

31 May 2000

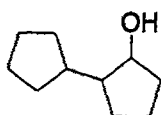
Cyclopentylalkyl-nitriles

The present invention refers to new cyclopentylalkyl-nitriles and to the use of odoriferous cyclopentylalkyl derivatives as fragrances.

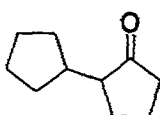
5

Despite the common occurrence of five-membered carbon rings in perfumery ingredients, mainly of terpenic origin (e. g. campholenic aldehyde derivatives of sandalwood-type odor note) or resulting from a Diels-Alder condensation with inexpensive cyclopentadiene, very few of them contain an unsubstituted, isolated (i. e. not making part of a polycyclic fused or spiro system) cyclopentyl, cyclopentenyl or cyclopentylidene radical. The following products figure among the few examples of such perfumery raw materials:

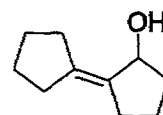
15



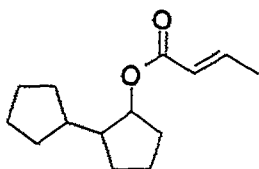
CAS 4884-25-7



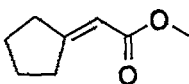
CAS 4884-24-6



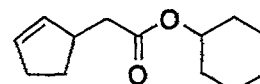
CAS 6261-30-9



20 CAS 68039-73-6



CAS 40203-73-4



CAS 65405-69-8

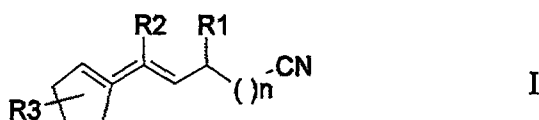
These compounds are also described in EP 0 016 650, EP 0 770 671 and DE 2 729 121.

25

There is a renewed interest in floral fragrances. Therefore, the object of the present invention is to

provide new perfumery ingredients exhibiting original, intense, diffusive and substantive (i. e. long-lasting) scents belonging to the floral family.

5 It has been found that new compounds of formula I,

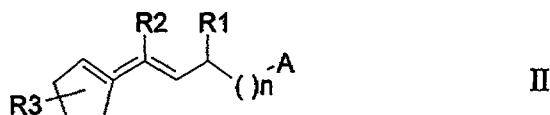


wherein

- 10 R^1 , R^2 and R^3 are independently H, C_{1-3} alkyl but R^1 and R^2 are not at the same time H;
 R^2 can also be methylene or ethylidene;
 $n = 0$ or 1 and
 --- stands for a single or a double bond, whereby
 15 maximum 2 double bonds are present

possess very intense, mainly rosy and orris notes.

20 It has further been found that compounds of formula II,



wherein

- 25 A is selected from the group of CR^4R^5OH ,
 $CR^4R^5OC(O)R^6$, CO_2R^6 , CN and $C(O)R^4$;
 R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are independently H or
 C_{1-3} -alkyl;
 R^2 can also be methylene or ethylidene;
 30 R^6 can also be a C_{2-4} alkenyl or alkynyl
 $n = 0$ or 1 and

This Sheet Has Been Replaced



--- stands for a single or a double bond, whereby maximum 2 double bonds are present

possess interesting olfactory properties. The odors are
5 mainly floral, e.g. lily of the valley, orris or ylang-ylang and fruity, e.g. citrus. They are intense, diffusive and long lasting. All compounds of the general formula II have substantive odors, a quality crucial for functional perfumery.

10

The heteroatoms in all compounds of formula I and II are in a more remote position relative to the lipophilic cyclopentane ring, than the oxygen atoms in the corresponding known perfumery ingredients.

15

The compounds of formula II may be used to impart odor to any perfumery composition such as fine and functional perfumery, e.g. perfume, fine fragrance accord or detergent, fabric softener, shower gel, soap, cosmetics,
20 scented candle, etc.

The compounds of formula I are new. The following compounds of formula II are also new:

25

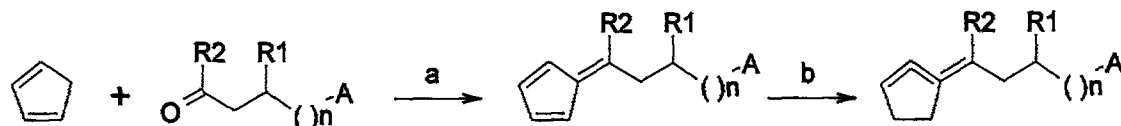
5-Cyclopentyl-3-methylpent-4-en-1-ol
5-Cyclopentyl-3-methylpent-4-enal
5-Cyclopentyl-3-methylpent-4-en-1-yl acetate
5-Cyclopentyl-3-methylpentan-1-ol
4-Cyclopentylpentan-1-ol
30 4-Cyclopentylpent-1-yl propanoate
4-Cyclopentylpentanal
Ethyl-4-cyclopentylpentanoate
5-Cyclopentylhexan-2-one

- 5-Cyclopentylhexanal
- 5-Cyclopentylhexan-1-ol
- 5-(2-Methylcyclopent-1-enyl)pentan-1-ol
- 5-(5-Methylcyclopent-1-enyl)pentan-1-ol
- 5 4-Cyclopentylidenebutan-1-ol
- 6-Cyclopentyl-3-methylhexan-3-ol
- 5-(Cyclopent-1-enyl)-2-methylpentan-2-ol
- 5-Cyclopentylpentan-2-ol
- 5-Cyclopentylidene-2-methylpentan-2-ol
- 10 5-Cyclopentylidenepent-2-yl propanoate

The following compounds of formula I are preferred:

- 5-Cyclopentyl-3-methylpentanenitrile
- 15 4-Cyclopentylpentanenitrile
- 5-Cyclopentylhexanenitrile
- 5-Cyclopentylidenehexanenitrile
- 5-(Cyclopent-1-enyl)hexanenitrile

- 20 The compounds of general formulae I and II can be advantageously prepared by different synthetic ways. Thereby, the five-membered ring is introduced with commercially available starting materials (cyclopentanone, cyclopentadiene, cyclopentylhalogenide and derivatives)
- 25 or, built e.g. via 1,4-dihalogenobutane derived Grignard reagent addition to lactones. Among the best methods of synthesis of functionalized cyclopentyl-, cyclopentenyl- or cyclopentylidene-alkanes figures the cyclopentadienyl anion addition to carbonyl group, followed by a total or
- 30 partial hydrogenation of the thus formed fulvene structure, as depicted in scheme I (e. g. Coe, J.; Vetelino, M. G.; Kemp, D. S. *Tetrahedron Lett.* **1994**, 35, 6627.).



