



The invention is concerned with aldehydes and ketones having a bicyclo[6.4.0]-
 dodec-1(8)-en-10-yl, bicyclo[5.4.0]undec-1(7)-en-9-yl, bicyclo[6.4.0]dodec-1(12)-en-10-
 yl or bicyclo[5.4.0]undec-1(11)-en-9-yl skeleton, especially 1-{bicyclo[6.4.0]dodec-1(8)-
 en-10-yl}ethan-1-ones, 1-{bicyclo[6.4.0]dodec-1(8)-en-10-yl}methanals, 1-{bicyclo[5.4.0]-
 5 undec-1(7)-en-9-yl}ethan-1-ones, 1-{bicyclo[5.4.0]undec-1(7)-en-9-yl}methanals, 1-
 {bicyclo[6.4.0]dodec-1(12)-en-10-yl}ethan-1-ones, 1-{bicyclo[6.4.0]dodec-1(12)-en-10-
 yl}methanals, 1-{bicyclo[5.4.0]undec-1(11)-en-9-yl}ethan-1-ones and 1-{bicyclo[5.4.0]-
 undec-1(12)-en-9-yl}methanals, which can be methyl- or ethyl-substituted on the six-
 membered ring, as well as their use as odorants.

10 Ionones and their linear derivatives (for example, Raldeine[®] or Timberol[®]) as well
 as their cyclic derivatives (for example, Iso E Super[®]) play a central rôle in perfumery. In
 particular, in the last ten years the classical perfumes with top, middle and base notes have
 been superseded more and more by monolithic creations, which are build around a main
 accord from relatively few olfactory substances of which some can be present in an amount
 15 of up to 25% and more in a composition [R. R. Calkin, J. S. Jellinek, Perfumery - Practice
 and Principles, Wiley, New York 1994, 138-140]. Ionones and their derivatives are
 preferred olfactory substances for the composition of such accords and perfumes, as they
 combine harmonically with a large number of olfactory building blocks, confer trans-
 parency and warmth to the compositions and their soft, floral-woody notes themselves
 20 remain pleasant in high concentration. On the other hand, ionones and ionone derivatives
 are a relatively old class of odorant substances and although they cover an entire spectrum
 from fresh floral to strong woody-amber like facets, there exists, however, a great need for
 novel compounds of similar tonality, but with new, individual olfactory characters in order
 to create new original accords which, in turn, can be used as components of new trend
 25 perfumes (for example, the so-called "sheer orientals").

In aldehydes and ketones having the bicyclo skeleton indicated in more detail above
 there has now been found a class of compounds which enriches the woody-floral olfactory
 spectrum of ionones and ionone derivatives by new facets and thereby satisfies the afore-

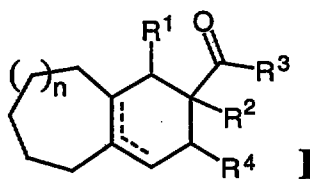
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mentioned requirements in an advantageous manner. This novel class of compounds is represented by formula I



wherein

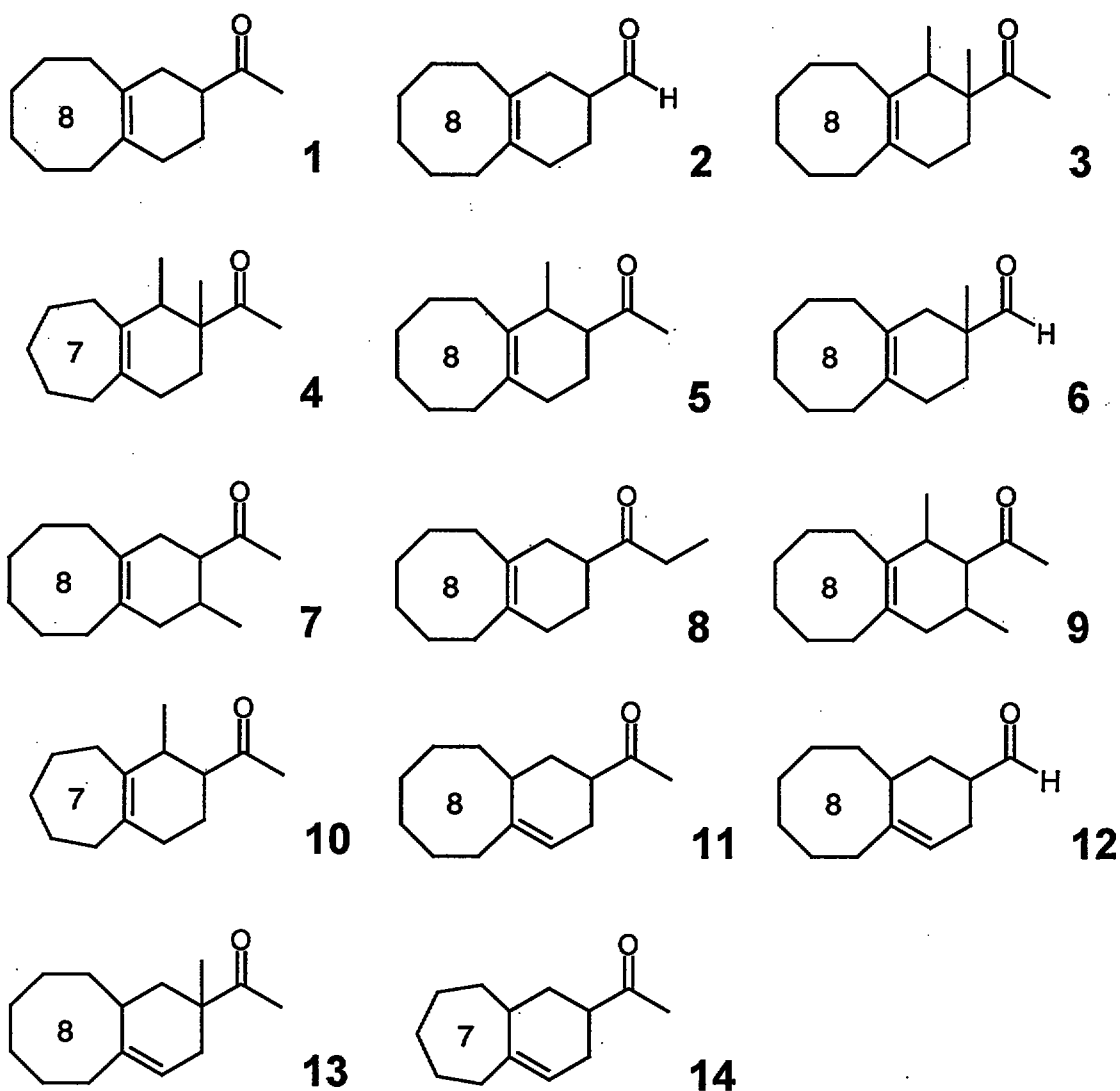
5 $n =$ 1 or 2;

R^1 and $R^4 =$ H or CH_3 ; and

R^2 and $R^3 =$ H, CH_3 or CH_2CH_3

 and the dotted line signifies a double bond between the two bridgehead atoms or between bridgehead atom 1 and ring atom 11 or 12.

