

- 1 -



166166

 α,β -UNSATURATED KETONES

G00002

The present invention relates to new α,β -unsaturated ketones exhibiting a green-galbanum, fresh (metallic, undecatriene type) and fruity-pineapple and/or fruity-cassis odor and to
5 the use of these new compounds as fragrance materials in different compositions.

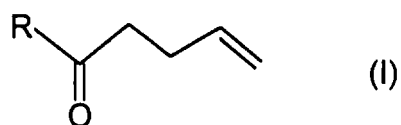
Inexpensive floral fruity and green fragrances with intense pineapple and galbanum undertones are highly desirable in the art of perfumery. However, many of the natural and
10 commercially available compounds e.g. galbanum oil are expensive and show lack of stability. Moderately weak galbanum type compounds became available in the mid seventies including allyl amyl glycolate (International Flavor and Fragrance Inc.) and Cyclogalbanate® (Dragocco S.A.). Another
15 member of this family, the allyl cyclopentyl glycolate is described in the US 4 735 932. However, glycolates are generally not stable in alkali, acid or oxidizing media.

1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one is described by Morris, A.F.; Näf, F; Snowdon, R. L. in Perfumer
20 & Flavorist 1991 (16), 33 as an important compound for the perfumery. This compound possesses a powerful metallic odor reminiscent of galbanum with pineapple and hyacinth character that adds fresh, green, floral and fruity aspects to perfumes and perfumed products.

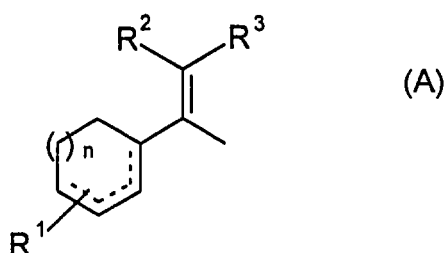
25 The object of the present invention is to provide new compounds which have an intense and long lasting green galbanum type of odor accompanied by various fruity, mainly pineapple undertones.

It has surprisingly been found that compounds of Formula I

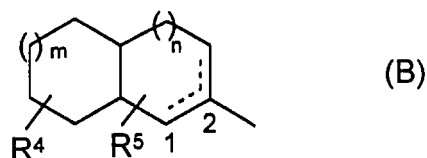
- 2 -



wherein R is a residue A



5 or a residue B

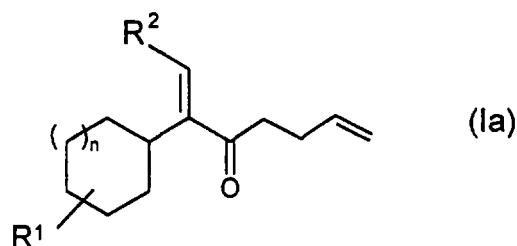


and R^1 , R^2 , R^3 , R^4 and R^5 are independently hydrogen, methyl or ethyl, R^1 , R^4 and R^5 being at any position of the ring structure, n and m are independently 0,1,2 or 3 and the
 10 dotted lines stand in formula A, if desired, for a double bond and the dotted lines in formula B stand, for a double bond either in position 1 or 2, have an intense, very long lasting green-galbanum type of odor with fruity undertones. These characteristics make the new compounds well suited for
 15 difficult functional perfumery applications, as well as for imparting unique green galbanum and fruity notes to fine perfumery products.

The above formulas include all different possible stereo- and double-bond isomers.

- 3 -

New compounds of formula Ia are preferred.



5 wherein R¹ and R² are independently hydrogen or methyl and n stands for 0 or 1.

Further preferred compounds are:

2-cyclohexylhepta-1,6-dien-3-one
 10 (E)- and (Z)-3-cyclohexylocta-2,7-dien-4-one
 2-cyclopentylhepta-1,6-dien-3-one
 1-(3,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-en-1-one
 1-(1,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-en-1-one

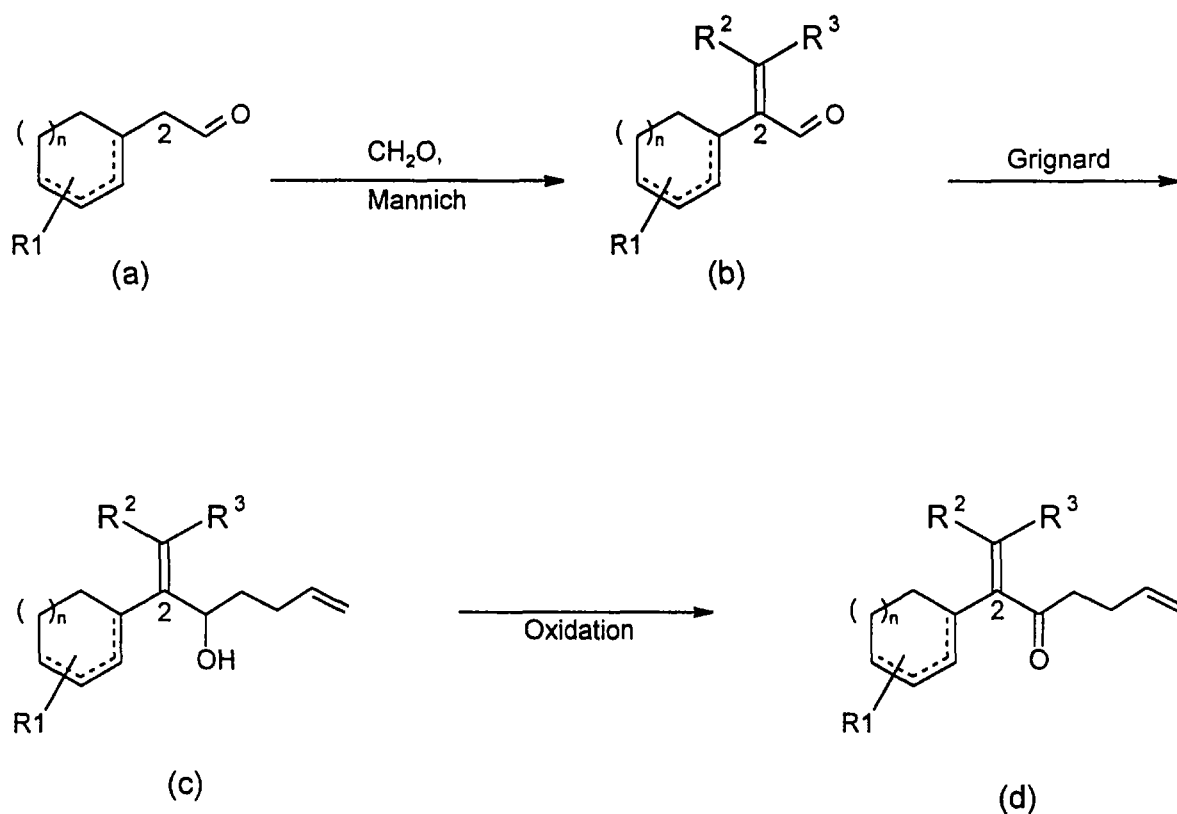
15 In addition to the above excellent qualities, it has been found that the compounds of the invention show outstanding diffusion and/or high substantivity, the latter meaning persistence of odor. The high diffusion and substantivity is well perceived on fabrics washed with a detergent or treated
 20 with a softener comprising one or more of the new α,β -unsaturated ketones. The typical fresh green odor is already perceived very strongly on the wet fabric and later also on the dry material.