5

a) piperidine; b) hydrogenation

Scheme 1

10

The odorants of formula II may be combined with numerous odorant ingredients of natural and/or synthetic origin, whereby the range of the natural odorants can include not only readily volatile, but also moderately and only slightly volatile components, and the synthetic ones can embrace representatives from practically all classes of substances. The following list comprises examples of known odorants which may be combined with the compounds of the invention:

20

natural products: such as tree moss absolute, basil oil, tropical fruit oils (such as bergamot oil, mandarine oil, etc.), mastix absolute, myrtle oil, palmarosa oil, galbanum oil, patchouli oil, petitgrain oil, wormwood oil, lavender oil, rose oil, jasmine oil, ylang-ylang oil, etc.;

25

alcohols: such as farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol, (Z)-hex-3-en-1-ol, menthol, α -terpineol, etc.;

30

This Sheet Has Been Replaced



-aldehydes: such as citral, α -hexyl cinnamaldehyde, Lilial® (Givaudan Roure), hydroxycitronellal, methylnonylacet-aldehyde, phenylacetaldehyde, anisaldehyde, vanillin, etc.;

5

ketones: such as allylionones, α -ionone, β -ionone, Isoraldeine® (Givaudan Roure), methylionone, verbenone, nootkatone, geranylacetone, etc.;

- 10 esters: such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, cis-3-hexenyl isobutyrate, cis-3-hexenyl salicylate, linalyl acetate, methyl
15 dihydrojasmonate, styrallyl propionate, vetiveryl acetate, benzyl acetate, geranyl acetate, etc.;

lactones: such as γ -undecalactone, δ -decalactone, pentadecanolide, 12-oxahexadecanolide, etc.;

20

acetals: such as Viridine (phenylacetaldehyde dimethylacetal), etc.;

- various components: often used in perfumery such as
25 indole, p-mentha-8-thiol-3-one, methyleugenol, eugenol, anethol, etc..

- The novel odorants harmonize particularly well with all other floral notes (lily of the valley, rose, orris,
30 jasmine, ylang-ylang, narcissus notes, etc.), as well as with woody, chypre and animalic notes, tobacco like and patchouli compositions, etc..

The percentage in which they are used in composition may vary within wide limits ranging from a few parts per thousand in mass market products (e.g. cleaning, 5 deodorant) up to a few percent in alcoholic extracts for (fine) perfumery. In all cases, even in small amounts, they provide odorant compositions with intense floral notes and increase the volume (strength, diffusivity) and the substantivity of the odor. In particular, the manner 10 in which they extend the diffusivity and the olfactory duration of the composition is remarkable.

There is really no restriction regarding the type of formulations and the destination of the actual finished 15 product thus, eau de cologne, toilet water, scented water, perfume, cream, shampoo, deodorant, soap, detergent powder, household cleaner, fabric softener, etc., come into consideration.

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

Convenient methods for preparing the compounds of the invention are outlined in the examples without limiting 25 the invention thereto.

All compounds were unambiguously identified by their ¹H-NMR-, IR- and MS-spectra that were measured under the following conditions:

30

- IR: Nicolet 510 FT-IR; neat ; ν in cm^{-1} ,
- ^1H NMR: Bruker DPX-400; at 250 and 400 MHz; in CDCl_3 if not otherwise stated; chemical shifts (δ) in ppm downfield from TMS; coupling constants J in Hz,
- 5 - MS and GC/MS: Finnigan MAT 212 (EI, 70eV); intensities (in brackets) in % rel. to the base peak.

They were always purified by fractional distillation, or bulb-to-bulb distillation if after flash chromatography
 10 (Merck silica gel 60; 230 - 400 mesh), and were olfactorily pure, colorless oils.

Example 1

15

5-Cyclopentyl-3-methylpent-4-en-1-ol

A solution of ethyl 5-cyclopentyl-3-methylpent-4-enoate (16.8 g; 80 mmol; obtained according to Streinz, L.;
 20 Romanuk, M.; Sorm, F.; Sehnal, F. DE 2 444 837, priority 20.09.1973) in diethyl ether (30 ml) was added dropwise to a suspension of lithium aluminum hydride (3.0 g; 80 mmol) in the same solvent (110 ml), and the reaction mixture was stirred at reflux for 1 h. Water (3.5 ml), then 15% NaOH
 25 solution and again water (3.5 ml) were added, the precipitate filtered off and washed with MTBE (30 ml). The combined organic phases were washed with 1 N HCl (200 ml) and brine (3 x 100 ml), dried (MgSO_4), concentrated in vacuo, and distilled (79-82°C/0.07 torr) to give 7.8 g
 30 (59 % yield) of 5-cyclopentyl-3-methylpent-4-en-1-ol.

IR: 3329, 2953, 2869, 1453, 1373, 1052, 999, 969. ^1H -NMR: 0.98 (δ , $J = 6.7$, 3H), 1.16-1.40 (m , 2H), 1.46-1.82 (m , 9H), 2.12-2.28 (m , 1H), 2.26-2.47 (m , 1H), 3.64 (t , $J =$

6.6, 2H), 5.25 (dd, $J = 15.3, 7.3$, 1H), 5.41 (dd, $J = 15.3, 7.0$, 1H). MS: 168 (1.3, M^+), 150 (3), 135 (8), 121 (9), 108 (8), 107 (9), 95 (64), 93 (31), 82 (63), 81 (93), 79 (40), 69 (35), 67 (100), 55 (59), 41 (57).

5

Odor: floral, fruity, hesperidic/citrus, very strong and substantive.

10 Example 2

5-Cyclopentyl-3-methylpent-4-enal

Diisobutylaluminum hydride (95 ml of 1.0 M solution in
 15 hexane) was added into a hexane (200 ml) solution of ethyl
 5-cyclopentyl-3-methylpent-4-enoate (used in example 1;
 20.0 g; 95 mmol), at -65°C . After 3 h stirring at the same
 temperature, ethanol (3 ml) was added, and the reaction
 mixture was poured into an ice-cold NH_4Cl solution (200
 20 ml) and diluted with 2 N HCl (100 ml). The organic layer
 was separated, washed with brine (3 x 200 ml), dried
 (MgSO_4), concentrated in vacuo, and purified by flash
 chromatography (hexane/MTBE 15 :1) to give 10.9 g (69 %
 yield) of 5-cyclopentyl-3-methylpent-4-enal.
 25 IR: 2954, 2870, 2716, 1727, 1453, 1375, 970. ^1H -NMR: 1.06
 (d, $J = 7.0$, 3H), 1.12-1.36 (m, 2H), 1.44-1.83 (m, 6H),
 2.25-2.49 (m, 3H), 2.61-2.81 (m, $J = 6.7$, 1H), 5.32 (dd,
 $J = 15.4, 6.1$, 1H), 5.44 (dd, $J = 15.4, 6.4$, 1H), 9.71 (t,
 $J = 2.3$, 1H). MS: 166 (1.5, M^+), 151 (3), 148 (3), 122
 30 (61), 107 (15), 98 (43), 97 (57), 95 (44), 93 (64), 81
 (63), 80 (36), 79 (47), 69 (47), 67 (100), 55 (71), 41
 (88), 39 (41).

