (400MHz, CDCl$_3$): δ6.70 (*dt*, J = 7.6, 16.3, H-C(3)), 5.33 (*dt*, J = 1.6, 16.3, H-C(2)), 2.12 (*ddd*, J = 1.5, 6.8, 7.5, 2 H-C(4)), 1.77 (*non.*, J = 6.7, H-C(5)), 0.93 (*d*, J = 6.7, 2 MeC(5)).

^{13}C-NMR (100MHz, $CDCl_3$): δ155.00 (*d*, C(3)), 117.46 (*s*, CN), 100.56 (*d*, C(2)), 42.44 (*t*, C(4)), 27.63 (*d*, C(5)), 22.10 (*q*, 2 *Me*C(5)).
MS (EI): 109 (1), 108 (1), 94 (3), 81 (1), 68 (6), 67 (100), 66 (10), 65 (4), 56 (26), 53 (4), 52 (4), 51 (4), 43 (56), 41 (42), 39 (21), 27 (11).
Data of (Z)-5-methylhex-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.51 (*dt*, J = 7.8, 10.8, H-C(3)), 5.36 (*dt*, J = 1.4, 10.8, H-C(2)), 2.33 (*ddd*, J = 1.3, 6.8, 8.0, 2 H-C(4)), 1.80 (*non.*, J = 6.7, H-C(5)), 0.96 (*d*, J = 6.7, 2 MeC(5)).
^{13}C-NMR (100MHz, $CDCl_3$): δ154.00 (*d*, C(3)), 116.10 (*s*, CN), 100.18 (*d*, C(2)), 40.66 (*t*, C(4)), 27.98 (*d*, C(5)), 22.10 (*q*, 2 *Me*C(5)).
MS (EI): 109 (1), 108 (1), 94 (2), 81 (1), 80 (1), 69 (1), 68 (5), 67 (100), 66 (6), 65 (3), 56 (6), 54 (2), 53 (3), 52 (3), 51 (3), 43 (24), 41 (28), 39 (15), 29 (1), 28 (1), 27 (7).

Example 5: 4-Methylpent-2-enenitrile

A mixture of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol), distilled isobutyraldehyde (1.2 g, 16.6 mmol), and distilled pentane (15 ml) was heated for 18 h at reflux, filtered, and concentrated (rotary evaporator at 50 °C without vacuum). The residue (E/Z 87:13) was then distilled using a Kugelrohr apparatus (ball-to-ball rotary distillation apparatus) at 10 mbar and 50 °C giving two fractions of (E/Z)-4-methylpent-2-enenitrile (first fraction: 0.16 g, 10%, E/Z 83:17; second fraction: 0.32 g, E/Z 91:9, 20%).
Boiling point: 50°C (10 mbar).

Odour description: green, fresh, fruity, slightly cuminic.

Data of (E)-4-methylpent-2-enenitrile:
^{1}H-NMR (400MHz, $CDCl_3$): δ6.71 (*dd*, J = 6.6, 16.4, H-C(3)), 5.28 (*dd*, J = 1.5, 16.4, H-C(2)), 2.48 (*oct.d*, J = 1.6, 6.8, H-C(4)), 1.07 (*d*, J = 6.8, 2 MeC(4)).
^{13}C-NMR (100MHz, $CDCl_3$): δ161.90 (*d*, C(3)), 117.69 (*s*, CN), 97.32 (*d*, C(2)), 32.05 (*d*, C(4)), 20.69 (*q*, 2 *Me*C(4)).
MS (EI): 95 (13), 94 (37), 80 (59), 68 (71), 67 (48), 55 (52), 54 (28), 53 (100), 52 (28), 51 (20), 42 (21), 41 (26), 39 (28), 27 (16).

Data of (Z)-4-methylpent-2-enenitrile:

^{1}H-NMR (400MHz, $CDCl_3$): δ6.31 (*dd*, J = 10.1, 10.9, H-C(3)), 5.21 (*dd*, J = 0.6, 10.9, H-C(2)), 2.92 (*dhept.d*, J = 0.5, 6.7, 10.1 H-C(4)), 1.09 (*d*, J = 6.6, 2 MeC(4)).

