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(54) **Fragrance composition comprising a mixture of nitriles**

(57) The present invention relates to a fragrance composition comprising a mixture (9E)-undecenitrile,

(9Z)-undecenitrile and 10-undecenitrile, which can be combined with additional fragrance ingredient and which is useful in perfumery.

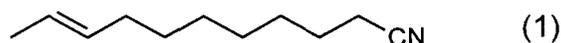
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Description

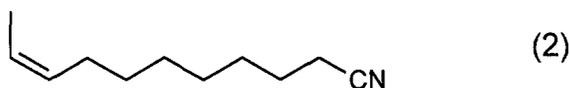
[0001] The present invention relates to fragrance compositions comprising a mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile, their use as well as a method for preparing scented consumer products containing said mixture.

[0002] Aldehydes with hesperidic and floral notes are important perfumery ingredients. Examples for such aldehydes are e.g. octanal, nonanal, decanal, undecanal, 10-undecenal and citral. However, these aldehydes are readily affected under oxidizing conditions or solutions having a pH lower than 5 or higher than 9. Under these conditions the above mentioned aldehydes are chemically modified and therefore lose their fragrance characteristics and/or generate additional off notes.

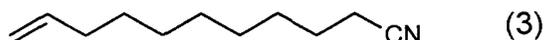
Nitriles such as (9E)-undecenitrile (1)



(9Z)-undecenitrile (2)



and 10-undecenitrile (3)



are already described in literature. Zhu et al. describe the synthesis of (9E)-undecenitrile (1) by oxidative addition of functionalized organozinc compounds with allylic halide mediated (Zhu L. et al., *J. Org. Chem.* **1991**, 56, 1445). In *Tetrahedron* **1999**, 55, 63 (9Z)-undecenitrile (2) has been described as an intermediate in the synthesis of pyridinoline. Miyaura et al. used 10-undecenitrile (3) as starting material for a Palladium catalyzed cross coupling reaction (Miyaura, N. et al., *J. Am. Chem. Soc.* **1989**, 111, 314). Further a mixture of 3-methyl-5-phenyl-pentanenitrile and 3-methyl-5-cyclohexyl-pentanenitrile is disclosed in WO 99/26601.

[0003] The use of other nitriles such as decanonitrile, dodecanonitrile, tetrahydrogeranonitrile, Geranonitrile (3,7-dimethyl-2,6-octadienenitrile) and Lemonile® (3,7-dimethyl-2(3),6-nonadienenitrile) is established in perfumery. These compounds are less affected under strong acid, basic and/or oxidizing conditions than aldehydes and they exhibit aldehydic and hesperidic notes with floral aspects which are similar to those of the above mentioned aldehydes. However, a harsh, metallic odor appears as concomitant of these nitriles, which confers a "synthetic" and "dirty, fatty" aspect to the compositions they are applied to.

[0004] An object of the present invention is to provide a fragrance composition which has a fresh sparkling, floral, fruity and warm odor and a high stability under aggressive alkaline conditions.

[0005] Further it is an object of the present invention to provide a fragrance composition which has a fresh sparkling, floral, fruity and warm odor and a high stability under aggressive acidic conditions.

[0006] It is further object of the present invention to provide a fragrance composition which has a fresh sparkling, floral, fruity and warm odor and a high stability under aggressive oxidative conditions.

[0007] The present invention relates to a fragrance composition comprising a mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile.

[0008] Surprisingly, it has been found that mixtures of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile have a well balanced fresh, sparkling floral, fruity and warm odor and do not have the typical greasy, fatty character of nitriles. These mixtures also exhibit a very nice natural and lactonic aspect which is new for nitriles compositions. Additionally, mixtures of the present invention exhibit an astonishing olfactory stability in hostile media. Mixtures of the present invention are characterized by their outstanding stability under aggressive acidic, alkaline and/or oxidizing conditions, by their excellent diffusive and pleasant odor and especially by lacking the greasy, fatty character of other nitriles. In many aspects the compositions of the present invention are better than the current benchmark compound decanonitrile and are therefore preferred.