10 The compounds of formula I are novel. Formula I accordingly embraces aldehydes as well as methyl ketones and ethyl ketones with bicyclo[6.4.0]dodec-1(8)-en-10-yl or bicyclo[5.4.0]undec-1(7)-en-9-yl substituents or, respectively, bicyclo[6.4.0]dodec-1(12)-en-10-yl or bicyclo[5.4.0]undec-1(11)-en-9-yl substituents, which can carry methyl or ethyl substituents on the cyclohexene ring. The following compounds 1-14 are preferred
15 examples of this novel class of compounds:



The compounds of formula I have woody-flowery notes, which are reminiscent of ionones, and in addition aldehydic, maritime, amber- and tobacco-like, to some extent also fruity-fresh, melon-like, or balsamic side-notes. In some cases, e.g. in the case of compounds 3 and 4, the woody character dominates strongly and the total olfactory impression is woody-amber like to dry-frankincense like, reminiscent of Iso E Super[®], as well as of vetiver oil. In addition to these compounds 3 and 4, which are outstanding in the scope of the invention, there are perfumistically interesting in an advantageous manner primarily the aldehydes 2 and 6, followed by the R¹-methyl substituted compounds 5 and 10. The compounds of formula I, and especially the compounds 1-13, are intended to embrace in accordance with the invention all possible stereomers and diastereomers of the respective compounds. In some instances these compounds in accordance with the invention differ greatly in their intensity and in their odour, but on the basis of their odour each of them can be used perfumistically. In the Examples which follow the respective

olfactory intensity and at the same time the especially interesting diastereomers are described and characterized in more detail.

The compounds of formula I harmonize with a large number of natural and/or synthetic raw materials which are frequently used in odorant compositions. Especially in the floral and chypre olfactory directions interesting accords and perfumes can be synthesized around the compounds of formula I. However, the compounds of formula I are outstandingly suitable for monolithic compounded perfumes of oriental-amber like olfactory directions. Further, extraordinary, new accentuated woody compositions such as, for example, of the "Féminité du Bois" (Shiseido 1992) type can be synthesized very advantageously with the compounds of formula I.

The use in accordance with the invention of the compounds of formula I is, however, limited neither to these types of perfume, nor to special olfactory directions, odorant derivatives or classes of chemical substances. Examples of classes of substances which harmonize especially well are:

- | | | |
|----|------------------------------------|---|
| 15 | - Ethereal oils and extracts, e.g. | bay oil, bergamot oil, cedarwood oil, geranium oil, guaiac wood oil, patchouli oil, petitgrain oil, rose oil, rosewood oil, vetiver oil, ylang-ylang oil; |
| 20 | - alcohols, e.g. | citronellol, Dimetol [®] , Ebanol [®] , cis-3-hexenol, geraniol, linalool, Peonile [®] , phenoxanol, Rosalva [®] , Rosaphen [®] , Sandalore [®] , cinnamic alcohol; |
| 25 | - aldehydes and ketones, e.g. | alpha-amylcinnamaldehyde, Cashmeran [®] , beta-damascenone, Dupical [®] , Florhydral [®] , Frambinon [®] , Givescone [®] , Hedion [®] , hydroxycitronellal, Lilial [®] , vanillin; |

- ethers and acetals, e.g.
 - Ambrox[®], Calone[®],
 - Galaxolide[®], Magnolan[®],
 - Rhubafuran[®], rose oxide,
 - Spirambrene[®];
- 5 - esters and lactones, e.g.
 - Agrumex[®], benzyl acetate,
 - benzyl salicylate, citronellyl
 - acetate, delta- and gamma-
 - decalactone, gamma-undecalactone;
- 10 - macrocycles, e.g.
 - Ambrettolide[®], Ambretone[®],
 - muscone, musk R-1,
 - Thibetolide[®], Trimofix O[®];
- heterocycles, e.g.
 - indole, skatole.

The synthesis of the compounds of formula I can be effected on the one hand, as enlarged upon by way of example in Examples 1 and 11, by Diels-Alder reaction of the

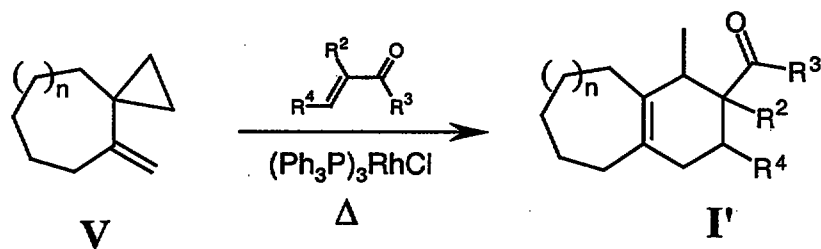
15 corresponding bis(methylene)cycloalkanes, ethyldidenemethylenecycloalkanes or 1-vinylcycloalkenes, accessible, for example, according to J. W. van Straten, J. J. van Norden, T. A. M. van Schaik, G.T. Franke, W. H. de Wolf, F. Bickelhaupt [Recl. Trav. Chim. Pays-Bas 1978, 97, 105] or W. Herz and R.-R. Juo [J. Org. Chem. 1985, 50, 618]. On the other

hand, in accordance with the invention there has now been found for the R¹-methyl

20 substituted compounds of formula I having a bridgehead-positioned double bond (formula I') a novel route via vinylcyclopropanes (V), which is enlarged upon by way of example in Example 6. Thereby, 4-methylenespiro[2.7]decane and, respectively, 4-methylenespiro[2.6]nonane, which are accessible from spiro[2.7]decan-4-one and, respectively, spiro[2.6]nonan-4-one, for example by a Wittig reaction, are heated under

25 reflux for several hours to a few days with a catalyst, preferably the Wilkinson catalyst, in a high-boiling, relatively non-polar solvent such as e.g. toluene or xylene. The compounds I' are then isolated regioselectively and in some cases, as in Example 6, also Z-diastereoselectively as the main product of this novel reaction. As the starting materials spiro[2.7]-decan-4-one and spiro[2.6]nonan-4-one are readily accessible according to a S. M. Ruder,

30 R. C. Ronald [Tetrahedron Lett. 1984, 25, 5501], this route is an attractive alternative for the synthesis of the compounds I' via exocyclic dienes:



wherein

$n = 1$ or 2 ; $\text{R}^4 = \text{H}$ or CH_3 ; and

5 R^2 and $\text{R}^3 = \text{H}$, CH_3 or CH_2CH_3 .

A further advantage of this process is that the intermediates V in which n is 1 or 2 are themselves novel, interesting fresh, green-minty, somewhat woody-fruity odorants, which likewise can be used in perfumery.

Example 1

10

1-{Bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (1)

The starting material, 1,2-bis(methylene)cyclooctane, was prepared according to J. W. van Straten, J. J. van Norden, T. A. M. van Schaik, G. T. Franke, W. H. de Wolf, F. Bickelhaupt [Recl. Trav. Chim. Pays-Bas 1978, 97, 105].