^{13}C-NMR (100MHz, $CDCl_3$): δ161.38 (*d*, C(3)), 117.69 (*s*, CN), 96.99 (*d*, C(2)), 31.57 (*d*, C(4)), 21.70 (*q*, 2 *Me*C(4)).

MS (EI): 95 (12), 94 (40), 80 (60), 68 (76), 67 (48), 55 (52), 54 (30), 53 (100), 52 (29), 51 (20), 42 (23), 41 (29), 39 (31), 27 (17).

Example 6: 3-Cyclopropylacrylonitrile

A mixture of (triphenylphosphoranilydene)acetonitrile (5 g, 16.6 mmol), distilled cyclopropanecarboxaldehyde (1.16 g, 16.6 mmol), and distilled pentane (15 ml) was heated for 19 h at reflux, filtered, and concentrated (rotary evaporator at 50 °C without vacuum). The residue was then distilled using a Kugelrohr apparatus (ball-to-ball rotary distillation apparatus) at 10 mbar and 67 °C giving two fractions of (E/Z)-3-cyclopropylacrylonitrile (first fraction: 0.27 g, 18%, E/Z 76:24; second fraction: 0.12 g, 8%, E/Z 85:15) having a boiling point of 67 °C at 10 mbar.

Odour description: green, apple, fruity, slightly fatty.

Data of (E)-3-cyclopropylacrylonitrile:

^{1}H-NMR (400MHz, $CDCl_3$): δ6.13 (*dd*, J = 10.0, 16.0, H-C(3)), 5.36 (*d*, J = 16.0, H-C(2)), 1.64-1.55 (*m*, CH-C(3)), 1.04-0.98 (*m*, 2 H), 0.69-0.64 (*m*, 2 H).

^{13}C-NMR (100MHz, $CDCl_3$): δ159.94 (*d*, C(3)), 117.89 (*s*, CN), 95.88 (*d*, C(2)), 15.49 (*d*, CH-C(3)), 8.91 (*t*, 2 C).

MS (EI): 94 (1), 93 (20), 78 (2), 67 (8), 66 (100), 65 (19), 64 (6), 63 (5), 54 (4), 53 (8), 52 (6), 51 (8), 50 (5), 41 (6), 40 (8), 39 (18), 38 (7), 37 (4), 27 (6).

Data of (Z)-3-cyclopropylacrylonitrile:

^{1}H-NMR (400MHz, $CDCl_3$): δ5.80 (*dd*, J = 10.8, 16.0, H-C(3)), 5.18 (*dd*, J = 0.5, 10.8, H-C(2)), 2.06-1.95 (*m*, CH-C(3)), 1.10-1.05 (*m*, 2 H), 0.70-0.64 (*m*, 2 H).

^{13}C-NMR (100MHz, $CDCl_3$): δ159.25 (*d*, C(3)), 117.83 (*s*, CN), 95.65 (*d*, C(2)), 14.84 (*d*, CH-C(3)), 8.78 (*t*, 2 C).

MS (EI): 94 (1), 93 (21), 78 (2), 67 (8), 66 (100), 65 (18), 64 (6), 63 (5), 54 (4), 53 (7), 52 (6), 51 (8), 50 (5), 41 (6), 40 (8), 39 (19), 38 (7), 37 (4), 27 (6).

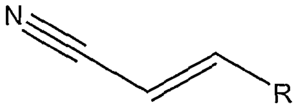
Example 7: A fragrance composition having a green apple accord