Odor: aldehydic, citrus, geranium.

Example 3

5

5-Cyclopentyl-3-methylpent-4-en-1-yl acetate

Acetyl chloride (1.7 g; 22 mmol) was added to a cooled solution of 5-cyclopentyl-3-methylpent-4-en-1-ol (obtained
10 in example 1; 2.6 g; 15 mmol), pyridine (2.4 g; 30 mmol), and DMAP (0.13 g; 0.1 mmol) in cyclohexane (65 ml). After 3 h stirring at r.t., the reaction mixture was poured into 1N HCl (130 ml) and MTBE (65 ml). The organic layer was separated, washed successively with 1N HCl (130ml), sodium
15 bicarbonate solution (100 ml) and brine (2 x 100 ml) and treated as in example 1 (distillation at 120°C/0.8 torr) to give 3.05 g (94 % yield) of 5-cyclopentyl-3-methylpent-4-en-1-yl acetate.

IR: 2954, 2869, 1743, 1454, 1366, 1238, 1048, 970. ¹H-NMR:
20 0.99 (d, J = 6.7, 3H), 1.13-1.34 (m, 2H), 1.44-1.83 (m, 8H), 2.04 (s, 3H), 2.08-2.30 (m, J = 7.0, 1H), 2.26-2.47 (m, 1H), 4.05 (t, J = 6.8, 2H), 5.20 (dd, J = 15.4, 7.3, 1H), 5.37 (dd, J = 15.4, 7.0, 1H). MS: 195 (0.1, M⁺ - CH₃), 150 (10), 135 (13), 121 (18), 108 (13), 107 (11), 95 (18),
25 93 (29), 82 (22), 81 (100), 80 (23), 79 (25), 67 (43), 55 (28), 41 (27).

Odor: fruity, pear, pineapple, floral.

30

Example 45-Cyclopentyl-3-methylpentan-1-ol

5 Ethyl 5-cyclopentyl-3-methylpent-4-enoate of example 1
 (22.4 g; 0.11 mol) was hydrogenated over 5% Pd/C in
 ethanol (220 ml), at r.t. and under atmospheric pressure.
 The catalyst was filtered off, the solvent evaporated in
 vacuo and the residue distilled (59°C/0.08 torr) to give
 10 19.5 g (92% yield) of 5-cyclopentyl-3-methylpentanoate
 that was reduced with lithium aluminum hydride as in
 example 1 to give 5-cyclopentyl-3-methylpentan-1-ol in
 76.5% yield.

IR: 3331, 2949, 2867, 1454, 1377, 1059, 1010. ¹H-NMR: 0.89
 15 (d, *J* = 6.4, 3H), 0.97-1.84 (m, 17H), 3.68 (m, 2H). MS:
 152 (0.4, *M*⁺ - H₂O), 137 (11), 124 (21), 123 (16), 110
 (12), 109 (14), 95 (85), 82 (100), 71 (28), 69 (72), 67
 (77), 55 (77), 41 (51).

20 Odor: very strong, rosy, geranium, woody.

Example 525 5-Cyclopentyl-3-methylpentanenitrilea) 5-Cyclopentyl-3-methylpentanal oxime

An aqueous (7 ml) solution of hydroxylamine hydrochloride
 (3.9 g; 56 mmol) was added to an ethanolic (20 ml)
 30 solution of 5-cyclopentyl-3-methylpentanal (8.0 g; 47
 mmol), obtained from ethyl 5-cyclopentyl-3-methyl-
 pentanoate of example 4 by diisobutylaluminum hydride
 reduction according to example 2 (73% yield). The reaction

mixture was heated to 50°C and treated with a solution of sodium hydroxide (2.7 g; 67 mmol) in water (5 ml). After 2 h stirring at r.t., ice (25 g) was added, and the mixture was saturated with carbon dioxide (solid). The organic layer was separated, dried (MgSO₄), concentrated in vacuo, and purified by flash chromatography (MTBE/hexane 1:4) to give 5.8 g (67% yield) of 5-cyclopentyl-3-methylpentanal oxime.

10 b) 5-Cyclopentyl-3-methylpentanenitrile

5-cyclopentyl-3-methylpentanal oxime (3.7 g; 20 mmol) and acetic anhydride (4.5 g; 40 mmol) were heated at 110°C during 1.5 h, poured into ice-water (100 ml), and extracted with MTBE (150 ml). The organic phase was washed with brine (4 x 150 ml), dried (MgSO₄), concentrated in vacuo, and purified by flash chromatography (MTBE/hexane 1:15) to give 1.9 g (57% yield) of 5-cyclopentyl-3-methylpentanenitrile.

IR: 2950, 2866, 2246, 1457, 1425, 1384. ¹H-NMR: 1.06 (d, J = 6.7, 3H), 1.25-1.91 (m, 14H), 2.22 (dd, J = 16.7, 6.3, 1H), 2.33 (dd, J = 16.7, 6.0, 1H). MS: 165 (0.5, M⁺), 164 (5), 150 (12), 136 (23), 124 (100), 122 (26), 109 (14), 97 (27), 94 (19), 83 (14), 82 (15), 69 (48), 68 (45), 55 (66), 41 (88).

25

Odor: citrus, geranitrile, peach, rosy.

Example 6

30

4-Cyclopentylpentan-1-ol

a) 4-Cyclopentylpentanoic acid

4-Cyclopenta-2,4-dienylidenepentanoic acid (25 g; 0.15 mol; obtained according to Coe, J. W.; Vetelino, M. G.; Kemp, D. S., *Tetrahedron Lett.*, **1994**, 35, 6627.) in ethyl acetate (270 ml) was hydrogenated as in example 4 to give 23.6 g (92% yield) of crude 4-cyclopentylpentanoic acid which was used in the next step without further purification.

10

b) 4-Cyclopentylpentan-1-ol

A solution of 4-cyclopentylpentanoic acid (16 g; 94 mmol) in diethyl ether (30 ml) and THF (30 ml) was added within 20 min. to lithium aluminum hydride (3.6 g; 94 mmol) suspended in the same solvent (100 ml). After 2 h at reflux, the reaction mixture was cooled with an ice-bath and quenched successively with water (4 ml), 15% sodium hydroxide (12 ml) and again water (4 ml). The white solid was filtered off, and the mixture diluted with MTBE (300 ml), washed with 1 N HCl (300 ml), sodium bicarbonate solution (300 ml) and brine (2 x 300 ml), dried (MgSO₄), concentrated in vacuo, and distilled (59°C/0.075 torr) to give 8.7 g (59 % yield) of 4-cyclopentylpentan-1-ol.