15 1.46 ml (17.8 mmol) of but-3-en-2-one were added while stirring to a solution of 2.00 g (14.7 mmol) of 1,2-bis(methylene)cyclooctane in 20 ml of dry toluene and the reaction mixture was cooled to 0°C. At this temp. 160 mg (1.20 mmol, 7 mol%) of aluminium trichloride were added thereto under nitrogen. After stirring at 0°C for 5 min. the cooling was removed, the reaction mixture was stirred at room temperature for 60 h. under

20 nitrogen and thereupon the mixture was poured into 400 ml of tert-butyl methyl ether/water (1:1). The organic phase was separated and the aqueous phase was extracted three times with 200 ml of tert-butyl methyl ether. The organic phases were combined, dried over sodium sulphate and concentrated on a rotary evaporator. After flash chromatography (n-pentane/tert-butyl methyl ether, 20:1, $R_f = 0.58$) on silica gel there were

25 obtained 2.54 g (84%) of 1-{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (1) as a colourless liquid.

- Odour: Woody-flowery after β -ionone, fruity-fresh, slightly aldehydic and amber-like. – IR (film): $\nu = 1711\text{ cm}^{-1}$ ($\nu\text{C=O}$); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.35\text{--}1.57$ (m, 10H, 3'-H₂–6'-H₂, 11'-H₂), 2.18 (s, 3H, 2-H₃), 1.93–2.14 (m, 8H, 2'-,7'-,9'-,12'-H₂), 2.55 (dddd, J 11.5, 10.1, 5.3, 2.8 Hz, 1H, 10'-H); – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 25.29$ (t, C-11'), 26.47/26.48 (t, C-3',-6'), 27.88 (q, C-2), 28.71/28.81 (t, C-4',-5'), 29.07/31.05 (t, C-2',-7'), 31.54/31.70 (t, C-9', -12'), 48.19 (d, C-10'), 128.79 (s, C-1'), 130.27 (s, C-8'), 211.86 (s, C-1); – MS (EI): m/z (%) = 43 (87) [$\text{C}_2\text{H}_3\text{O}^+$], 67 (100) [C_5H_7^+], 81 (68) [C_6H_9^+], 93 (20)/107 (15)/121 (15)/135 (7)/149 (5) [$\text{C}_n\text{H}(2n-5)^+$ series], 163 (49) [$\text{M}^+ - \text{C}_2\text{H}_3\text{O}$], 191 (4) [$\text{M}^+ - \text{CH}_3$], 206 (23) [M^+]; – $\text{C}_{14}\text{H}_{22}\text{O}$ (206.33): calc. C 81.50, H 10.75; found C 81.49, H 10.57.
- 10 The compounds of Examples 2-5 are accessible in an analogous manner from 1,2-bis(methylene)-cyclooctane. With respect to these there are therefore set forth only the olfactory characteristics, the spectroscopic data and in some cases the elementary analysis.

Example 2

15 1-{Bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}methanal (2)

- Odour: Maritime, reminiscent of watermelons, tobacco or cigarette-like and somewhat ionone like-fruity. – IR (film): $\nu = 1726\text{ cm}^{-1}$ ($\nu\text{ HC=O}$); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.41\text{--}1.65$ (m, 10H, 3'-H₂–6'-H₂, 11'-H₂), 1.93–2.13 (m, 8H, 2'-,7'-,9'-,12'-H₂), 2.47 (m_C, 1H, 10'-H), 9.69 (d, J 1.2 Hz, 1H, CHO); – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 22.78$ (t, C-11'), 26.49/26.52 (t, C-3',-6'), 27.99/28.52 (t, C-4',-5'), 28.79/28.81 (t, C-2',-7'), 31.70/31.77 (t, C-9',-12'), 46.81 (d, C-10'), 128.43 (s, C-1'), 130.82 (s, C-8'), 204.82 (d, C-1); – MS (EI): m/z (%) = 29 (33) [CHO], 41 (72) [C_3H_5^+], 67 (90) [C_5H_7^+], 91 (98) [C_7H_7^+], 107 (51)/121 (34)/135 (29)/149 (12) [$\text{C}_n\text{H}(2n-5)^+$ series], 164 (31) [$\text{M}^+ - \text{CO}$], 192 (100) [M^+].

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Example 3

1-{10'-Methylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}methanal (6)

Odour: Fruity-ionone like, amber- and tobacco-like, with a watermelon note. – IR (film): $\nu = 1727\text{ cm}^{-1}$ ($\nu\text{ HC=O}$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.04$ (s, 3H, 10'-Me), 1.37–1.54 (m,

10H, 3'-H₂-6'-H₂, 11'-H₂), 1.78 (d, J 16.0 Hz, 1H, 9'-H_b), 2.01-2.12 (m, 6H, 2'-,7'-,12'-H₂), 2.29 (d, J 16.0 Hz, 1H, 9'-H_a), 9.47 (s, 1H, CHO); - ¹³C-NMR (CDCl₃): δ = 20.68 (q, 10'-Me), 26.42/26.48 / 26.61 (t, C-3',-6',-11'), 28.80/28.91 (t, C-4',-5'), 29.09 (t, C-12'), 31.63/31.86 (t, C-2',-7'), 35.88 (t, C-9'), 45.08 (s, C-10'), 128.17 (s, C-1'), 130.07 (s, C-8'),
 5 206.19 (d, C-1); - MS (EI): m/z (%) = 29 (36) [CHO], 41 (78) [C₃H₅⁺], 67 (65) [C₅H₇⁺], 81 (100) [C₆H₉⁺], 95 (61) [C₇H₁₁⁺], 121 (39)/135 (29)/149 (20)/163 (28) [C_nH(2n-5)⁺ series], 177 (70) [M⁺-CHO], 191 (9) [M⁺-CH₃], 206 (31) [M⁺].

Example 4

10 (r-10',c-11')-1-{11'-Methylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (7)

Odour: Woody, ionone-like, somewhat reminiscent of coffee. - IR (film): ν = 1710 cm⁻¹ (ν C=O); - ¹H-NMR (CDCl₃): δ = 0.93 (d, J 6.4 Hz, 3H, 11'-Me), 1.35-1.55 (m, 8H, 3'-H₂-6'-H₂), 1.76-2.16 (m, 9H, 2'-,7'-,9'-,12'-H₂, 11'-H_{ax}), 2.17 (s, 3H, 2-H₃), 2.36 (ddd, J 10.3, 10.3, 5.4 Hz, 1H, 10'-H_{ax}); - ¹³C-NMR (CDCl₃): δ = 19.48 (q, 11'-Me), 26.44/26.25 (t, C-3',-6'), 28.70/28.74 (t, C-4',-5'), 29.21 (q, C-2), 30.83 (d, C-11'), 31.30/31.42/32.47 (t, C-2',-7',-9'), 37.78 (t, C-12'), 55.17 (d, C-10'), 128.26 (s, C-1'), 129.95 (s, C-8'), 213.01 (s, C-1);
 15 -MS (EI): m/z (%) = 43 (61) [C₂H₃O⁺], 67 (100) [C₅H₇⁺], 95 (63) [C₇H₁₁⁺], 177 (52) [M⁺-C₂H₃O], 205 (5) [M⁺-CH₃], 220 (19) [M⁺]; - C₁₅H₂₄O (220.35): calc. C 81.76, H 10.98; found C 81.46, H 10.95.