Due to the excellent odor and application qualities, the new
 25 compounds are excellent fragrances for use in any field of

- 4 -

fine and functionary perfumery, such as perfumes, household products, laundry products, body care products and cosmetics.

The new α,β -unsaturated ketones of formula I, wherein R is a residue of formula A, may be prepared according to procedures
5 known in the art as shown in Scheme 1.



Scheme 1

The starting materials of formula (a) in Scheme 1 may be
10 prepared by oxidation of the corresponding alcohols. By methylenation with formaldehyde (Mannich reaction) aldehydes of formula (b), wherein R^2 and R^3 are hydrogen are obtained.

- 5 -

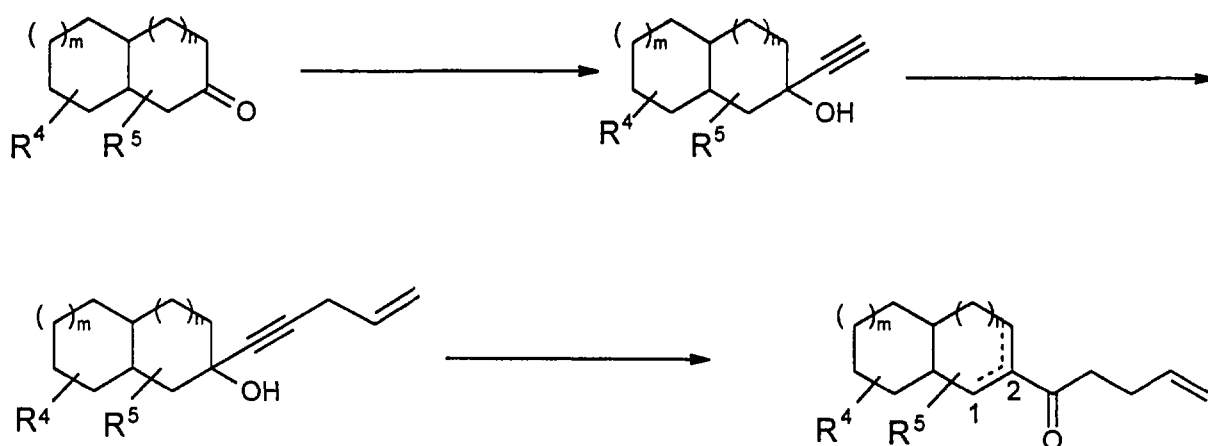
The α,β -unsaturated aldehydes corresponding to compounds of Formula I wherein R is a residue of formula A and R² and/or R³ are not hydrogen may be for example prepared via cross-aldol condensation using Mukaiyama conditions followed by
5 dehydration (T. Mukaiyama, K. Banno, K. Narasaka: J. Amer. Chem. Soc. **1974** (96), 7503).

Alternatively, the Grignard reaction may be carried out using appropriately substituted nitriles. This one pot reaction gives good yields of α,β -unsaturated ketones. 2-Substituted-
10 3-trimethylsilyloxypropionitriles are especially well suited for this transformation. The latter can for example be prepared from the respective cyclic ketones and ethyl cyanoacetate according to J.A. Marshall, R.D. Carroll: J. Org. Chem. **1965** (30), 2748 followed by protection of the
15 hydroxy-group with trimethylchlorosilane.

Another possible preparation of the α,β -unsaturated ketones of Formula I in which R is a residue A proceeds via Claisen transposition of the corresponding vinyl ether in analogy to
T. Masso, A. Portella, E. Rus (in Perfumer & Flavorist **1990**
20 (15), 39) starting with the suitably substituted 3-butene-2-ones (e.g. prepared according to R.A. Cormier, W.L. Schreiber, W.C. Agosta: J. Amer. Chem. Soc. **1973** (95), 4873).

The new α,β -unsaturated ketones of Formula I wherein R is a residue of formula B can be prepared from the corresponding
25 bicyclic ketones according to the process illustrated in Scheme 2.

- 6 -



Scheme 2

The starting ketones are either commercially available, or can be synthesized by Robinson annulation from the corresponding ketones with substituted or unsubstituted methyl vinyl ketones, followed by selective hydrogenation with Pd/C (e.g. G. Stork, A. Brizzolara, H. Landesman, J. Szmuskovicz, R. Terrell: J. Amer. Chem. Soc **1963** (85), 207).

The α,β -unsaturated ketones wherein R is a residue of formula B, are generally obtained as mixtures of cis-/trans-isomers. The double bond is either in position 1 or 2. The odors of the different isomers are all of the same „green“ type, however the GC thresholds are varying within broad ranges. Cis-1-(1,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-ene-1-one, the most powerful isomer of $n=m=1$, $R^4=R^5=H$, has a GC-threshold of only 10 pg/l.

The new odorants may be combined with numerous odorant ingredients of natural and/or synthetic origin. The range of the natural odorants includes in addition to readily volatile, also moderately and only slightly volatile components. The synthetic odorants embrace representatives from practically all classes of odorant substances. The

- 7 -

following list comprises examples of known odorants which may be combined with the compounds of the invention:

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

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

aldehydes: citral, α -hexyl cinnamaldehyde, Lilial, methylionone, verbenone, nootkatone, geranylacetone, etc.;

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

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

acetals: Viridine (phenylacetaldehyde dimethylacetal), etc.;

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

25 The novel compounds of the invention harmonize particularly well with floral notes (lily of the valley, rose, iris, jasmine, ylang-ylang, narcissus notes, etc.) as well as with

- 8 -

woody, chypre and animalic notes, tobacco like an patchouli compositions, etc.