IR: 3329, 2950, 2867, 1451, 1377, 1056, 894. ¹H-NMR: 0.88 (d, J = 6.4, 3H), 1.0-1.81 (m, 15H), 3.62 (m, 2H);. MS: 138 (3, M⁺ - H₂O), 123 (3), 110 (42), 109 (14), 97 (58), 96 (40), 95 (35), 87 (24), 81 (27), 68 (38), 67 (51), 55 (60), 41 (43).

30 Odor: floral, woody, citrus, metallic.

Example 74-Cyclopentylpent-1-yl propanoate

5 4-Cyclopentylpentan-1-ol (4.0 g; 23 mmol) was esterified with propionyl chloride (3.1 g; 34 mmol) according to example 3 to give 4.4 g (84.5% yield) of 4-cyclopentylpent-1-yl propanoate.

IR: 2951, 2868, 1743, 1456, 1366, 1239, 1048. ¹H-NMR: 0.87
 10 (d, *J* = 6.4, 3H), 1.00-1.87 (m, 14H), 1.14 (t, *J* = 7.5, 3H), 2.32 (q, *J* = 7.6, 2H), 4.05 (t, *J* = 6.6, 2H). MS: 226 (0.01, *M*⁺), 197 (4), 152 (10), 137 (12), 124 (17), 123 (18), 110 (22), 96 (32), 95 (88), 83 (50), 82 (100), 81 (42), 75 (40), 69 (44), 67 (59), 57 (67), 55 (53), 41
 15 (32).

Odor: orange, fruity, ozonic, floral.

20 Example 8Ethyl 4-cyclopentylpentanoate

1,1'-Carbonyldiimidazole (101 g; 0.62 mmol) was added
 25 portionwise to 4-cyclopentylpentanoic acid (100 g; 0.58 mol) in THF (500 ml). After the gas evolution ceased, the reaction mixture was reacted with sodium ethylate solution prepared from sodium (0.3 g; 13 mmol) and ethanol (500 ml), stirred at r.t. for 2.5 h, and the solvent evaporated
 30 in *vacuo*. The residue was dissolved in ether (300 ml), washed successively with water (300 ml), 1 N NaOH (300 ml), and 1 N HCl (300 ml), dried (MgSO₄), concentrated in *vacuo*, and distilled over a 10 cm Vigreux column

(66°C/0.08 torr) to give 59.4 g (52% yield) of ethyl 4-cyclopentylpentanoate.

IR: 2953, 2869, 1738, 1451, 1376, 1253, 1181, 1104, 1037, 939. ¹H-NMR: 0.87 (d, *J* = 6.4, 3H), 1.26 (t, *J* = 7.2, 3H),

5 1.01-1.91 (m, 12H), 2.23 (ddd, *J* = 15.3, 8.8, 6.4, 1H), 2.37 (ddd, *J* = 15.3, 9.8, 5.5, 1H), 4.12 (q, *J* = 7.1, 2H).

MS: 183 (0.1, *M*⁺ - CH₃), 153 (3), 141 (16), 135 (32), 129 (23), 111 (65), 110 (31), 101 (98), 88 (85), 69 (49), 67 (36), 55 (100), 41 (67).

10

Odor: green, fruity (pineapple), floral (rosy).

Example 9

15

4-Cyclopentylpentanal

Ethyl 4-cyclopentylpentanoate was reduced to 4-cyclopentylpentanal with diisobutylaluminum hydride as in
20 example 2 (68% yield).

IR: 2952, 2868, 2714, 1727, 1450, 1411, 1379, 1012. ¹H-NMR: 0.88 (d, *J* = 6.4, 3H), 1.01-1.91 (m, 12H), 2.29-2.57 (m, 2H), 9.77 (t, *J* = 2.0, 1H). MS: 154 (4, *M*⁺), 139 (10), 136 (18), 121 (19), 110 (77), 97 (44), 95 (53), 85 (36),
25 81 (35), 69 (62), 68 (76), 67 (100), 55 (76), 41 (60).

Odor: aldehydic, melon, mandarine, green ivy, floral.

30

Example 104-Cyclopentylpentanenitrile

- 5 4-Cyclopentylpentanal was transformed into 4-cyclopentylpentanenitrile as in example 5 (56% yield).
 IR: 2953, 2869, 2246, 1450, 1428, 1381. ¹H-NMR: 0.91 (d, J = 6.1, 3H), 1.04-1.26 (m, 2H), 1.36-1.93 (m, 10H), 2.21-2.49 (m, 2H). MS: 151 (0.1, M⁺), 150 (0.5), 136 (4), 123
 10 (3), 110 (45), 109 (43), 97 (11), 83 (18), 69 (63), 68 (19), 67 (21), 55 (83), 41 (100).

Odor: hesperidic, floral, green, cumin.

15

Example 115-Cyclopentylhexanenitrile

- 20 a) 5-(Cyclopenta-2,4-dienylidene)hexanenitrile
 Pyrrolidine (18.5 g; 0.26 mol) was added to a solution of cyclopentadiene (10.8 g; 0.16 mol; freshly prepared by cracking of dicyclopentadiene) and 5-oxohexanenitrile (15.4 g; 0.13 mol) in methanol (175 ml) at 0°C. After 1 h
 25 stirring at this temperature, the reaction mixture was poured into ice-cold 2 N HCl (500 ml), saturated with sodium chloride and extracted with MTBE (400 ml). The organic phase was washed with brine (3 x 300 ml), dried (MgSO₄), concentrated *in vacuo*, and used in the next step
 30 without further purification.

b) 5-Cyclopentylhexanenitrile

Hydrogenation as in example 4 gave 5-cyclopentylhexanenitrile.

IR: 2952, 2868, 2245, 1458, 1427, 1378. $^1\text{H-NMR}$: 0.88 (d, J = 6.1, 3H), 1.01-1.86 (m, 14H), 2.28-2.37 (m, 2H). MS: 165 (2, M^+), 164 (12), 150 (25), 136 (17), 124 (67), 122 (39), 98 (61), 97 (100), 96 (47), 82 (34), 69 (80), 68 (38), 67 (25), 55 (71), 41 (49).

10 Odor: floral, orris, spicy, powdery, cumin.

Example 1215 5-Cyclopentylhexan-2-one

4-Cyclopentylpentanoic acid (3.4 g; 20 mmol; prepared in example 6) in diethyl ether (90 ml) was added at 0°C to 1.6 M diethyl ether solution of methyllithium (25 ml; 40 mmol), diluted with the same solvent (75 ml). After 3.5 h stirring at 5°C, water (100 ml) was added, and the separated organic layer was washed with brine (3 x 400 ml), dried (MgSO_4), concentrated in vacuo, and bulb-to-bulb distilled (125°C/0.2 torr) to give 1.8 g (53.5 yield) of 5-cyclopentylhexan-2-one.