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Example 5

1-{Bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}propan-1-one (8)

Odour: Reminiscent of β-ionone, fruity-floral, fresh, somewhat pear-like. - IR (film): ν = 1711 cm⁻¹ (ν C=O); - ¹H-NMR (CDCl₃): δ = 1.06 (t, J 7.2 Hz, 3H, 3-H₃), 1.35-1.58 (m, 10H, 3'-H₂-6'-H₂, 11'-H₂), 1.99-2.18 (m, 8H, 2'-,7'-,9'-,12'-H₂), 2.48 (dq, J 17.6, 7.3 Hz, 1H, 2-H_b), 2.54 (dq, J 17.6, 7.3 Hz, 1H, 2-H_a), 2.57 (dddd, J 11.6, 10.4, 5.2, 2.9 Hz, 1H, 10'-H); - ¹³C-NMR (CDCl₃): δ = 7.68 (q, C-3), 25.45 (t, C-11'), 26.45/26.47 (t, C-3',-6'), 28.70/28.80 (t, C-4',-5'), 29.12/31.31 (t, C-2',-7'), 31.53/31.69 (t, C-9',-12'), 33.68 (t, C-2), 47.23 (d, C-10'), 128.90 (s, C-1'), 130.17 (s, C-8'), 214.31 (s, C-1); - MS (EI): m/z (%) =
 25 29 (33) [C₂H₅⁺], 57 (40) [C₃H₅O⁺], 67 (100) [C₅H₇⁺], 81 (81) [C₆H₉⁺], 91 (29)

[C₇H₇⁺], 107 (13)/121 (15)/135 (5) [C_nH(2n-5)⁺ series], 163 (49) [M⁺ - C₂H₅-CO], 191 (16) [M⁺ - C₂H₅], 220 (18) [M⁺]; - C₁₅H₂₄O (220.35): calc. C 81.76, H 10.98; found C 81.80, H 10.90.

Example 6

5 (r-9',c-10')-1-{9',10'-Dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (3)

a) Preparation of the intermediate 4-methylenespiro[2.7]decane (V, n = 2)

The starting material, spiro[2.7]decan-4-one, was prepared according to S. M. Ruder, R. C. Ronald [Tetrahedron Lett. 1984, 25, 5501].

64.3 g (180 mmol) of methyltriphenylphosphonium bromide were added while stirring
 10 under nitrogen to a solution of 19.1 g (170 mmol) of potassium tert-butyrate in 350 ml of dry tetrahydrofuran and the mixture was heated to reflux. Thereupon, a solution of 22.8 g (150 mmol) of spiro[2.7]decan-4-one in 50 ml of dry tetrahydrofuran was added dropwise to the boiling reaction mixture and the mixture was heated under reflux for a further 2 h. After cooling, the reaction mixture was poured into 1 l of tert-butyl methyl ether/water
 15 (1:1), the organic phase was separated and the aqueous phase was extracted twice with 500 ml of tert-butyl methyl ether. The organic extracts were combined, dried over sodium sulphate and concentrated on a rotary evaporator. After flash chromatography (n-pentane, R_f = 0.97) on silica gel there were obtained 17.1 g (76%) of 4-methylenespiro[2.7]decane (V, n = 2) as a colourless liquid.

20 Odour: fresh minty, green-resinous, somewhat woody-fruity. - IR (film): ν 2922/2851/2997/3076 cm⁻¹ (ν C-H), 1444 cm⁻¹ (δ H-C-H), 879/1014 cm⁻¹ (δ C=C-H), 1632 cm⁻¹ (ν C=C); - ¹H-NMR (CDCl₃): δ = 0.45 (dd, J 5.8, 3.6 Hz, 2H, 2-H₂), 0.59 (dd, J 5.8, 4.0 Hz, 2H, 1-H₂), 1.45-1.59 (m, 8H, 7-H₂-10-H₂), 1.67-1.73 (m, 2H, 6-H₂), 2.25 (ddd, J 14.6, 6.4, 1.2 Hz, 2H, 5-H₂), 4.71 (dd, J 3.6, 1.2 Hz, 2H, 11-H₂); - ¹³C-NMR (CDCl₃): δ =
 25 14.85 (2t, C-1,-2), 25.00 (s, C-3), 25.24 (t, C-6), 26.38/26.41 (t, C-7,-8), 29.53 (t, C-9), 34.36 (t, C-5), 37.09 (t, C-10), 108.88 (t, C-11), 155.76 (s, C-4); - MS (EI): m/z (%) = 67 (85) [C₅H₇⁺], 79 (100)/93 (61)/107 (29)/121 (21)/135 (13) [C_nH(2n-5)⁺ series], 150 (3) [M⁺].

b) Preparation of (*r*-9',*c*-10')-1-{9',10'-dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}-ethan-1-one (3)

2.20 g (14.6 mmol) of 4-methylenespiro[2.7]decane were dissolved in 20 ml of dry toluene and treated under nitrogen with 550 mg (0.59 mmol, 4 mol%) of tris(triphenylphosphine)-rhodium(I) chloride. 1.80 ml (17.5 mmol) of 3-methyl-3-buten-2-one were introduced by injection while stirring under an inert gas atmosphere and the reaction mixture was thereupon heated to reflux for 40 h. After cooling, the catalyst was separated by filtration over silica gel, the filtrate was poured into 400 ml of tert-butyl methyl ether/water (1:1) and the organic phase was separated. The aqueous phase was extracted three times with 200 ml of tert-butyl methyl ether and the organic extracts were subsequently combined. After drying over sodium sulphate, concentration on a rotary evaporator and flash chromatography (n-pentane/tert-butyl methyl ether, 40:1, $R_f = 0.41$) on silica gel there were obtained 1.62 g (47%) of (*r*-9',*c*-10')-1-{9',10'-dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (3) as a colourless solid.

Odour: Intensive woody-amber like, fresh-dry frankincense-like, reminiscent of Iso E Super[®] and of vetiver oil. – M.p. 56.3°C; – IR (KBr): $\nu = 1704 \text{ cm}^{-1}$ ($\nu \text{ C=O}$); – ¹H-NMR (CDCl₃): $\delta = 0.83$ (d, J 6.8 Hz, 3H, 9'-Me), 1.10 (s, 3H, 10'-Me), 1.42-2.06 (m, 15H, 2'-,7'-H_b, 3'-H₂-6'-H₂, 9'-H, 11'-,12'-H₂), 2.14 (s, 2-H₃), 2.23-2.40 (m, 2H, 2'-,7'-H_a); – ¹³C-NMR (CDCl₃): $\delta = 17.06$ (q, 9'-Me), 21.04 (q, 10'-Me), 22.73 (t, C-11'), 25.36 (q, C-2), 26.62/26.67 (t, C-3',-6'), 26.98 (t, C-4'), 28.75 (t, C-5'), 29.73 (t, C-12'), 30.81 (t, C-7'), 31.68 (t, C-2'), 40.74 (d, C-9'), 49.86 (s, C-10'), 128.85 (s, C-1'), 133.09 (s, C-8'), 214.22 (s, C-1); – MS (EI): m/z (%) = 95 (31) [C₇H₁₁⁺], 191 (100) [M⁺-C₂H₃O], 219 (3) [M⁺-CH₃], 234 (12) [M⁺]; – C₁₆H₂₆O (234.38): calc. C 81.99, H 11.18, O 6.83; found C 81.68, H 11.15, O 6.89.