The percentage in which the compounds of the invention are used in a composition may vary within wide limits ranging
5 from a few parts per thousand in mass market products (e.g. cleaning compositions, deodorant, etc.) up to a few percents in alcoholic extracts for fine perfumery. In all cases, even in small amounts, the compounds of Formula I provide odorant
10 compositions with green-galbanum and intense fresh green-fruity notes and a remarkable increase of the volume (strength, diffusivity) and of the duration (substantivity) of the odor.

There is no restriction regarding the type of formulations and the destination of the actual finished product: thus, eau
15 de cologne, toilet water, scented water, perfume, body care and cosmetic products such as cream, shampoo, soap, household products such as detergent, household cleaner, fabric softener, etc., come into consideration.

The invention will be further described, by way of
20 illustration, in the following examples without limiting the invention thereto.

All compounds were unambiguously identified by their ^1H -NMR- (chemical shifts (δ) are given in ppm downfield from TMS; coupling constants J in Hz), IR- and MS-spectra.

25 Compounds of Formula I and R = A

Example 1

2-Cyclohexylhepta-1,6-dien-3-one

- 9 -

a) 2-Cyclohexylprop-2-en-1-al

Successively, sulfuric acid 62% (79.4 g, 0.5 mol), aqueous formaldehyde 35% (82 g, 1.0 mol) and cyclohexyl acetaldehyde
5 (100.8 g, 0.8 mol) were added slowly to diethylamine (73 g, 1.0 mol) at 0°C. After stirring at 80°C overnight, the reaction mixture was extracted with MTBE. The combined organic phases were washed with H₂O until neutral pH, dried (MgSO₄) and concentrated in vacuo. The crude product was
10 distilled under reduced pressure using a Widmer column (10 Torr, 80°C) yielding 89.5 g (81 %) of pure product as colorless oil. ¹H-NMR (200MHz, CDCl₃): 9.5 (s, 1H, -CHO), 6.22 (s, 1H, H-C(3)), 5.95 (s, 1H, H'-C(3)), 2.48 (m, 1H, -CH-), 1.9-1.6 (m, 5H, -CH₂-), 1.5-1.0 (m, 5H, -CH₂-). MS
15 (EI): 138(M⁺,40), 123(22), 109(73), 95(90), 91(28), 79(61), 67(100), 55(39), 41(53). IR (neat): 2927vs, 2853 s, 1694vs, 1449m cm⁻¹.

b) 2-Cyclohexylhepta-1,6-dien-3-ol

20

2-Cyclohexylprop-2-en-1-al (69 g, 0.5 mol) in 100 ml of ether was slowly added to but-1-enylmagnesium bromide prepared by slow addition of 4-bromo-but-1-ene (81.0 g, 0.6 mol) in 100 ml of ether at 0°C to magnesium turnings (13.2 g, 0.55 mol)
25 in 300 ml of ether. After the addition was complete, the reaction mixture was allowed to warm to RT and was stirred for additional 3h. After quenching with 2N HCl the organic phase was separated, washed until neutral pH with H₂O, dried (MgSO₄) and the solvent was evaporated in vacuo. The crude
30 product was distilled over a Vigreux column (0.15 Torr, 91°C) yielding 85 g (88%) of pure product as colorless oil. ¹H-NMR (200MHz, CDCl₃): 5.85 (ddt, J = 17.2, 10.4, 6.6, 1H, H-C(6)), 5.05 (ddt, J = 17.2, 2.0, 1.6, 1H, H-C(7)), 5.02 (dd, J =

- 10 -

1.0, 1.0, 1H, H-C(1)), 4.98 (ddt, $J = 10.2, 2.1, 1.2$, 1H, H'-C(7)), 4.88 (d, $J = 1.0$, 1H, H'-C(1)), 4.09 (t, $J = 6.2$, 1H, H-C(3)), 2.22-2.10 (m, 2H, H-C(5)), 1.89 (m, 1H, -CH-), 1.80-1.52 (m, 8H, -CH₂-, -OH), 1.38-1.24 (m, 5H, -CH₂-). MS (EI):
 5 194(M⁺,1), 176(4), 165(3), 151(9), 139(11), 122(11), 109(15), 95(37), 83(66), 79(43), 71(34), 67(50), 55(100), 41(50). IR (neat): 3361s, 2926vs, 2852s, 1641w, 1448m cm⁻¹.

c) 2-Cyclohexylhepta-1,6-dien-3-one

10

2-Cyclohexyl-hepta-1,6-dien-3-ol (85 g, 0.44 mol) were oxidized with MnO₂ (804 g, 9.2 mol) in 2 l of hexane at RT. After stirring for 96 h the reaction mixture was filtered over Celite and concentrated in vacuo yielding 71 g of a
 15 yellow oil. Distillation (0.04 Torr/ 70°C) yielded 43.5 g (51%) of pure product.

Odor: green-galbanum, fruity-pineapple, metallic.

¹H-NMR (400MHz, CDCl₃): 5.95 (s, 1H, H-C(1)), 5.85 (ddt, $J =$
 20 17.0, 10.2, 6.4, 1H, H-C(6)), 5.65 (d, $J = 1.2$, 1H, H'-C(1)), 5.05 (ddt, $J = 17.1, 1.6, 1.6$, 1H, H-C(7)), 4.96 (ddt, $J = 10.2, 1.6, 1.2$, 1H, H'-C(7)), 2.78 (t, $J = 7.4$, 2H, H-C(4)), 2.59 (m, 1H, -CH-), 2.35 (m, 2H, H-C(5)), 1.80-1.65 (m, 5H, -CH₂-), 1.41-1.28 (m, 2H, -CH₂-), 1.22-1.00 (m, 3H, -CH₂-). MS
 25 (EI): 192(M⁺,11), 177(4), 163(50), 149(29), 137(78), 121(9), 109(65), 95(22), 81(34), 77(12), 67(100), 55(61), 41(29). IR (neat): 2926vs, 2852s, 1681vs, 1449m cm⁻¹.

The following examples are prepared according to the general
 30 procedure described for example 1. Only the spectroscopic data and olfactory properties are given below.