[0009] The mixture comprised in the fragrance composition of the present invention as well as the fragrance com-

position according to the present invention may be used alone or in combination with numerous fragrance ingredients of natural and/or synthetic origin. The range of the natural fragrances includes in addition to volatile, also moderately and only slightly volatile components. The synthetic fragrance ingredients belong to practically all classes of fragrant substances. Examples for such natural and synthetic ingredients are listed e.g. in "Perfume and Flavor Materials of Natural Origin", S. Arctander, Ed., Elizabeth, N.J., 1960 and "Perfume and Flavor Chemicals", S. Arctander, Ed., Vol. I & II, Allured Publishing Corporation, Carol Stream, USA, 1994.

[0010] To the mixture comprised in the fragrance composition according to the present invention an additional fragrance ingredient can be added. A fragrance ingredient is defined as a substance with olfactory characteristics. Such an additional fragrance ingredient may consist of one or several ingredients. The compositions of the present invention harmonize particularly well with additional fragrance ingredients such as fresh, hesperidic notes (lemon, mandarin, etc.), fruity accords (peach, apricot, etc.), floral notes (lily of the valley, rose, iris, jasmine, ylang-ylang, narcissus notes, etc.), green and agrestic notes (galbanum, tagete, lavender, thyme, ect).

[0011] (9E)-undecenitrile is the major compound in these mixture comprised in the fragrance composition according to the present invention, comprising more than 30% by weight of it. Preferably, the said mixture comprises between about 30% and about 80% of (9E)-undecenitrile, more preferably between about 40% and about 60%. In a preferred embodiment 10-undecenitrile is the minor component in said mixture, comprising less than 40% by weight of it. Preferably, said mixture comprises 10-undecenitrile between about 0.01% and about 30%, more preferably between 5% and 20%.

[0012] Due to the excellent odor and application qualities, the compositions of the present invention are excellent for use in any field of perfumery, especially in functional perfumery. Consumer products with a non-hostile or a hostile media comprising a fragrant composition according to the present invention as well as an additional ingredient are preferred. Consumer products with a non-hostile media include alcoholic solutions, shampoos, hair conditioners, bath oils, air freshners, cosmetics and skin care products. Consumer products with aggressive alkaline media include soaps, laundry detergents, bleaches, automatic dishwashing powders, scouring powders. Consumer products with aggressive acidic media include fabric softeners, deodorants, antiperspirants and cleaners containing citric acid, hydrochloric acid, sulfonic acid or phosphoric acid. Consumer products with aggressive oxidizing media include hair colorants and bleaches.

[0013] The amount of fragrant compositions of the present invention, alone or in combination with other fragrance ingredients, varies depending on the nature of the product, and the intensity of the desired odor. These factors are known to those skilled in the art. Preferably the compositions of the present invention are present in the range of 0.01% to 1% in the product.

[0014] As apparent from the above examples, the compositions of the present invention can be used in a variety of cleansing products for household and commercial applications, including bleaches, laundry detergents, dishwasher detergents, stain removers, scouring agents, fabric softeners, soaps, all purpose and special cleaners, in various forms including liquids, gels, sprays, bars sticks and powders.

[0015] The fragrance compositions according to the present invention can be obtained either by a one-pot reaction from a mixture of the corresponding aldehydes or by mixing the purified nitriles (1)-(3), obtained from the pure corresponding aldehydes. It is not necessary but possible to purify the aldehyde mixture before starting the one-pot reaction.

[0016] The scented consumer products for functional perfumery are prepared by admixing the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile, other optional fragrance ingredients, liquid and/or solid ingredients as well as a medium.

[0017] The invention will be further described in the following examples, by way of illustration.

Example 1

(E,Z)-9-Undecenitrile

a) (E,Z)-9-Undecenal oxime

[0018] To a solution of hydroxylamine hydrochloride (125.2 g, 1.8 mol) and sodium acetate (118.0 g, 1.44 mol) in H₂O (480 ml) is added rapidly Aldehyde Iso C11 [(E,Z)-9-undecenal, 201.6 g, 1.2 mol, origin: Givaudan SA, Vernier, Switzerland] and then methanol (170 ml). The mixture is heated for 3 h to 60° C, allowed to cool to room temperature and diluted with hexane (600 ml). The organic solution is washed 1x with saturated NaHCO₃ solution (300 ml), 2x with H₂O (500 ml each), dried over MgSO₄ and concentrated in vacuo to give a crystalline solid (225 g) which is directly used in the next step. Yield: quantitative.