The compounds of Examples 7-10 are accessible in an analogous manner from 4-methylenespiro[2.7]decane. With respect to these there are therefore given, just as in Examples 2-5, only the olfactory description and the analytical data.

Example 7

(*r*-8',*c*-9')-1-{8',9'-Dimethylbicyclo[5.4.0]undec-1'(7')-en-9'-yl}ethan-1-one (4)

Odour: Woody-cedar like, vetiver, floral, sandalwood-like. – IR (film): $\nu = 1703 \text{ cm}^{-1}$ ($\nu \text{C=O}$); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.77$ (d, J 6.8 Hz, 3H, 8'-Me), 1.06 (s, 3H, 9'-Me),
 5 1.34-1.44 (m, 5H, 4'-H₂, 8'-H, 10'-H₂), 1.68-1.75 (m, 4H, 3'-,5'-H₂), 1.93-2.08 (m, 6H, 2',
 6'-,11'-H₂), 2.11 (s, 3H, 2-H₃); – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 16.32$ (q, 8'-Me), 20.59 (q, 9'-Me), 22.97 (t, C-10'), 25.39 (q, C-2), 26.26/26.82 (t, C-3',-5'), 28.83 (t, C-4'), 32.76 (t, C-11'), 34.40/34.58 (t, C-2',-6'), 43.34 (d, C-8'), 49.54 (s, C-9'), 132.12 (s, C-1'), 135.45 (s, C-7'), 214.14 (s, C-1); – MS (EI): $m/z = 43$ (52) [$\text{C}_2\text{H}_3\text{O}^+$], 95 (100) [$\text{C}_7\text{H}_{11}^+$], 107
 10 (40)/121 (32)/149 (4) [$\text{C}_n\text{H}(2n-5)^+$ series], 177 (81) [$\text{M}^+-\text{C}_2\text{H}_3\text{O}$], 220 (7) [M^+].

Example 8

(*r*-9',*c*-10')-1-{9'-Methylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (5)

Odour: Woody, reminiscent of vetiver and β -ionone, with a slight amber note. – IR (film): $\nu = 1709 \text{ cm}^{-1}$ ($\nu \text{C=O}$); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.84$ (J 6.8 Hz, 3H, 9'-Me), 1.39-1.61
 15 (m, 8H, 3'-H₂-6'-H₂), 1.72 (m_c, 2H, 11'-H₂), 1.93-2.08 (m, 4H, 2'-H₂, 7'-,12'-H_b), 2.16 (s, 3H, 2-H₃), 2.19-2.31 (m, 2H, 7'-,12'-H_a), 2.52 (m_c, 1H, 9'-H), 2.56 (m_c, 1H, 10'-H); –
 $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 14.65$ (q, 9'-Me), 18.07 (t, C-11'), 26.38/26.90 (t, C-3',-6'), 28.39 (q, C-2), 28.46/29.20 (t, C-4',-5'), 30.21/30.83 (t, C-2',-7'), 31.40 (C-12'), 34.50 (d, C-9'), 52.63 (d, C-10'), 130.53/134.38 (s, C-1',-8'), 211.46 (s, C-1); – MS (EI): m/z (%) = 43 (65)
 20 [$\text{C}_2\text{H}_3\text{O}^+$], 81 (100) [C_6H_9^+], 95 (50) [$\text{C}_7\text{H}_{11}^+$], 177 (38) [$\text{M}^+-\text{C}_2\text{H}_3\text{O}$], 205 (3) [M^+-CH_3], 220 (14) [M^+]; – $\text{C}_{15}\text{H}_{24}\text{O}$ (220.35): calc. C 81.76, H 10.98; found C 81.60, H 10.87.

Example 9

25 (*r*-9',*c*-10', *t*-11')-1-{9',11'-Dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (9)

Odour: Woody, balsamic, fruity, relatively weak and slightly reminiscent of β -ionone. – IR (film): $\nu = 1710 \text{ cm}^{-1}$ ($\nu \text{C=O}$); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.84$ (d, J 7.2 Hz, 3H, 11'-Me), 0.91 (d, J 6.0 Hz, 3H, 9'-Me), 1.42-1.55 (m, 8H, 3'-H₂-6'-H₂), 1.67 (dd, J 16.8, 10.4 Hz,

1H, 12-H_b), 1.89-2.27 (m, 5H, 2'-H₂, 7'-H₂, 12'-H_a), 2.09 (m, 1H, 11-H_{ax}), 2.15 (s, 3H, 2-H₃), 2.37 (dq, J 6.0, 4.8 Hz, 1H, 9-H_{eq}), 2.45 (dd, J 11.1, 4.8 Hz, 1H, 10-H_{ax}); – ¹³C-NMR (CDCl₃): δ = 15.30 (q, 9'-Me), 19.93 (q, 11'-Me), 23.85 (d, C-11'), 26.37/26.90 (t, C-3', -6'), 28.41 (t, C-5'), 30.14 (t, C-4'), 30.52 (q, C-2), 30.65 (t, C-7'), 31.23 (t, C-2'), 35.26 (d, C-9'), 38.46 (t, C-12'), 59.06 (d, C-10'), 129.88 (s, C-1'), 134.10 (s, C-8'), 211.05 (s, C-1); – MS (EI): m/z (%) = 43 (68) [C₂H₃O⁺], 95 (100) [C₇H₁₁⁺], 109 (45) [C₈H₁₃⁺], 191.1797 (38) [M⁺-C₂H₃O], 219 (5) [M⁺-CH₃], 234 (11) [M⁺].

Example 10

1-{8'-Methylbicyclo[5.4.0]undec-1'(7')-en-9'-yl}ethan-1-one (10)

10 Odour: Ionone-like, green-floral, woody, creamy. – IR (film): ν = 1709 cm⁻¹ (ν C=O), 1353 / 1376 cm⁻¹ (δ CH₃); – ¹H-NMR (CDCl₃): δ = 0.80 (d, 7.1 Hz, 3H, 8'-Me), 1.34-1.76 (m, 8H, 3'-H₂-5'-H₂, 10'-H₂), 1.99-2.15 (m, 6H, 2', -6', -11'-H₂), 2.16 (s, 3H, 2-H₃), 2.45 (quint, J 6.2 Hz, 1H, 8'-H), 2.58 (ddd, J 12.1, 6.2, 3.2 Hz, 1H, 9'-H); – ¹³C-NMR (CDCl₃): δ = 14.12 (q, 8'-Me), 18.26 (t, C-10'), 26.23/27.25 (t, C-3', -5'), 28.44 (q, C-2), 31.59/32.71 (t, C-2', -6'), 34.12/34.68 (t, C-4', -11'), 36.82 (d, C-8'), 52.32 (d, C-9'), 134.00/137.29 (s, C-1', -7'), 211.53 (s, C-1); – MS (EI): m/z (%) = 28 (38) [CO⁺], 43 (68) [C₂H₃O⁺], 81 (100) [C₆H₉⁺], 91 (34) [C₇H₇⁺], 105 (24) [C₇H₇O⁺], 121 (13) [C₉H₁₃⁺], 163 (38) [M⁺-C₂H₃O], 191 (2) [M⁺-CH₃], 206 (7) [M⁺].