- 11 -

Example 22-Cyclopentylhepta-1,6-dien-3-one

Odor: green-galbanum, anisic, metallic

5 $^1\text{H-NMR}$ (400MHz, CDCl_3): 5.95 (s, 1H, H-C(1)), 5.85 (ddt, J = 17.2, 10.4, 6.6, 1H, H-C(6)), 5.70 (d, J = 1.2, 1H, H'-C(1)), 5.04 (ddt, J = 17.1, 1.8, 1.6, 1H, H-C(7)), 4.98 (ddt, J = 10.2, 1.6, 1.2, 1H, H'-C(7)), 2.95 (m, 1H, -CH-), 2.80 (t, J = 7.5, 2H, H-C(4)), 2.40 (m, 2H, H-C(5)), 1.94-1.81 (m, 2H, -CH₂-), 1.75-1.55 (m, 4H, -CH₂-), 1.35-1.12 (m, 2H, -CH₂-). MS (EI): 178(M^+ , 1), 163(2), 149(18), 137(5), 123(43), 110(8), 95(100), 83(9), 79(15), 67(73), 55(61), 41(23). IR (neat): 2953vs, 2869s, 1681vs, 1641m cm^{-1} .

10

15 Example 32-(4-Methylcyclohexyl)hepta-1,6-dien-3-one (cis/trans isomers ~1:1)

Odor: green-galbanum, fruity-pineapple

$^1\text{H-NMR}$ (400MHz, CDCl_3): 5.96 + 5.95 (2s, 1H, H-C(1)), 5.83 (ddt, J = 17.2, 10.4, 6.6, 1H, H-C(6)), 5.69 + 5.65 (2d, J = 1.4, 1H, H'-C(1)), 5.00 (m, 2H, H-C(7)), 2.77 (t, J = 7.6, 2H, H-C(4)), 2.55 (m, 1H, -CH-), 2.35 (m, 2H, H-C(5)), 1.94-1.22 (m, 7H, -CH-, -CH₂-), 1.19-1.00 (m, 2H, -CH₂-), 1.00 + 0.89 (2d, J = 7.2, 6.4, 3H, -CH₃). MS (EI): 206 (M^+ , 4), 191(6), 177(44), 163(7), 151(44), 149(33), 123(22), 110(17), 109(17), 107(14), 105(10), 95(34), 81(100), 79(24), 67(42), 55(65), 41(28). IR (neat): 2922vs, 2850s, 1681vs, 1641m cm^{-1} .

20

25

- 12 -

Example 42-(3-Methylcyclohexyl)hepta-1,6-dien-3-one (cis/trans isomers ~1:1)

5 Odor: green-fruity, pineapple with galbanum-aspects

¹H-NMR (400MHz, CDCl₃): 5.96 + 5.95 (2s, 1H, H-C(1)), 5.83 (ddt, J = 16.8, 10.4, 6.6, 1H, H-C(6)), 5.70 (2d, J = 1.2, 1H, H'-C(1)), 5.00 (m, 2H, H-C(7)), 2.9 (m, 0.5H, -CH-), 2.77 (m, 2H, H-C(4)), 2.61 (m, 0.5H, -CH-), 2.46 (m, 2H, H-C(5)), 2.01-1.09 (m, 9H, -CH-, -CH₂-), 1.03 + 0.88 (2d, J = 7.2, 6.8, 3H, -CH₃). MS (EI): 206(M⁺,4), 191(6), 177(30), 163(18), 151(49), 149(11), 123(20), 110(22), 109(15), 107(13), 105(8), 95(33), 81(100), 79(22), 67(42), 55(60), 41(28). IR (neat): 2923vs, 2850s, 1681vs, 1641m cm⁻¹.

Example 52-(2-Methylcyclohexyl)hepta-1,6-dien-3-one (cis/trans isomers ~1:1)

20

Odor: green-galbanum, mushroom, fruity-pineapple with jasmin aspects

¹H-NMR (400MHz, CDCl₃): 6.06 + 6.02 (2s, 1H, H-C(1)), 5.82 (m, 1H, H-C(6)), 5.70 + 5.52 (2d, J = 1.2, 1H, H'-C(1)), 5.00 (m, 2H, H-C(7)), 2.80 (m, 2.5H, H-C(4), -CH-), 2.38 (m, 2H, H-C(5)), 1.95 (m, 0.5H, -CH-), 1.82-1.00 (m, 9H, -CH-, -CH₂-), 0.71 + 0.69 (2d, J = 6.4, 7.2, 3H, -CH₃). MS (EI): 206(M⁺,15), 191(10), 177(33), 164(23), 151(50), 149(32), 133(124), 123(27), 109(28), 107(22), 105(22), 95(49), 81(89), 79(35), 67(51), 55(100), 41(44). IR (neat): 2925vs, 2853s, 1681vs, 1641m cm⁻¹.

- 13 -

Example 6

5 2-(2-Methylcyclopentyl)hepta-1,6-dien-3-one (cis/trans isomers)

Odor: green-galbanum, pineapple, grapefruit with anisic aspects

10 $^1\text{H-NMR}$ (400MHz, CDCl_3): 6.08 + 6.01 (2s, 1H, H-C(1)), 5.82 (m, 1H, H-C(6)), 5.70 + 5.66 (2d, $J = 1.2$, 1H, H'-C(1)), 5.02 (m, 2H, H-C(7)), 3.10 - 1.20 (5m, 12H), 0.90 + 0.54 (2d, $J = 6.4$, 6.8, 3H, $-\text{CH}_3$). MS (EI): 192(M^+ ,4), 177(14), 163(68), 150(23), 137(63), 133(124), 123(11), 119(25), 109(63), 15 107(23), 105(9), 95(37), 81(56), 79(33), 67(95), 55(100), 41(47). IR (neat): 2954vs, 2869s, 1681vs, 1641m cm^{-1} .

Example 7

20 2-Cycloheptylhepta-1,6-dien-3-one

Odor: green-galbanum, fruity, floral (lindenblossom)

$^1\text{H-NMR}$ (400MHz, CDCl_3): 5.95 (s, 1H, H-C(1)), 5.85 (ddt, $J = 17.2$, 10.4, 6.4, 1H, H-C(6)), 5.68 (d, $J = 1.2$, 1H, H'-C(1)), 5.05 (ddt, $J = 17.2$, 1.6, 1.6, 1H, H-C(7)), 4.96 (ddt, $J = 10.4$, 1.6, 1.2, 1H, H'-C(7)), 2.77 (t, $J = 7.2$, 2H, H-C(4)), 2.72 (m, 1H, $-\text{CH}-$), 2.37 (m, 2H, H-C(5)), 1.74-1.29 (m, 12H, $-\text{CH}_2-$). MS(EI): 206(M^+ ,3), 191(2), 177(27), 165(9), 151(38), 149(22), 135(6), 123(11), 121(13), 109(22), 95(30), 81(100), 67(96), 55(100), 41(51). IR (neat): 2924vs, 2855s, 1680vs, 30 1641m cm^{-1} .