b) (E,Z)-9-Undecenitrile

[0019] The reaction flask is charged with acetic anhydride (612 g, 6 mol) and heated to 120°C. A solution of (E,Z)-9-undecenal oxime (225 g, 1.2 mol) in toluene (890 ml) is added slowly over a period of 2.5 h. The reaction mixture is kept at reflux temperature for 4 h, cooled to room temperature and diluted with hexane (600 ml). The organic solution is washed 3x with H₂O (800 ml each), 3x with 5N NaOH (300 ml each) and 3x with brine (600 ml each), dried over MgSO₄ and concentrated in vacuo to give a yellowish oil (217 g). Distillation over a 25 cm Widmer column (87°C/0.05 mbar) afforded (E,Z)-9-undecenitrile (124.8 g; 63%, 2 steps) in form of a colorless oil. The product comprises (9E)-undecenitrile: 56%, (9Z)-undecenitrile 26% and 10-undecenitrile 8%.

¹H-NMR (400 MHz, CDCl₃): 1.22-1.40 (m, 6H); 1.40-1.50 (m, 2H); 1.58-1.70 (m, 5H); 1.93-2.14 (m, 2H); 2.33 (t, J = 7.1 Hz, 2H); 5.33-5.48 (m, 2H).

MS [m/z (EI)]: 165 (M⁺, 1), 136 (48), 122 (61), 69 (41), 55 (100), 41 (56).

Example 2

[0020] Stability of the perfumery material of the invention in liquid bleach.

[0021] A mixture of the perfumery material of the invention, obtained according to example 1, was added at 0.15 % to a liquid bleach solution composed of 5% by weight of sodium hypochlorite and 95% by weight of water, adjusted to a pH of about 11.5 to 12.0 by the addition of sodium hydroxide (sample I). A similar mixture was prepared with decanonitrile as control experiment (sample IV). The odor of both solutions were then evaluated by a panel of 14 perfumers. Both solutions were then divided into two aliquots, which were stored for 1 month at 4° C (samples II and V) and 37° C (samples III and VI), respectively. All solutions were then again assessed olfactorily by a panel of 14 perfumers. Furthermore, the content of free chlorine was determined for all samples by titration according to standard procedures known to a person skilled in the art, e.g. as described by Fritz et al., Quantitative Analytical Chemistry, 2nd Ed. (1969), 101-118, 239-284.

[0022] The data in the table below show that the tested mixture of the compounds of the invention is chemically acceptably stable, comparable to the stability of the benchmark compound decanonitrile. It is also clear from the data that the mixture is olfactorily stable and the odor is perceived much more stronger and diffusive than an equal amount of decanonitrile. All 14 perfumers preferred the solution comprising the mixture of the invention for being nicely citrusy, floral/fruity over decanonitrile which was perceived citrusy, greasy/fatty.

Table 1:

Chemical Stability				
Sample	Composition	Active fresh	Chlorine 30d/0°C	Content [%] 30d/37°C
I	mixt. of example 1, 0.15%	4.04	-	-
II	mixt. of example 1, 0.15%	-	3.73	-
III	mixt. of example 1, 0.15%	-	-	2.82
IV	decanonitrile, 0.15%	4.02	-	-
V	decanonitrile, 0.15%	-	3.81	-
VI	decanonitrile, 0.15%	-	-	3.16

Table 2:

Olfactory Stability			
Sample	Stability ¹⁾	Olfactory description	Bleach coverage
I	+++	citrusy, floral/fruity	good, preferred over IV
II	+++	citrusy, floral/fruity	good, preferred over V
III	+++	citrusy, floral/fruity	good, preferred over VI
IV	+++	citrusy, fatty/greasy	good, more greasy fatty than I
V	++	citrusy, fatty/greasy	good, more greasy fatty than II
VI	++	citrusy, fatty/greasy	good, more greasy fatty than III

¹⁾ Olfactory Stability: +++ = stable; ++ = acceptably stable, slight change; + = unstable, not disagreeable; - = unstable, off-odor.