Example 11

20 (*r*-8',*c*-10')-1-{Bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}ethan-1-one (11)

The required diene, 1-vinylcyclooct-1-ene, was synthesized according to W. Herz and R.-R. Juo [J. Org. Chem. 1985, 50, 618].

3.60 ml (44.1 mmol) of but-3-en-2-one were added while stirring to a solution of 3.50 g (36.8 mmol) of 1-vinylcyclooct-1-ene in 40 ml of dry toluene. After cooling to 0°C 0.41 g (3.05 mmol, 8 mol%) of aluminium trichloride was added thereto under nitrogen. After stirring at 0°C for 15 min. the cooling bath was removed and the mixture was left to warm to room temperature. The mixture was then stirred at this temperature for 6 days under nitrogen and thereupon poured into 200 ml of water. The mixture was extracted three times with 200 ml of tert-butyl methyl ether each time, the combined organic extracts were

dried over magnesium sulphate and the solvent was removed on a rotary evaporator. Flash chromatography (n-pentane/tert-butyl methyl ether, 50:1, $R_f = 0.46$) on silica gel yielded 1.79 g (24%) of (*r*-8',*c*-10')-1-{bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}ethan-1-one (11) as the main component in admixture with the regioisomeric (*r*-8',*c*-9')-1-{bicyclo[6.4.0]-
 5 dodec-1'(12')-en-9'-yl}ethan-1-one. Although both isomers have a similar smell, the odour of the mixture is determined by the more intensive (*r*-8',*c*-10')-1-{bicyclo[6.4.0]-dodec-1'(12')-en-10'-yl}ethan-1-one (11).

Odour: Woody-fruity, ionone-like, Raldeine, Vertenex, cedar-like. – IR (film): $\nu = 1709$ cm^{-1} (ν OC=O); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.33\text{--}1.72$ (m, 11H, 2'-H, 4'-H₂-7'-H₂, 9'-H₂),
 10 1.92-2.16 (m, 4H, 3'-,11'-H₂), 2.18 (s, 3H, 2-H₃), 2.19-2.39 (m, 2H, 2'-,8'-H), 2.66 (m_C, 1H, 10'-H), 5.42 (t, J 3.1 Hz, 1H, 12'-H); – $^{13}\text{C-NMR}$ data of the main isomer (CDCl_3): $\delta = 24.64 / 25.17$ (t, C-3',-6'), 25.93 (t, C-11'), 27.10/27.79 (t, C-4',-5'), 28.00 (q, C-2), 29.59 (t, C-7'), 32.62 (t, C-2'), 36.80 (t, C-9'), 38.17 (d, C-8'), 48.37 (d, C-10'), 120.24 (d, C-12'), 143.46 (s, C-1'), 211.98 (s, C-1); – MS (EI): m/z (%) = 43 (100) [$\text{C}_2\text{H}_3\text{O}^+$], 55 (29)
 15 [C_4H_7^+], 67 (62) [C_5H_7^+], 81 (67) [C_6H_9^+], 91 (38) [C_7H_7^+], 107 (13)/121 (15) [$\text{C}_n\text{H}_{(2n-5)}^+$ series], 163 (30) [$\text{M}^+ - \text{C}_2\text{H}_3\text{O}$], 191 (3) [$\text{M}^+ - \text{CH}_3$], 206 (6) [M^+]; – $\text{C}_{14}\text{H}_{22}\text{O}$ (206.33): calc. C 81.50, H 10.75; found C 81.38, H 10.56.

The compounds of the following Examples are accessible in an analogous manner from 1-vinylcyclooct-1-ene. As they likewise occur in admixture with the regioisomeric and
 20 diastereoisomeric Diels-Alder adducts some of the compounds, for unequivocal characterization, were purified micropreparatively and analyzed.

Example 12

25 (*r*-8', *c*-10')-1-{Bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}methanal (12)

Odour: maritime, reminiscent of watermelons, tobacco and wood, somewhat ionone like-fruity and slightly ozone-like. – IR (film): $\nu = 1724$ cm^{-1} (ν CHO); – $^1\text{H-NMR}$ (CDCl_3): $\delta = 1.29\text{--}1.92$ (m, 10H, 3'-H₂-6'-H₂,7'-,9'-H_b), 1.87 (m_C, 1H, 9'-H_a), 1.99 (ddd, J 13.8, 13.6, 3.1 Hz, 1H, 2'-H_b), 2.10 (m_C, 1H, 7'-H_a), 2.07-2.26 (m, 2H, 11'-H₂), 2.27 (m_C, 1H, 2'-H_a),
 30 2.36 (m_C, 1H, 8'-H), 2.55 (m_C, 1H, 10'-H), 5.42 (t, J 2.5 Hz, 1H, 12'-H), 9.70 (d, J 1.6 Hz, 1H, 1-H); – $^{13}\text{C-NMR}$ data of the main isomer (C_6D_6): $\delta = 24.68/25.54/25.38/26.28$ (t, C-

3'-C-6'), 25.45 (t, C-11'), 27.44 (t, C-7'), 28.33 (t, C-9'), 32.81 (t, C-2'), 38.12 (d, C-8'), 47.58 (d, C-10'), 120.43 (d, C-12'), 143.64 (s, C-1'), 202.72 (d, C-1); – MS (EI): m/z (%) = 29 (10) [CHO⁺], 41 (32) [C₃H₅⁺], 67 (26) [C₅H₇⁺], 91 (100) [C₇H₇⁺], 79 (45)/93 (34)/107 (41)/121 (33)/135 (14)/149 (6) [C_nH_(2n-5)⁺ series], 192 (63) [M⁺].

5

Example 13

(*r*-8',*c*-10')-1-[10'-Methylbicyclo[6.4.0]dodec-1'(12')-en-10'-yl]ethan-1-one (13)

Odour: woody-ionone like, creamy, warm, sweet, amber-like, after Iso E Super and Vertofix. Compared with the samples of the regioisomers and diastereoisomers, likewise obtained by preparative GC, compound 13 has the most interesting odour and the lowest threshold value. – IR (benzene): ν = 1705 cm⁻¹ (ν OC=O); – ¹H-NMR (CDCl₃): δ = 1.14 (s, 3H, 10'-Me), 1.34–1.73 (m, 8H, 3'-H₂-6'-H₂), 1.42 (m_c, 1H, 7'-H_b), 1.52 (dd, *J* 13.0, 4.9 Hz, 1H, 9'-H_b), 1.66 (dd, *J* 13.0, 12.2 Hz, 1H, 9'-H_a), 1.83 (m_c, 1H, 7'-H_a), 1.89 (dd, 1H, *J* 15.0, 3.3 Hz, 1H, 11'-H_b), 1.99 (ddd, *J* 13.4, 12.5, 3.5 Hz, 1H, 2'-H_b), 2.17 (s, 3H, 2-Me), 2.26 (m_c, 1H, 2'-H_a), 2.29 (m_c, 1H, 8'-H), 2.31 (dd, 1H, *J* 15.0, 3.3 Hz, 1H, 11'-H_a), 5.37 (t, *J* 3.3 Hz, 1H, 12'-H); – ¹³C-NMR (CDCl₃): δ = 20.26 (q, 10'-Me), 24.77 (q, C-2), 24.78/25.23 (t, C-3',-6'), 26.02/27.07 (t, C-4',-5'), 32.56 (t, C-2'), 32.78 (t, C-7'), 33.60 (t, C-11'), 34.47 (d, C-8'), 34.72 (t, C-9'), 46.65 (s, C-10'), 119.42 (d, C-12'), 142.04 (s, C-1'), 214.48 (s, C-1); – MS (EI): m/z (%) = 43 (75) [C₂H₃O⁺], 55 (37) [C₄H₇⁺], 59 (58) [C₃H₇O⁺], 67 (29) [C₅H₇⁺], 81 (100) [C₆H₉⁺], 95 (54) [C₇H₁₁⁺], 107 (14)/121 (19)/135 (8)/149 (3) [C_nH_(2n-5)⁺ series], 177 (30) [M⁺-C₂H₃O], 205 (29) [M⁺-CH₃], 220 (16) [M⁺].