Example 82-Cyclooctylhepta-1,6-dien-3-one

Odor: green-galbanum, woody, fatty with marine aspects

5 $^1\text{H-NMR}$ (400MHz, CDCl_3): 5.95 (s, 1H, H-C(1)), 5.85 (ddt, J = 17.1, 10.1, 6.6, 1H, H-C(6)), 5.69 (d, J = 1.1, 1H, H'-C(1)), 5.05 (ddt, J = 17.1, 1.7, 1.7, 1H, H-C(7)), 4.96 (ddt, J = 10.2, 1.6, 1.2, 1H, H'-C(7)), 2.96 (m, 1H, -CH-), 2.75 (t, J = 7.4, 2H, H-C(4)), 2.35 (m, 2H, H-C(5)), 1.80-1.45 (m, 14H, -CH₂-). MS(EI): 220(M^+ , 4), 205(2), 191(30), 179(19), 177(14),
10 149(28), 137(15), 135(17), 123(21), 121(24), 109(32), 110(22), 95(94), 81(79), 67(54), 55(100), 41(47). IR (neat): 2920vs, 2851s, 1680vs, 1641m cm^{-1} .

15 Example 93-Cyclohexylocta-2,7-dien-4-onea) 3-Cyclohexylbut-2-enal

20

A mixture of [(2-cyclohexylethenyl)oxy]trimethylsilane (19.8 g, 0.1 mol) and acetaldehyde (4.4 g, 0.1 mol) was added slowly at -70°C to a mixture of titantetrachloride (11 ml, 0.1 mol) and titanium(IV) isopropoxide (0.59 ml, 0.02 mol) in
25 CH_2Cl_2 (50 ml). After stirring for 1 h, the reaction was quenched with saturated NH_4Cl -solution and extracted twice with ether (2 x 100 ml). The combined organic phases were washed to neutral pH, dried (MgSO_4) and concentrated in vacuo. The crude product was dehydrated by distillation with
30 I_2 (200 mg) over a 5 cm Widmer column (0.1 Torr, 120°C) yielding 7.7 g (50 %) of 3-cyclohexylbut-2-enal as E/Z-

- 15 -

mixture of ~7:1. $^1\text{H-NMR}$ ((*E*)-isomer, 200MHz, CDCl_3): 9.31 (*d*, $J = 1.0$, 1H, -CHO), 6.48 (*q*, $J = 7.5$, 1H, H-C(3)), 2.55 (*m*, 1H, -CH-), 2.05 (*d*, $J = 7.5$, 3H, CH_2), 2.00-1.05 (*m*, 10H, - CH_2 -). MS (EI): 152(M^+ , 72), 137(29), 134 (14), 123(100),
 5 119(24), 109(43), 105(25), 95(57), 91(37), 84(21), 81(68), 79(45), 77(24), 69(31), 67(72), 55(48), 41(50). IR (neat): 2927vs, 2853s, 2704w, 1689s, 1634m, 1449m cm^{-1} .

b) 3-Cyclohexylocta-2,7-dien-4-one (E/ Z mixture of 10:1)

10 was prepared following the experimental procedure described in example 1a and 1c.

Odor: green-galbanum, pineapple, cassis

15 $^1\text{H-NMR}$ ((*E*)-isomer, 400MHz, CDCl_3): 6.50 (*q*, $J = 7.0$, 1H, H-C(2)), 5.80 (*ddt*, $J = 16.8$, 10.4, 6.4, 1H, H-C(7)), 5.01 (*ddt*, $J = 17.1$, 1.6, 1.6, 1H, H-C(8)), 4.96 (*ddt*, $J = 10.2$, 1.8, 1.2, 1H, H'-C(8)), 2.68 (*t*, $J = 7.6$, 2H, H-C(5)), 2.55 (*tt*, $J = 12.2$, 3.4, 1H, -CH-), 2.35 (*m*, 2H, H-C(6)), 1.88 (*d*,
 20 $J = 6.8$, - CH_3), 1.85-1.60 (*m*, 5H, - CH_2 -), 1.50-1.10 (*m*, 5H, - CH_2 -). MS (EI): 206(M^+ , 10), 191(15), 177(16), 164 (9), 151 (100), 123(19), 109(8), 95(12), 81(80), 79(18), 67(43), 55(49), 41(20). IR (neat): 2926vs, 2852s, 1672s, 1641m, 1450m cm^{-1} .

25

Example 10

4-Cyclohexylnona-3,8-dien-5-one (20:1 E/Z mixture)

30 was prepared according to the general procedure described for 3-cyclohexylocta-2,7-dien-4-one (Example 9).

Odor: green-fruity, apple, pineapple, galbanum, anisic

- 16 -

¹H-NMR ((*E*)-isomer, 400MHz, CDCl₃): 6.35 (t, *J* = 7.4, 1H, H-C(3)), 5.82 (ddt, *J* = 17.0, 10.4, 6.4, 1H, H-C(8)), 5.01 (ddt, *J* = 17.1, 1.8, 1.7, 1H, H-C(9)), 4.96 (ddt, *J* = 10.2, 1.8, 1.2, 1H, H'-C(9)), 2.70 (t, *J* = 7.6, 2H, H-C(6)), 2.51 (tt, *J* = 12.0, 3.6, 1H, -CH-), 2.39-2.30 (m, 2H, H-C(7)), 2.29 (q, *J* = 7.6, H-C(2)), 1.82-1.60 (m, 5H, -CH₂-), 1.45 (m, 2H, -CH₂-), 1.32-1.18 (m, 3H, -CH₂-), 1.08 (t, *J* = 7.6, -CH₃). MS (EI, (*E*)-isomer): 220(M⁺,10), 191(43), 177(9), 165 (100), 149 (5), 137(11), 123(7), 109(12), 95(86), 81(72), 79(23), 67(34), 55(63), 41(26). IR (neat): 2927vs, 2852s, 1672s, 1641m, 1450m cm⁻¹.