Compound / Ingredient	parts by weight 1/1000
Butyl Acetate	20
Geranyl Acetate	10
Hexenyl-3 cis Acetate	3
Hexyl Acetate	50
Nonanyl Acetate	60
Agrumex™ (2-tert-butylcyclohexyl acetate)	140
Cyclal C™ (2,4-dimethyl-3-cyclohexen-1-carbaldehyde)	6
Allyl Cyclo Hexyl Propionate (2-propenyl 3-cyclohexylpropanoate)	8
Delta Damascone	2
Gamma Decalactone	7
Dimyrcetol™ (mixture of 2,6-dimethyl-7octen-2-ol and 2,6-dimethyl-7-octen-2-yl formate)	30
Citronellyl Formate (3,7-dimethyloct-6-enyl formate)	6
Fructone™ (ethyl methyl dioxolane acetate)	50
Geraniol	40
Givescone® (mixture of ethyl 2-ethyl-6,6-dimethyl-2-cyclohexenecarboxylate & ethyl 2,3,6,6-tetramethyl-2-cyclohexenecarboxylate)	5
Ionone Beta	20
Labienoxime (2,4,4,7-tetramethyl-6,8-nonadiene-3-one oxime) 1% solution in mixture of isopropyl myristate and triethyl citrate	3
Linalool (3,7-dimethyl-1,6-octadien-3-ol)	30
Diethyl Malonate	160
Ethyl 2-methylbutyrate	10
Isopropyl 2-methylbutyrate	10
Pharaone (2-cyclohexyl-1,6-heptadien-3-one) 10% in DPG	10
Dipropylene Glycol (DPG)	300
Hex-2-enenitrile	**20**

In this apple accord 2% of hex-2-enenitrile provides a typical green apple volume and makes it more fresh-natural and tasty.

Claims

1. Use as flavour or fragrance ingredient of a compound of formula (I)



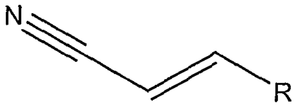
(I)

wherein R is selected from linear, branched C_{3-4} alkyl and C_{3-4} cycloalkyl; and the double bond is in E or Z configuration;

or a mixture thereof.

2. The use according to claim 1 wherein the compound of formula (I) is selected from the group consisting of hex-2-enenitrile, hept-2-enenitrile, 4-methylhex-2-enenitrile, 5-methylhex-2-enenitrile, 4-methylpent-2-enenitrile and 3-cyclopropylacrylonitrile.

3. A fragrance composition comprising a compound of formula (I)

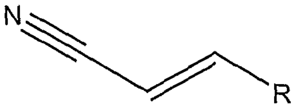


(I)

wherein R is selected from linear, branched C_{3-4} alkyl and C_{3-4} cycloalkyl; and the double bond is in E or Z configuration;

or a mixture thereof; and a base material.

4. A method of manufacturing a fragrance composition, comprising incorporating a compound of formula (I)



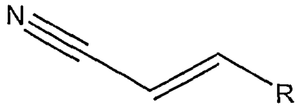
(I)

wherein R is selected from linear, branched C_{3-4} alkyl and C_{3-4} cycloalkyl; and the double bond is in E or Z configuration;

or a mixture thereof;

into a base material.

5. A method of improving, enhancing or modifying a fragrance application through the addition of an olfactory acceptable amount of a compound of formula (I)



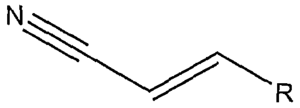
(I)

wherein R is selected from linear, branched C_{3-4} alkyl and C_{3-4} cycloalkyl; and the double bond is in E or Z configuration;

or a mixture thereof.

6. A method according to claim 4 or claim 5 wherein the fragrance application is selected from the group consisting of perfumes, household products, laundry products, body care products and cosmetics.

7. A compound of formula (I)



(I)

wherein R is 1-methylprop-1-yl; and the double bond is in E or Z configuration;

or a mixture thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/CH2007/000472

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61K8/40 C07C255/07 C07C255/31 C11B9/00 A61Q13/00

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)
A61K C07C C11B A61Q

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, WPI Data, BEILSTEIN Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 395 982 A (BASF AG [DE]) 7 November 1990 (1990-11-07) the whole document	1-7

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☒ Further documents are listed in the continuation of Box C.

☒ 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

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"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 19 November 2007	Date of mailing of the international search report 31/01/2008
Name and mailing address of the ISA/ 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	Authorized officer Cooper, Simon

INTERNATIONAL SEARCH REPORT

International application No
PCT/CH2007/000472

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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PCT/CH2007/000472

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