Example 14

(*r*-7',*c*-9')-1-[Bicyclo[5.4.0]undec-1'(11')-en-9'-yl]ethan-1-one (14)

25 Odour: sweet, ionone-like-fruity, woody-fresh, somewhat reminiscent of raspberry. – IR (film): ν = 1709 cm⁻¹ (ν OC=O); – ¹H-NMR (CDCl₃): δ = 1.36–1.88 (m, 10H, 3'-H₂-6'-H₂, 8'-H₂), 2.08–2.22 (m, 4H, 2',-10'-H₂), 2.17 (s, 3H, 2-H₃), 2.32 (m_c, 1H, 7'-H), 2.63 (dddd, *J* 12.0, 11.6, 5.7, 2.9 Hz, 1H, 9'-H), 5.41 (m_c, 1H, 11'-H); – ¹³C-NMR (CDCl₃): δ = 26.30/27.32 (t, C-3',-5'), 27.86 (q, C-2), 29.85 (t, C-4'), 31.13 (t, C-6'), 33.35/33.39 (t, C-

8',-10'), 35.70 (t, C-2'), 39.21 (d, C-7'), 48.10 (d, C-9'), 120.34 (d, C-11'), 143.06 (s, C-1'), 211.68 (s, C-1); – MS (EI): m/z (%) = 43 (24) [C₂H₃O⁺], 55 (6) [C₄H₇⁺], 67 (44) [C₅H₇⁺], 91 (44) [C₇H₇⁺], 79 (18)/93 (16)/107 (12)/121 (8) [C_nH_(2n-5)⁺ series], 149 (100) [M⁺-C₂H₃O], 159 (3) [M⁺-CH₃-H₂O], 177 (14) [M⁺-CH₃], 192 (34) [M⁺].

5

Example 15

Feminine extrait perfume with compound 3

Compound/ingredient		Weight content in ‰
10	1. AMBRAROME	15
	2. CEDARWOOD OIL VIRGINIA	50
	3. CITRONELLOL EXTRA	30
	4. CYCLOPENTADECANOLIDE (THIBETOLIDE)	50
15	5. 4-(1-ETHOXYETHENYL)-3,3,5,5-TETRAMETHYL-CYCLOHEXANONE (KEPHALIS)	40
	6. 2-ETHYL-6,6-DIMETHYLCYCLOHEX-2-ENE-CARBOXYLIC ACID ETHYL ESTER (GIVESCONE)	15
	7. ETHYL LINALOOL	50
	8. EUGENOL PURE	30
20	9. 3-(4-METHOXYPHENYL)-2-METHYLPROPANAL	60
	10. 1,2,3,5,6,7-HEXAHYDRO-1,1,2,3,3-PENTAMETHYL-4H-INDENONE (CASHMERAN)	15
	11. INDOLE 10% DPG	2
	12. ISOAMBRETTOLIDE (AMBRETTOLIDE)	15
25	13. CUMIN OIL ROMAN 10% DPG	4
	14. LINALYL ACETATE SYNTHETIC	30
	15. MANDARINE OIL	20
	16. METHYL ANTHRANILATE 10% DPG	3
	17. METHYLIONONE (ISORALDEINE 95)	120
30	18. NECTARYL	10
	19. 3-METHYL-5-(2,2,3-TRIMETHYLCYCOPENT-3-EN-1-YL)PENTAN-2-OL (SANDALORE)	90
	20. OLIBANUM OIL PURE	5

	21. PATCHOULI OIL PURE	40
	22. PHENYLETHYL ALCOHOL EXTRA	32
	23. ROSE OIL	2
	24. VANILLIN	4
5.	25. COMPOUND 3	250
	26. JUNIPER BERRY OIL	10
	27. YLANG-YLANG OIL EXTRA	5
	28. CINNAMALDEHYDE	3

1000

- 10 Compound 3 forms, together with methylionone, patchouli, Sandalore and Thibetolide/
Ambrettolide, the main accord of this modern, monolithic feminine-woody chypre
perfume. In spite of the high dosage of 25%, the composition remains harmonic and
transparent, and lives by the cedar-like-amber-like, pleasant warmth of compound 3. This
already unfolds refreshingly in the aromatic scent and develops into a spicy-floral bouquet
15 which is long-lasting. In olfactory intensity, diffusion and adhesive resistance compound 3
in the same dosage is clearly superior to the odorants Iso E Super and Vertofix in this
composition.

Example 16

Perfume oil for conditioner with compound 3

20

	Compound/ingredient	Weight content in ‰
	1. AMYL SALICYLATE	50
	2. BENZYL ALCOHOL EXTRA	100
	3. CITRONELLOL EXTRA	50
25	4. COUMARIN PURE CRYSTALLINE	20
	5. CYCOPENTADECANOLIDE (THIBETOLIDE)	30
	6. 2-METHYL-3-[4-(1,1-DIMETHYL)ETHYL]- PHENYLPROPANAL (LILIAL)	250
	7. DYNASCONE 10	1
30	8. 3-(4-ETHYLPHENYL)-2,2-DIMETHYLPROPANAL (FLORALOZONE)	4
	9. 2-ETHYL-4-(2,2,3-TRIMETHYLCYCLOPENT-3-EN-1-YL)-	

	BUT-2-EN-1-OL (RADJANOL)	10
	10. ALPHA-HEXYLCINNAMALDEHYDE	150
	11. LINALOOL SYNTHETIC	100
	12. PARA-METHYLACETOPHENONE	5
5	13. METHYLIONONE (ISORALDEINE 70)	100
	14. PHENYLETHYL ACETATE	30
	15. TERPINEOL PURE	50
	16. COMPOUND 3	50
10		1000

Compound 3 confers to the composition a pleasant fresh-dry note with a soft, frankincense note, which underlines the soft caring character of the product. It rounds off the composition, has a very good adhesion to the washing and has a fixative action on the remaining odorants.