15 Compounds of Formula I and R = B

Example 11

1-(1,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one
20 1-(3,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one
1-(1,2,3,4,5,6,7,8,-Octahydronaphth-2-yl)pent-4-ene-1-one

a) 2-Ethynyldecahydronaphthalen-2-ol

25 Acetylene was bubbled for 4h through a mixture of tBuOK (95.8 g, 0.85 mol) in THF (1 l) at 0°C. 2-Decalone (100 g, 0.66 mol) was added slowly at RT to the slightly yellow suspension and the resulting mixture was stirred for additional 3.5 h, quenched with saturated NH₄Cl (500 ml) solution and extracted
30 with MTBE (2 x 700 ml). The combined organic phases were washed with NH₄Cl (500 ml), H₂O (2 x 500 ml), saturated NaCl (500 ml) solution until neutral pH, dried (MgSO₄) and concentrated in vacuo. The crude orange oil was flash

- 17 -

distilled (0.01 Torr, 88-90°C) yielding 100.6 g (86%) of 2-ethynyldecahydro-naphthalen-2-ol.

b) 2-(Pent-4-en-1-ynyl)decahydronaphth-2-ol

5

A solution of 2-ethynyldecahydronaphthalen-2-ol (100.6 g, 0.56 mol) in iPrOH (300 ml) was added slowly at 0°C under nitrogen atmosphere to a mixture of KOH (47.5 g), K₂CO₃ (6.5 g) and CuCl (4.4 g) in MeOH (300 ml). After stirring for
10 additional 30 min at 0°C, allylbromide (102 g, 0.85 mol) was added slowly over a period of 25 min. The reaction mixture was stirred overnight at RT, quenched with NH₄Cl and concentrated in vacuo. The residue was taken up in saturated NH₄Cl (500 ml) solution, extracted with MTBE (2 x 400 ml).
15 The combined organic phases were washed with saturated NH₄Cl solution (500 ml), H₂O (2 x 500 ml), saturated NaCl solution (500 ml) until neutral pH, dried (MgSO₄) and evaporated in vacuo to yield quantitatively 120 g of crude product which was used without further purification in the next step.

20

c) 1-(1,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one
1-(3,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one
1-(1,2,3,4,5,6,7,8,-Octahydronaphth-2-yl)pent-4-ene-1-one

25 A solution of 2-(pent-4-en-1-ynyl)decahydronaphthalen-2-ol (120 g, 0.55 mol) in HCOOH 80% (200 ml) was heated at 90°C for 16 h. After cooling to RT, the resulting brown mixture was neutralized with saturated Na₂CO₃ and extracted with MTBE (2 x 400 ml). The combined organic phases are washed with NaHCO₃
30 (2 x 400 ml), H₂O (2 x 400 ml) and dried over MgSO₄. After distillation with a Vigreux column, 54.2 g (45%) of the olfactorily pure product was obtained as a mixture of 5 isomers.

Odor (mixture of 5 isomers): green-galbanum, fruity

¹H-NMR (200MHz, CDCl₃): 6.90 (m, ~0.9H), 6.85 (m, 1H), 5.00
5 (m, 2H), 2.82-1.20 (m, 18H). MS (EI): Peak 1 (22%):
218(M⁺,18), 176(6), 163(30), 135(100), 119(7), 107(9),
105(8), 93(23), 91(38), 79(22), 67(24), 55(33), 41(12); Peak
2 (8%): 218(M⁺,55), 177(54), 163(100), 145(19), 135(92),
119(13), 107(24), 105(18), 93(47), 91(57), 79(49), 67(68),
10 55(54), 41(25); Peak 3 (15%): 218(M⁺,46), 177(50), 163(87),
145(19), 135(100), 119(12), 107(24), 105(16), 93(47), 91(50),
79(47), 67(67), 55(47), 41(27); Peak 4 (13%): 218(M⁺,11),
177(1), 163(100), 145(2), 135(11), 107(7), 93(25), 91(15),
79(20), 67(20), 55(18), 41(11); Peak 5 (42%): 218(M⁺,8),
15 177(2), 163(100), 145(4), 135(11), 107(12), 93(24), 91(16),
79(21), 67(21), 55(20), 41(11). IR (mixture of 5 isomers,
neat): 2923s, 2853m, 1669vs, 1640m cm⁻¹.

The main and most powerful isomer, cis-1-(1,4,4a,5,6,7,8,8a-
20 octahydronaphth-2-yl)pent-4-ene-1-one, with a GC-odor
threshold of 10 pg was isolated by preparative GLC for ¹H-NMR
analysis. ¹H-NMR (400MHz, CDCl₃): 6.85 (m, 1H, CH=C), 5.85
(ddt, 1H, J = 17.0, 10.2, 6.6, H-C(4)), 5.05 (ddt, J = 17.1,
1.6, 1.6, 1H, H-C(5)), 4.98 (ddt, J = 10.1, 1.8, 1.2, H'-
25 C(5)), 2.74 (t, J = 7.6, H-C(2)), 2.35 (m, 2H, -CH₂-), 2.30-
2.13 (m, 4H, -CH₂-), 1.85 (m, 2H, -CH-), 1.57 (m, 2H, -CH₂-),
1.47-1.32 (m, 6H, -CH₂-).

The compounds of the following examples were all prepared
30 according to the general procedure described in Example 11.
Only the spectroscopic data and olfactory properties for each
example are given below.

- 19 -

Example 121-(2,3,3a,4,7,7a-hexahydro-1H-indene-5-yl)pent-4-ene-1-one1-(2,3,3a,6,7,7a-hexahydro-1H-indene-5-yl)pent-4-ene-1-one5 1-(2,3,4,5,6,7-hexahydro-1H-indene-5-yl)pent-4-ene-1-one

Odor (mixture of 3 isomers): green-galbanum, cassis,
boysenberry, metallic

10 ¹H-NMR (200MHz, CDCl₃): 6.90 (m, ~0.8H), 6.85 (m, 1H), 5.00
(m, 2H), 2.82-1.20 (m, 16H). MS (EI): Peak 1 (16%):
204(M⁺, 18), 162(7), 149(34), 121(100), 107(5), 105(7),
93(25), 91(37), 79(39), 67(14), 55(35), 41(11); Peak 2 (61%):
204(M⁺, 14), 163(16), 149(100), 131(17), 121(22), 107(13),
15 105(11), 93(25), 91(23), 79(34), 67(12), 55(18), 41(10); Peak
3 (23%): 204(M⁺, 7), 163(2), 149(100), 131(6), 121(7), 107(5),
105(7), 93(26), 91(16), 79(32), 67(13), 55(19), 41(9). IR
(mixture of 3 isomers, neat): 2943s, 2867m, 1710w, 1668vs,
1639m cm⁻¹.