IR: 2952, 2868, 1718, 1450, 1412, 1357, 1162. $^1\text{H-NMR}$: 0.86 (d, J = 6.1, 3H), 1.02-1.85 (m, 12H), 2.15 (s, 3H), 2.28-2.57 (m, 2H). MS: 168 (5, M^+), 150 (12), 135 (21), 121 (96), 111 (79), 110 (70), 108 (46), 81 (27), 71 (46), 69 (58), 67 (58), 58 (55), 55 (57), 43 (100), 41 (35).

Odor: fruity, lavender, orris, lactonic, pineapple.

Example 13

5 5-Cyclopentylidenehexanenitrile and 5-(cyclopent-1-enyl)-
hexanenitrile

a) 5-Cyclopentyl-5-hydroxyhexanenitrile

5-Oxohexanenitrile (11.1 g; 0.10 mmol) was added at 20 °C to a suspension of anhydrous cerium(III) chloride (30 g; 0.12 mol) in THF (250 ml). After 1 h stirring at r.t.,
10 cyclopentylmagnesium chloride (60 ml of 2.0 M solution in diethyl ether; 0.12 mol) was added dropwise at 5°C and stirring continued for more 0.5 h at the same temperature. 2 N HCl (60 ml) was added, and the reaction mixture was
15 extracted with MTBE (2 x 200 ml). The combined organic phases was washed with 2 N HCl (100 ml), and brine (2 x 100 ml), dried (MgSO₄), and concentrated in vacuo, to give 13 g of crude (83% GC pure; 60% yield) 5-cyclopentyl-5-hydroxyhexanenitrile, used without further purification in
20 the next step.

b) 5-Cyclopentylidenehexanenitrile and 5-(cyclopent-1-enyl)hexanenitrile

Crude 5-cyclopentyl-5-hydroxyhexanenitrile (18 g; 0.1 mol)
25 was added into a solution of sulphuric acid (15 ml) in acetic acid (150 ml). The reaction mixture was stirred at 5°C for 1 h, then poured into ice (100 g), diluted with MTBE (100 ml), washed with saturated sodium bicarbonate solution (5 x 300 ml), and brine (2 x 300 ml), dried
30 (MgSO₄), concentrated in vacuo, and bulb-to-bulb distilled to give 2.1 g (13 % yield) of 5-cyclopentylidenehexanenitrile and 5-(cyclopent-1-enyl)-hexanenitrile mixture (GC: 43 + 57%).

IR: 2953, 2867, 2245, 1457, 1433, 1377. $^1\text{H-NMR}$: 1.03 (d, J = 6.7, 1.5H), 1.41-1.66 (m, 4H), 1.60 (s, 1.5H), 1.75 (m, J = 7.3, 1H), 1.84 (m, J = 7.4, 1H), 2.11-2.38 (m, 7.5H), 5.36 (m, 0.5H). MS (major product): 163 (26, M^+), 148

5 (62), 135 (20), 134 (23), 120 (32), 107 (66), 95 (77), 91 (24), 79 (32), 77 (25), 67 (100), 55 (29), 41 (42); MS (minor product): 163 (13, M^+), 163 (6), 148 (28), 135 (18), 134 (12), 120 (38), 107 (31), 95 (100), 91 (18), 79 (24), 77 (20), 67 (93), 55 (20), 41 (33).

10

Odor: cumin, orris, spicy, floral, stronger than 5-cyclopentylhexanenitrile.

15 **Example 14**

5-Cyclopentylhexanal

Diisobutylaluminum hydride (60 ml of 1.0 M solution in
20 hexane) was added at -65°C to a hexane (50 ml) solution of 5-cyclopentylhexanenitrile (5.0 g; 30 mmol; from example 11). After stirring at -70°C for 0.5 h, and at r.t. for 3 h, methanol (1.8 ml) was added, and the stirring continued for 20 min.. 10% H_2SO_4 (48 ml) was added, and the reaction
25 mixture was diluted with MTBE (150 ml). The organic layer was separated, washed with saturated sodium bicarbonate solution (300 ml), and brine (3 x 300 ml), dried (MgSO_4), concentrated in vacuo, and bulb-to-bulb distilled ($100^\circ\text{C}/0.2$ torr) to give 2.6 g (51.5 % yield) of 5-
30 cyclopentylhexanal.

IR: 2950, 2867, 2715, 1727, 1452, 1410, 1377. $^1\text{H-NMR}$: 0.90 (d, J = 6.4, 3H), 1.01-1.91 (m, 14H), 2.35-2.46 (m, 2H), 9.77 (t, J = 1.8, 1H). MS: 168 (19, M^+), 150 (1), 135

(27), 121 (19), 109 (29), 97 (57), 96 (100), 95 (34), 81 (65), 69 (50), 68 (43), 67 (56), 55 (98), 41 (48).

Odor: aldehydic, green, fresh, hesperidic, linear.

5

Example 15

5-Cyclopentylhexan-1-ol

10

5-Cyclopentylhexanal (4.2 g; 25 mmol) in ethanol (40 ml) was added to sodium borohydride (1.2 g; 32 mmol) suspended in the same solvent (50 ml), at 10°C, and the reaction mixture was stirred at r.t. for 2 h. 1 N HCl (50 ml) was added dropwise at 0°C. The mixture was diluted with MTBE (150 ml), the organic layer separated, washed with brine (3 x 250 ml), dried (MgSO₄), concentrated in vacuo, and bulb-to-bulb distilled (125°C/0.2 torr) to give 3.4 g (80 % yield) of 5-cyclopentylhexan-1-ol.

15

IR: 3326, 2949, 2865, 1452, 1376, 1059. ¹H-NMR: 0.86 (d, J = 6.4, 3H), 1.01-1.82 (m, 17H), 3.63 (t, J = 6.5, 2H). MS: 152 (0.7, M⁺ - H₂O), 137 (3), 123 (4), 110 (14), 109 (18), 101 (14), 97 (72), 96 (49), 95 (28), 83 (80), 82 (53), 69 (33), 68 (33), 67 (47), 55 (100), 41 (35).

25

Odor: floral, sweet, fruity, raspberry, powdery, rosy.