Example 3**[0023]** Citrus fragrance composition for a bleach containing consumer product

Ingredients	Parts per weight	
	(+)	(-)
Agrumex	14.0	14.0
Amberketal, 10% in IPM ¹⁾	0.4	0.4
Ambrofix ¹⁾	0.4	0.4
Clonal	2.0	2.0
Cumin nitrile	0.1	0.1
Damascone alpha ²⁾	0.4	0.4
Dihydromyrcenol	25.0	25.0
Diphenyl oxide	10.0	10.0
Dipropylene glycol	24.0	25.0
Ethyl vanilline ²⁾	0.4	0.4
Eucalyptol	3.0	3.0
Fenchyl alcohol	0.5	0.5
Fructose	0.5	0.5
Irisantheme	2.0	2.0
Rhubafuran	0.5	0.5
Rosalva	0.8	0.8
Tetrahydro linalool	15.0	15.0
(E,Z)-9-undecenitrile ³⁾	1.0	0
Total	100	100

¹⁾ at 10% in MIP.²⁾ at 10% in DPG.³⁾ Mixture prepared as described in example 1.

[0024] The presence of (E,Z)-9-undecenitrile with its fresh, sparkling floral, fruity and warm odor gives richness, volume and a lot of diffusion power to the fragrance. It nicely promotes the rosy note of this accord, adds a touch of a fruity/peach aspect and its character reminiscent of "Aldehyde Iso C11" makes the fragrance more perfumistic in the classical "Floral Aldehydic" tradition.

Claims

1. A fragrance composition comprising a mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile.
2. Fragrance composition according to claim 1 comprising an additional fragrance ingredient.
3. Fragrance composition according to any of the preceding claims comprising an additional ingredient with fresh hesperic notes.
4. Fragrance composition according to any of the preceding claims comprising additional ingredients with fruity accords.
5. Fragrance composition according to any of the preceding claims comprising additional ingredients with floral notes.
6. Fragrance composition according to any of the preceding claims comprising additional ingredients with green agrestic notes.
7. Fragrance composition according to any of the preceding claims, wherein the mixture of (9E)-undecenitrile,

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(9Z)-undecenitrile and 10-undecenitrile comprises at least 30% by weight of (9E)-undecenitrile.

- 5
8. Fragrance composition according to any of the preceding claims, wherein the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile comprises 40% to 60% by weight of (9E)-undecenitrile.
- 10
9. Fragrance composition according to any of the preceding claims, wherein the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile comprises less than 40% by weight of 10-undecenitrile.
10. Fragrance composition according to any of the preceding claims, wherein the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile comprises 0.01% to 30% by weight of 10-undecenitrile.
11. Fragrance composition according to any of the preceding claims, wherein the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile comprises 5% to 20% by weight of 10-undecenitrile.
- 15
12. Consumer products comprising a fragrance composition according to any of the preceding claims having neutral characteristics.
13. Consumer products comprising a fragrance composition according to any of the preceding claims having aggressive acidic characteristics.
- 20
14. Consumer products comprising a fragrance composition according to any of the preceding claims having aggressive oxidizing characteristics.
- 25
15. Consumer products comprising a fragrance composition according to any of the preceding claims having aggressive alkaline characteristics.
16. Consumer product comprising 0.01 to 1% of a fragrance composition according to any of the preceding claims.
- 30
17. Use of a fragrance composition according to any of the preceding claims in perfumery.
18. Use of a fragrance composition according to claim 17 in functional perfumery.
- 35
19. Method for preparing scented consumer products for functional perfumery by admixing the mixture of (9E)-undecenitrile, (9Z)-undecenitrile and 10-undecenitrile obtained by a one-pot reaction, another optional fragrance ingredient, liquid and/or solid ingredients as well as a medium.
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European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 01 11 6983

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	US 3 325 369 A (W.T. SOMERVILLE AND ALL) 13 June 1967 (1967-06-13) * column 1, line 56 - line 63 * ---	1-19	A61K7/46 C11B9/00 C07C255/07
Y	ARCTANDER: "Perfume and flavor chemicals" , S. ARCTANDER. , MONCLAIR, USA XPO02155807 * examples 839, ,3035, ,3034 * ---	1-19	
A	US 5 892 092 A (GROSCHE GEORG HEINRICH ET AL) 6 April 1999 (1999-04-06) * the whole document * ---	1-19	
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A	US 5 888 962 A (PAGANO ALEX R ET AL) 30 March 1999 (1999-03-30) * abstract * ---	1-19	
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
			A61K C11B C07C
Place of search	Date of completion of the search	Examiner	
THE HAGUE	25 October 2001	Dauksch, H	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

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