20

Example 131-(4a-Methyl-3,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-ene-1-one25 1-(4a-Methyl-1,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-ene-1-one

Odor (mixture of 4 isomers): violet, woody, green-galbanum,
pineapple

30

- 20 -

$^1\text{H-NMR}$ (200MHz, CDCl_3): 6.85 + 6.75 (2m, 1H, $\text{CH}=\text{C}$), 5.85 (m, 1H, $\text{CH}=\text{CH}_2$), 5.00 (m, 2H, $\text{CH}=\text{CH}_2$), 2.75 (m, 2H), 2.60-1.00 (m, 15H), 0.95 + 0.89 + 0.78 (3s, 3H). MS (EI): Peak 1 (32%): 232 (M^+ , 56), 217 (32), 204 (3), 191 (44), 177 (100), 159 (20), 149 (26), 135 (18), 121 (16), 109 (84), 96 (23), 93 (24), 91 (55), 81 (52), 79 (39), 67 (65), 55 (68), 41 (30); Peak 2 (52%): 232 (M^+ , 15), 217 (5), 204 (3), 191 (2), 177 (100), 159 (3), 149 (16), 137 (7), 121 (3), 109 (9), 107 (9), 96 (10), 93 (13), 91 (16), 81 (73), 67 (14), 55 (23), 41 (10); Peak 3 (2%): 232 (M^+ , 46), 217 (25), 191 (35), 177 (43), 161 (12), 159 (11), 149 (100), 135 (13), 121 (12), 109 (70), 107 (27), 93 (42), 91 (48), 81 (52), 67 (55), 55 (67), 41 (30); Peak 4 (14%): 232 (M^+ , 8), 217 (3), 204 (2), 191 (2), 177 (100), 159 (3), 149 (8), 121 (5), 109 (7), 107 (16), 93 (16), 91 (12), 81 (34), 67 (14), 55 (20), 41 (10); IR (mixture of 4 isomers, neat): 2925vs, 2860s, 1668vs, 1640m cm^{-1} .

Example 14

20 1-(4-Methyl-1,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-ene-1-one
1-(4-Methyl-3,4,4a,5,6,7,8,8a-octahydronaphth-2-yl)pent-4-ene-1-one
1-(4-Methyl-1,2,3,4,5,6,7,8-octahydronaphth-2-yl)pent-4-ene-
 25 1-one

Odor (mixture of 3 isomers): woody, green-galbanum, fruity, fatty

- 21 -

¹H-NMR (200MHz, CDCl₃): 6.62 + 6.59 (2m, ~0.8H, CH=C), 5.82 (m, 1H, CH=CH₂), 5.00 (m, 2H, CH=CH₂), 2.75 (m, 2H), 2.68-0.70 (m, 18H). MS (EI): Peak 1 (11%): 232(M⁺,4), 217(1), 203(3), 190(8), 177(22), 159(3), 149(100), 133(14), 121(6), 119(8), 105(37), 91(39), 81(24), 79(22), 67(15), 55(53), 41(20); Peak 2 (56%): 232(M⁺,42), 217(5), 203(3), 191(33), 177(100), 159(11), 149(75), 135(9), 133(14), 121(16), 109(31), 107(26), 93(40), 91(44), 81(48), 67(57), 55(74), 41(44); Peak 3 (33%): 232(M⁺,78), 217(7), 203(3), 191(73), 177(100), 159(15), 149(32), 135(13), 121(21), 109(57), 107(35), 93(47), 91(43), 81(56), 67(68), 55(80), 41(50). IR (mixture of 3 isomers, neat): 2922vs, 2852s, 1711m, 169vs, 1640m cm⁻¹.

15

Example 151-(3a,4,5,6,7,7a-hexahydro-1H-indene-2-yl)pent-4-ene-1-one1-(2,3,4,5,6,7-hexahydro-1H-indene-2-yl)pent-4-ene-1-one

20 Odor (mixture of 3 isomers): fruity, pineapple, green-galbanum

¹H-NMR (400MHz, CDCl₃): 6.69 (m, 0.8H, CH=C), 5.83 (m, 1H, CH=CH₂), 5.05 (m, 1H, CH=CH₂), 4.98 (m, 1H, CH=CH₂), 2.75 (m, 2H), 2.60-2.20 (m, 5H), 1.90 (m, 1H), 1.78-0.25 (m, 8H). MS (EI): Peak 1 (3%): 204(M⁺,5), 149(3), 121(100), 105(3), 93(20), 91(13), 79(30), 77(12), 67(12), 55(13), 41(6); Peak 2 (16%): 204(M⁺,16), 189(9), 162(4), 149(34), 131(2), 121(100), 107(9), 105(5), 93(18), 91(28), 79(27), 77(14), 67(11), 55(20), 41(9); Peak 3 (79%): 204(M⁺,12), 189(1), 163(14), 149(100), 131(11), 121(47), 107(7), 105(8), 93(29), 91(21),

- 22 -

79(37), 77(17), 67(14), 55(18), 41(9); IR (mixture of 3 isomers, neat): 2925vs, 2851s, 1667vs, 1641m cm^{-1} .

Example 16

5 Feminine composition for toiletries

	parts per weight
Adoxal (10% DPG)	10
Ambrofix	3
Beta-ionone	10
Bergamote oil abergapt	50
Calone 1951 (10% DPG)	10
Cepionate	200
Citronellol	30
Dasmascenone (10% DPG)	10
Dihydromyrcenol	30
Ethyllinalool	40
Florhydral	5
Galaxolide 50% PHT	200
α -Hexyl cinnamic aldehyde	80
Phenylethyl alcohol	50
Indol (10% DPG)	5
Iso E super	40
Isoraldeine 95	50
Jasmone cis (10% DPG)	10
Lilial	50
Melonal (10% DPG)	5
Methyl anthranilate (10% DPG)	10
Methyl pamplemousse (1,1-dimethoxy-2,2,5-trimethyl-4-hexene)	20
Nectaryl	2
Radjanol	20
Tropional	15
Tricyclal (10% DPG)	10
Vanilline (10% DPG)	5
Viridine (10% DPG)	10
Ylang Ylang oil.	10
2-Cyclohexyl-hepta-1,6-dien-3-one (10% DPG)	10
	1000

In this feminine accord, 2-cyclohexyl-hepta-1,6-dien-3-one enhances the fruity hesperidic part giving a vibrant character to the fragrance. Its long-lasting effects is very useful to keep the fragrance fresh over time.