Example 16

30

5-(2-Methylcyclopent-1-enyl)pentan-1-ol and 5-(5-methylcyclopent-1-enyl)pentan-1-ol

1,4-Dibromopentane (76 g; 0,33 mol) dissolved in THF (450 ml) was added at reflux within 70 min. to magnesium turnings (15.8g; 0,66 mol) in THF (50 ml). The mixture was refluxed for 90 min., cooled to room temperature and
 5 diluted with THF (250 ml). This solution was added within 160 min. to caprolactone (37.6 g; 0,33 mol) dissolved in THF (400 ml), the temperature being kept at 5°C. After further stirring for 90 min. without cooling, the mixture was poured into ice-water (1.2 l), acidified to pH 2 (HCl)
 10 and extracted with MTBE (2 x 600 ml). The organic phases were washed with water (4 x 800 ml), dried (Na₂SO₄), concentrated in vacuo and distilled (0,02 torr) over KHSO₄ (1.3 g) to give 23 g of an oil which was further purified by flash-chromatography (MTBE/hexane 1:5) to give 4.8 g
 15 (9% yield) of a mixture of the two isomers.
 IR: 3334, 2930, 2856, 1456, 1379, 1072, 1052. ¹H-NMR: 0.99 (d, J = 8, ca. 0,85H), 1.23-1.50 (m, ca. 5H), 1.52-1.69 (m, ca. 5H), 1.72-1.79 (m, 1H), 1.91-2.32 (m, 5H, 3.58-3.66 (m, 2H), 5.29 (bs, ca. 0.3H). MS: 168(18, M⁺), 81
 20 (1), 95 (2), 67 (3), 55(4), 41 (5), 107 (6), 135 (7), 121 (8).

Odor: floral, rosy, fruity (melon), marine.

25

Example 17

4-(Cyclopent-1-enyl)butan-1-ol and 4-cyclopentylidene-
butan-1-ol

30

1,4-Dibromobutane (64.8 g; 0.3 mol) dissolved in THF (300 ml) was added within 45 min. to magnesium (14.6 g; 0,6 mol) in the same solvent (35 ml). After 3h stirring at

reflux, the solution was cooled to r.t., diluted with THF (30 ml) and added within 30 min. to δ -valerolactone (30 g; 0,3 mol) dissolved in THF (450 ml), the temperature being kept at 10°. After stirring at r.t. for 2h, the reaction
 5 mixture was poured into ice-water (500 ml), acidified to pH 2 (10% HCl) and extracted with MTBE (3 x 200 ml). The organic phases were washed with water (3 x 500 ml) dried (Na₂SO₄), concentrated *in vacuo* and distilled (0,1 Torr) over KHSO₄ (0.5 g) to afford 10.5 g of an oil which after
 10 flash-chromatography (MTBE/hexane 1:5) gave 3.4 g (8% yield) of the two isomers.

IR: 3334, 2934, 2844, 1652, 1436, 1056, 1032. ¹H-NMR: 1.46-1.69 (m, ca. 4.5H), 1.8-1.89 (m, ca. 1.5H), 2.0-2.12 (m, 2H), 2.14-2.32 (m, 4H), 2.78 (bm, 1H), 3.61 (t, J = 7, 2H), 5.24 (m, ca. 0.25H), 5.33 (t, J = 1, ca. 0,75H); MS: 140 (19, M⁺), 79(1), 67 (2), 93 (3), 41 (4), 53 (5), 31 (6), 107 (7), 122 (8).

Odor: rosy, aldehydic, green.

20

Example 18

6-Cyclopentyl-3-methylhexan-3-ol

25

a) 1-Ethenylcyclopentanol

A solution of vinylbromide (146.6 g; 1.37 mol) in 250 ml of THF was added during 4 h to a mixture of magnesium fine turnings (33.3 g; 1.37 mol) and a crystal of iodine in 150
 30 ml of THF at t < 50°C. The resulting dark grey mixture was stirred for 1 h, treated with a solution of cyclopentanone (104.8 g; 1.25 mol) in 100 ml of THF at 35- 45°C, and

stirred overnight at r.t.. Saturated NH_4Cl solution (1 l) was added at $\sim 0^\circ\text{C}$ and the reaction mixture was acidified to pH $\sim 6-7$ with 2N HCl. The organic layer was separated, washed with brine (3 x 100 ml), dried over MgSO_4 and concentrated in vacuo. Distillation using a Widmer column ($32^\circ\text{C}/0.06$ torr) yielded 67.6 g (48% yield) of 1-ethenylcyclopentanol.

b) 5-Cyclopentylidenepentane-2-one

10 A 600 ml autoclave containing 1-ethenyl-cyclopentanol (172.0 g; 1.54 mol), isopropenyl methyl ether (218.8 g; 3.04 mol), triethylamine (1.65 ml) and 85% H_3PO_4 (0.72 ml) was pressurised with N_2 at 2 bar and heated up to 125°C . An increase of the pressure to 7 bar was observed. After 15 14 h stirring, the autoclave was cooled down to r.t. and depressurised. The mixture was taken in MTBE (1.5 l), washed with H_2O (4 x 25 ml) until neutral pH, dried (MgSO_4) and concentrated. Distillation ($61^\circ\text{C}/0.1$ torr) yielded 161.3 g (69% yield) of 5-cyclopentylidenepentane-2-one.

20

c) 6-Cyclopentylidene-3-methylhex-1-yn-3-ol

Acetylene was bubbled for 50 min. through a solution of $t\text{BuOK}$ (33.8 g; 0.30 mol) in THF (240 ml), cooled down to 0°C . The resulting beige suspension was treated with 5-cyclopentylidenepentane-2-one (41.7 g; 0.27 mol) added dropwise for 15 min. at 0°C . The resulting mixture was warmed gently to r.t. and quenched with sat. NH_4Cl (180 ml). The aqueous phase was separated and extracted with MTBE (2 x 120 ml). The combined organic layers were washed 30 with H_2O (240 ml), brine (100 ml), dried over MgSO_4 and concentrated in vacuo. Distillation ($69-71^\circ\text{C}/0.09$ torr) afforded 38.95 g (81% yield) of 6-cyclopentylidene-3-methylhex-1-yn-3-ol.

d) 6-Cyclopentyl-3-methylhexan-3-ol

Hydrogenation of 6-cyclopentylidene-3-methylhex-1-yn-3-ol (5.0 g, 28 mmol) under standard conditions: H₂ 1 atm, r.t., over 5% Pd/C (0.57 g) in EtOH (30 ml) afforded after distillation (56°C/0.06 torr) 4.57 g (89% yield) of 6-cyclopentyl-3-methylhexan-3-ol.

IR (neat): 3378, 2942, 2866. ¹H NMR: 0.89 (t, *J* = 7.5 Hz, 3H), 1.00-1.13 (m, 2H), 1.14 (s, 3H), 1.48 (q, *J* = 7.5 Hz, 2H), 1.24-1.65 (m, 11H), 1.69-1.84 (m, 3H). MS: 169 (2, *M*⁺ - CH₃), 155 (6), 137 (8), 95 (32), 81 (23), 73 (100), 67 (14), 55 (32), 43 (18), 41 (18).

Odor: floral (rosewood), fruity (apricot), hesperidic, neroli.

Example 1920 5-(Cyclopent-1-enyl)-2-methylpentan-2-ola) 5-(Cyclopent-1-enyl)-2-pentanone

A mixture of 5-cyclopentylidene-2-pentanone (9.92 g; 65 mmol) and *p*-TsOH (100 mg; 0.53 mmol) in toluene (150 ml) was heated at 90°C for 8 h, then cooled down to r.t., diluted with MTBE (100 ml), washed with sat. NaHCO₃ (50 ml), H₂O (50 ml), brine (50 ml), dried over MgSO₄ and concentrated in vacuo. Distillation under reduced pressure (48°C/0.065 torr) yielded 7.13 g of 5-(cyclopent-1-enyl)-2-pentanone (purity ~80%), further purified by flash chromatography to give 6.1 g (61% yield) of 89% pure product containing 11% of 5-cyclopentylidene-2-pentanone.

b) 5-(Cyclopent-1-enyl)-2-methylpentan-2-ol

5-(Cyclopent-1-enyl)-2-pentanone (5.95 g; 39 mmol) in ethyl ether (6 ml) was added dropwise to a 3M solution of methylmagnesium bromide in the same solvent (17 ml; 51 mmol) during 15 min.. After 2 h at reflux, the mixture was cooled down to r.t., poured into ice (20 g), acidified with 5N HCl (20 ml) and extracted with MTBE (60 ml). The aqueous phase was separated and extracted again with MTBE (2 x 100 ml). The combined organic phases were washed with sat. NaHCO₃ (80 ml), H₂O (80 ml), brine (80 ml), dried over MgSO₄ and concentrated *in vacuo*. Bulb to bulb distillation (80°C/0.06 torr) yielded quantitatively 5.84 g of 5-(cyclopent-1-enyl)-2-methylpentan-2-ol containing 11% of 5-cyclopentylidene-2-methylpentan-2-ol.

IR: 3364, 2967, 2939, 2867, 2844, 1468, 1377, 1296, 1195, 1149, 1047, 910, 772. ¹H NMR: 1.21 (s, 6H), 1.41-1.56 (m, 4H), 1.80-1.90 (m, 2H), 2.02-2.11 (m, 2H), 2.18-2.26 (m, 2H), 2.26-2.33 (m, 2H), 5.31-5.35 (m, 1H). MS: 168 (0.5, M⁺), 150 (28), 135 (50), 95 (25), 94 (100), 93 (16), 81 (12), 80 (14), 79 (91), 69 (22), 67 (22), 59 (34), 43 (10), 41 (12).

Odor: floral (rosy, geranium), fruity (plum), agrestic.

25

Example 205-Cyclopentylpentan-2-ol30 a) 5-Cyclopentylpentan-2-one

Hydrogenation of 5-cyclopentylidenepentan-2-one synthesized in example 18b (30.4 g; 0.2 mol) under standard conditions (cf. example 19d) gave, after

distillation (61-67°C/0.1 torr), 25.8 g (84% yield) of 5-cyclopentylpentan-2-one.

b) 5-Cyclopentylpentan-2-ol

5 NaBH₄ (3.15 g; 83 mmol) was added portionwise to a solution of 5-cyclopentylpentan-2-one (16.0 g; 104 mmol) in MeOH (125 ml) at 0°C. The mixture was stirred at 0°C for 1 h then at r.t. for 2 h. Water (100 ml) was added cautiously and the mixture extracted with MTBE (3 x 250
10 ml). The organic phases were combined, washed with brine (3 x 50 ml), dried over MgSO₄, concentrated *in vacuo* and distilled (52-56°C/0.045 torr) to give 14.5 g (90% yield) of 5-cyclopentylpentan-2-ol.

IR: 3347, 2947, 2861, 1453, 1374, 1308, 1116, 1077, 942.

15 ¹H NMR: 1.00-1.12 (m, 2H), 1.18 (d, *J* = 6.0, 3H), 1.23-1.38 (m, 3H), 1.38-1.64 (m, 7H), 1.67 (bs, 1H), 1.70-1.80 (m, 3H), 3.73-3.85 (m, 1H). MS: 141 (6, *M*⁺ - CH₃), 123 (18), 111 (16), 110 (22), 96 (52), 95 (48), 83 (28), 82 (70), 81 (60), 69 (42), 68 (36), 67 (84), 58 (12), 55
20 (34), 45 (100), 43 (16), 41 (35), 39 (12).

Odor: floral (tuberose), lily of the valley, coconut, celery.

25

Example 21

5-Cyclopentylidene-2-methylpentan-2-ol

30 5-Cyclopentylidene-2-pentanone (13.4 g; 88 mmol) in ether (13 ml) was added dropwise during 30 min. to a 3M solution of methylmagnesium bromide in ether (38 ml; 114 mmol). After addition of more ether (25 ml), the mixture was

heated under reflux for 2h, then cooled down to r.t., poured into ice (40 g), acidified with 5N HCl (50 ml) and extracted with MTBE (130 ml). The aqueous phase was separated and extracted with MTBE (2 x 130 ml). The
 5 combined organic phases were washed with sat. NaHCO₃ (2 x 130 ml), water (130 ml), dried over MgSO₄ and concentrated in vacuo. Distillation (52-55°C/0.06 torr) yielded 11.24 g (76% yield) of 5-cyclopentylidene-2-methylpentan-2-ol.
 IR: 3366, 2959, 2867, 1451, 1377, 1218, 1147, 910. ¹H NMR:
 10 1.21 (s, 6H), 1.48-1.70 (m, 6H), 2.00-2.09 (m, 2H), 2.15-2.24 (m, 4H), 5.20-5.28 (m, 1H). MS: 168 (0.5, M⁺), 150 (65), 135 (100), 121 (12), 107 (26), 95 (46), 94 (68), 93 (32), 82 (30), 81 (13), 80 (10), 79 (63), 67 (40), 59 (42), 55 (10), 43 (12), 41 (16).

15

Odor: floral ionone, linalool, raspberry, agrestic, tea.

Example 22

20

5-Cyclopentylidenepent-2-yl propanoate

a) 5-Cyclopentylidenepent-2-ol

5-cyclopentylidenepent-2-one (22.7 g; 149 mmol) was
 25 reduced as in example 20b to give 24.5 g of crude 5-cyclopentylidenepent-2-ol that was used without further purification in the following step.

b) 5-Cyclopentylidenepent-2-yl propanoate

30 DMAP (0.03 g; 0.24 mmol, 0.8) was added to a mixture of 5-cyclopentylidenepent-2-ol (5.0 g; 32 mmol), propionic anhydride (6.7 ml, 52 mmol) and Et₃N (7.2 ml, 52 mmol). After 1.5 h stirring at r.t., the reaction mixture was

diluted with MTBE (140 ml), washed with 2N HCl (60 ml), water (60 ml), sat. NaHCO₃ (60 ml), again with water (60 ml), and brine (60 ml), dried over MgSO₄ and concentrated in vacuo. Distillation under reduced pressure (87-
 5 92°C/0.04 torr) afforded 5.38 g (80% yield) of 5-cyclopentylidenepent-2-yl propanoate.