5

Example 17

Green-marine composition for toiletries

	parts per weight
Acetal CD (phenylacetaldehyde glycerylacetal)	40
Acetal R (acetaldehyde phenylethyl propyl acetal)	2
Adoxal 10% DPG (2,6,10-trimethyl-9-undecenal)	1.5
Phenoxyethyl alcohol	70
Linalyl benzoate	100
Bigarade oil	10
Clonal (10% DPG)	5
Beta-damascone	5
Dimetol (2,6-dimethyl-2-heptanol)	25
Disopropylene glycol	375
Florhydral	20
Glycollierral	60
(Z)-Hex-3-en-1-ol	5
(Z)-Hex-3-en-1-yl acetate	2.5
(Z)-Hex-3-en-1-yl formiate	5
(Z)-Hex-3-en-1-yl salycilate	5
Hexyl propionate	10
Beta-ionone	10
Linalool	100
Linalool oxyde (1% DPG)	2.5
Melonal (10% DPG)	2.5
Menthe Crepue Ess USA (10% DPG)	10
Nerol	80
Nerolidol	40
Radjanol	5
Viridine (10% PE)	5
2-Cyclohexylhepta-1,6-dien-3-one	4
	1000

- 24 -

The new compound, namely 2-cyclohexylhepta-1,6-dien-3-one, brings a fresh, natural galbanum note to the perfumed composition, enhancing its diffusion and adding a fresh pineapple top note.

5

Example 18

Floral composition for fabric softener

	parts per weight
Acetate PA (2-propenyl phenoxyacetate)	15
Allyl amyl glycolate	15
Ambrofix	1
Benzyl acetate	60
Citronellol extra	50
Citronellyl acetate	30
Cyclal C	10
Dihydromyrcenol	50
Ebanol	10
Freskomenthe	5
Galaxolide 50% PHT	60
Geranitrite	12
Givescone	7
α -Hexylcinnamic aldehyde	200
Iso E Super	30
Linalool	60
Lilial	60
Nectaryl	5
Neroline crist.	5
Rosacetol	20
Roseoxyde	8
Terpineol	60
10-Undecenal	2
Verdyl acetate	200
Ylang Oil	15
2-Cyclohexylhepa-1,6-dien-3-one (10% DPG)	10
	1000

- 25 -

In this floral accord 2-cyclohexylhepta-1,6-dien-3-one with its green-galbanum note gives a fresh and clean effect to the fragrance, both on wet and on dry laundry.

5 Example 19

Fresh floral composition for softeners

	parts per weight
Adoxal (10% DPG)	1
Agrumex	40
Amberketal (10% IPM)	15
Ambretone	10
Bigarade oil	20
Citronellol	35
Beta-Damascone	2.5
Dimethylbenzylcarbiny l acetate	75
Ebanol	20
Fixambrene	10
Florhydral	10
Gardenol	7.5
α -Hexylcinnamic aldehyde	70
Hexyl salicylate	100
Beta-ionone	40
Isoraldeine	30
Jasmin reconst.	15
Jasmonyl	25
Lilial	70
2-Methylundecanal	5
Oranger crystals	4
Phenylethylalcohol	85
Rosacetol	30
Tetrahydro linalool	100
Thibetolide	20
Undecavertol	25
9-Undecenal	5
Verdylpropionate	55
Vertofix coeur	55

- 26 -

1-(1,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one 20
1-(3,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one

1000

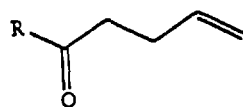
The novel compound adds a fresh, fruity galbanum note to the perfumed composition, enhancing its volume, diffusion and long-lastingness.

5

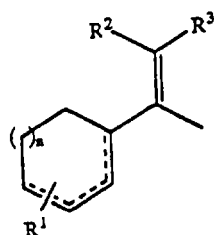
For the exact definition of the trivial names mentioned above, see Flavor and Fragrance materials 1998, Allured publishing Corporation, Carol Stream, Illinois, U.S.A. or Arctander, Perfume and Flavor Chemicals - 1969, published by
10 the author, Montclair, New Jersey, U.S.A.

What is claimed is:

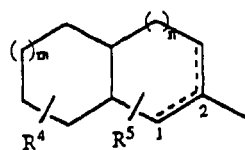
1. A compound of formula I



wherein R is a residue A

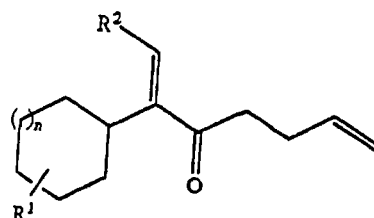


or a residue B



and R^1 , R^2 , R^3 , R^4 , and R^5 are independently hydrogen, methyl or ethyl, and further wherein R^1 , R^4 , and R^5 are located at any position of the ring structure, n and m are independently 0, 1, 2, or 3 and the dotted lines represent in formula A an optional double bond and in formula B a double bond either in position 1 or 2.

2. A compound according to claim 1 of formula Ia



wherein R^1 and R^2 are independently hydrogen or methyl and n is for 0 or 1.

3. A compound according to claim 1 wherein the compound is 2-Cyclohexylhepta-1,6-dien-3-one.
4. A compound according to claim 1 wherein the compound is (E)- and/or (Z)-3-Cyclohexylocta-2,7-dien-4-one.
5. A compound according to claim 1 wherein the compound is 2-Cyclopentylhepta-1,6-dien-3-one.
6. A compound according to claim 1 wherein the compound is 1-(3,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one.
7. A compound according to claim 1 wherein the compound is 1-(1,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one.
8. A composition comprising at least 1 compound according to claim 1.
9. A composition according to claim 8 comprising 1-(3,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one and 1-(1,4,4a,5,6,7,8,8a-Octahydronaphth-2-yl)pent-4-ene-1-one.
10. A composition according to claim 8 wherein the composition exhibits a green-galbanum fresh (metallic type) and fruity-pineapple and/or fruity-cassis odor.

α,β -UNSATURATED KETONES

Abstract

The present invention relates to new α,β -unsaturated ketones of formula I. The symbols in formula I have the meaning as defined in claim 1. The new compounds exhibit an intense,
5 very long lasting green galbanum-type odor with fruity undertones.