IR: 2943, 2868, 1736, 1462, 1370, 1192, 1129, 1082. ¹H NMR: 1.14 (t, J = 7.6, 3H), 1.21 (d, J = 6.0, 3H), 1.46-1.70 (m, 6H), 1.91-2.07 (m, 2H), 2.10-2.18 (m, 2H), 2.18-
 10 2.25 (m, 2H), 2.30 (q, J = 7.6, 2H), 4.85-4.95 (m, 1H), 5.17-5.25 (m, 1H). MS: 195 (0.5, M⁺ - CH₃), 136 (100), 121 (57), 107 (60), 95 (54), 94 (72), 93 (66), 91 (14), 81 (18), 80 (28), 79 (73), 77 (11), 68 (31), 67 (35), 57 (34), 41 (15).

15

Odor: floral, fruity, pear, ionone, apple.

Example 23

20

Shower gel perfume

5-Cyclopentylhexanenitrile 10% DPG	7.5
Aldehyde C 12 lauric 10% DPG	10
Ambrettolide	10
Benzyl acetate	30
Bergamote abergapt oil	115
Berryflor	3
Cetone alpha	40
Citronellol E	20
Citronellyl acetate	10
Coumarin pure crist.	20
Dipropylene glycol	117

Ethyl linalool	35
Ethyl vanillin	5
Ethylene brassylate	130
Eucalyptol	4
Eugenol pur	5
Givescone	3
Hexyl cinnamic aldehyde	200
Ionone beta	10
Lemonile	3
Lilial	30
Myraldene	3
Orange Floride oil	30
Prunolide	10
Radjanol	40
Rhodinol 70	10
Tricyclal	3
Tuberose base (reconstitution)	7.5
Verdantiol	4
Vertofix coeur	50
Ylang ylang oil	35
	1000

5-Cyclopentylhexanenitrile brings a lot of diffusion to the fragrance, imparting a very rich orris, ionone effect to the composition; the floral rosy/lily of the valley part of the fragrance is also considerably enhanced; this compound brings both power and elegance to this shower gel perfume.

Example 24Fine fragrance for men

5	5-Cyclopentylhexan-1-ol 10% DPG	30
	Amyris oil	50
	Benzoin tears Siam 50% DEP	50
	Bergamote Italy oil	175
	Cepionate	60
10	Citronellyl acetate	25
	Damascenone 10% DPG	10
	Dihydrolinalool	50
	Dimethylbenzylcarbinol isobutyrate	6
	Dimetol	40
15	Fennaldehyde	15
	Fixambrene	4
	Florhydral	5
	Florol	50
	Gardenol	5
20	Laurine	80
	Lemon Italy oil	40
	Magnolione	80
	Mandarine green Italy oil	10
	Olibanum res. 50% DEP	45
25	Orange Florida oil	60
	Thibetolide	10
	Tricyclal 10% DPG	25
	Tropional	40
	Undecavertol	15
30	Velvione	20
		1000

5-Cyclopentylhexan-1-ol brings on the whole higher diffusion to the blend. It enhances hesperidic notes, particularly mandarine effect. The aldehydic rosy effect it imparts adds to the transparency of the fragrance and to its modernity through marine undertones.

Example 25

10 Deodorant fragrance

	5-Cyclopentylhexanal 10% DPG	30
	Bergamote base	50
	Cedryl acetate	25
15	Cepionate	50
	Coumarin	5
	Cyclohexyl salicylate	12
	Dipropylene glycol	105
	Dynascone 10	15
20	Elemi oil	5
	Fixambrene	5
	Folrosia	6
	Hydro Rose C (rose oil reconstitution)	300
	Iso E Super	85
25	Junniper berries oil	20
	Kephalis	30
	Lemon Italy oil	50
	Mate absolute 10%DPG	35
	Metambrate	45
30	Methyl Pamplemousse	8
	Nutmeg oil	8
	Okoumal	10
	Patchouli SF oil	8

Sandalore	35
Spearmint USA 10%DPG	20
Thibetolide	30
	1000

5

5-Cyclopentylhexanal brings higher harmony to the blend; it imparts anisic, tarragon type of nuances, along with its natural rosy/geranium effect; through evaporation the anisic undertones evolve towards a floral, marine, anisic cocktail which underlines the modern transparent and clean effect of the fragrance in the deodorant application.

10

For the exact definition of the trivial names mentioned above, see *Flavor and Fragrance Materials 1998*, Allured Publishing Corporation, Carol Stream, Illinois, U.S.A. or Arctander, *Perfume and Flavor Chemicals - 1969*, published by the author, Montclair, New Jersey, U.S.A.

20

25

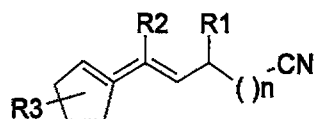
30

Claims



1. Compounds of general formula I

5



I

wherein

10 R^1 , R^2 and R^3 are independently H, C_{1-3} alkyl but R^1
and R^2 are not at the same time H;
 R^2 can also be methylene or ethylidene;
 $n = 0$ or 1 and

15 --- stands for a single or a double bond, whereby
maximum 2 double bonds are present

2. 5-Cyclopentyl-3-methylpentanenitrile according to claim 1.

20 3. 4-Cyclopentylpentanenitrile according to claim 1.

4. 5-Cyclopentylhexanenitrile according to claim 1.

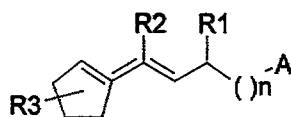
5. 5-Cyclopentylidenehexanenitrile according to claim 1.

25

6. 5-(Cyclopent-1-enyl)hexanenitrile according to claim 1.

7. Use of the compounds of general formula II

30



II

This Sheet Has Been Replaced



wherein

A is selected from the group of $\text{CR}^4\text{R}^5\text{OH}$,
 $\text{CR}^4\text{R}^5\text{OC(O)R}^6$, CO_2R^6 , CN and C(O)R^4 ;

R^1 , R^2 , R^3 , R^4 , R^5 and R^6 are independently H or
5 C_{1-3} -alkyl;

R^2 can also be methylene or ethylidene;

R^6 can also be a C_{2-4} alkenyl or alkynyl

$n = 0$ or 1 and

--- stands for a single or a double bond, whereby

10 maximum 2 double bonds are present.

8. Use according to claim 7 as fragrance.

9. Use according to claim 8 in fine and functional
15 perfumery.