Example 17

Floral-maritime perfume composition with compound 2

20

	Compound/ingredient	Amount by weight in ‰
	1. BERGAMOT OIL	100
	2. LEMON OIL ITALIAN PURE	20
	3. ALLYL 3-CYCLOHEXYLPROPIONATE	
25	10% DPG	5
	4. ALPHA-DAMASCONONE 10% DPG	3
	5. 2,6-DIMETHYLHEPTAN-2-OL	1
	6. 1,1-DIMETHYL-3-PHENYLPROPANOL	3
	7. DIPROPYLENE GLYCOL (DPG)	90
30	8. ETHYL LINALOOL	85
	9. GERANIOL PURE	1
	10. 1,3,4,6,7,8-HEXAHYDRO-4,6,6,7,8,8-HEXAMETHYL-CYCLOPENTA[G]-2-BENZOPYRAN	

	(GALAXOLIDE) 50 BB	140
	11. BETA-IONONE SYNTHETIC	2
	12. LINALOOL SYNTHETIC	35
	13. LINALYL ACETATE SYNTHETIC	15
5	14. 7-METHYL-2H-BENZO-1,5-DIOXEPIN-3(4H)-ONE (CALONE 1951)	6
	15. 2-METHYL-3-[4-(1,1-DIMETHYL)ETHYL]- PHENYLPROPANAL (LILIAL)	120
	16. METHYLDIHYDROJASMONATE (CEPIONAT)	320
10	17. NONA-2(E),6(Z)-DIENAL 10%/TEC 10% DPG	5
	18. PHENYLACETALDEHYDE (HYACINTH ALDEHYDE) 85%/PEA 10% DPG	5
	19. ALPHA-TERPINEOL (LINDENOL)	2
	20. GAMMA-UNDECALACTONE (PEACH PURE)	2
15	21. COMPOUND 2	40
		1000

Compound 2 shapes the floral-maritime note of this perfume composition, and also confers to it fruity-ionone-like aspects and a pleasant tobacco-like note. It fixes and
20 harmonizes the creation by its floral, maritime and woody facets and brings naturalness and transparency into the modern "aqueous-flowery" perfumistic theme.

Example 18

Floral hesperidic note with compound 2

25	Compound/ingredient	Amount by weight in ‰
	1. MUGWORT OIL 10% DPG	6
	2. BERGAMOT OIL	70
	3. CARDAMON OIL CEYLON	15
	4. CEDARWOOD OIL BROWN VIRGINIAN	150
30	5. CITRONELLOL EXTRA	20
	6. CORIANDER OIL	2
	7. COUMARIN PURE CRYSTALLINE	2
	8. CUMIN OIL (ROMAN CUMIN OIL) 10% DPG	5

	9. CYPRESS OIL	3
	10. 2,4-DIHYDROXY-3,6-DIMETHYLBENZOIC ACID METHYL ESTER (EVERNYL) 10% DPG	5
	11. DIPROPYLENE GLYCOL (DPG)	109
5	12. ETHYL LINALOOL	45
	13. (3Z)-HEX-3-EN-1-OL 10% DPG	5
	14. ALPHA-HEXYLCINNAMALDEHYDE	17
	15. BETA-IONONE SYNTHETIC	30
	16. MACE OIL (NUTMEG OIL) USP	10
10	17. MANDARINE OIL YELLOW ITALIAN	10
	18. METHYLDIHYDROJASMONATE (CEPIONATE)	120
	19. MUSCONE 10% DPG	6
	20. ORANGE OIL BITTER	10
	21. 2-PHENYLETHAN-1-OL WHITE	10
15	22. COMPOUND 2	350

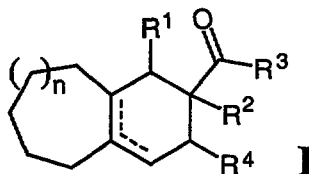
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Compound 2 increases the intensity and the character of the perfume, emphasizes the fresh-hesperidic like facets and reduces the dry-woody elements.



Claims

1. Compounds of formula I



5

wherein

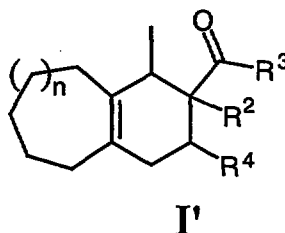
$n =$ 1 or 2;

R^1 and $R^4 =$ H or CH_3 ; and

R^2 and $R^3 =$ H, CH_3 or CH_2CH_3 .

10

2. Compounds according to claim 1 of formula I'



15

wherein

$n =$ 1 or 2;

R^1 and $R^4 =$ H or CH_3 ; and

R^2 and $R^3 =$ H, CH_3 or CH_2CH_3 .

20

3. A compound according to claim 1 selected from the group consisting of 1-

{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (1), 1-{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}methanal (2), 1-{9',10'-dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one

(3), 1-{8',9'-dimethylbicyclo[5.4.0]undec-1'(7')-en-9'-yl}ethan-1-one (4), 1-{9'-methylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (5), 1-{10'-methylbicyclo[6.4.0]dodec-

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1'(8')-en-10'-yl}methanal (6), 1-{11'-methylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-

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one (7), 1-{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}propan-1-one (8), 1-{9',11'-dimethyl-
bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (9), 1-{8'-methylbicyclo[5.4.0]undec-
1'(7')-en-9'-yl}ethan-1-one (10), 1-{bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}ethan-1-one
(11), 1-{bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}methanal (12), 1-{10'-methylbicyclo[6.4.0]-
5 dodec-1'(12')-en-10'-yl}ethan-1-one (13) and 1-{bicyclo[5.4.0]undec-1'(11')-en-9'-
yl}ethan-1-one (14).

4. A compound according to claim 2, selected from the group consisting of 1-{9',10'-
dimethylbicyclo[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (3), 1-{8',9'-dimethyl-
bicyclo[5.4.0]undec-1'(7')-en-9'-yl}ethan-1-one (4), 1-{9'-methylbicyclo[6.4.0]dodec-
10 1'(8')-en-10'-yl}ethan-1-one (5) and 1-{8'-methylbicyclo[5.4.0]undec-1'(7')-en-9'-
yl}ethan-1-one (10).

5. A compound according to claim 3 selected from the group consisting of 1-
{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}methanal (2) and 1-{10'-methylbicyclo[6.4.0]dodec-
1'(8')-en-10'-yl}methanal (6).

15 6. A compound according to claim 3 selected from the group consisting of 1-
{bicyclo[6.4.0]dodec-1'(8')-en-10'-yl}methanal (2) and 1-{9',10'-dimethylbicyclo-
[6.4.0]dodec-1'(8')-en-10'-yl}ethan-1-one (3).

7. A compound according to claim 3 selected from the group consisting of 1-
{bicyclo[6.4.0]dodec-1'(12')-en-10'-yl}ethan-1-one (11), 1-{bicyclo[6.4.0]dodec-1'(12')-en-
20 10'-yl}methanal (12), 1-{10'-methylbicyclo[6.4.0]dodec-1'(12')-en-10'-yl}ethan-1-one (13)
and 1-{bicyclo[5.4.0]undec-1'(11')-en-9'-yl}ethan-1-one (14) in admixture with their
corresponding regioisomeric Diels-Alder adducts.

8. The use of a compound according to any one of claims 1 to 7 as an odorant.

9. An odorant composition, which contains at least one compound set forth in any
25 one of claims 1-7.

10. A process for the manufacture of the R¹-methyl substituted compounds of
formula I' in accordance with claim 2, which process comprises reacting a spirocyclic
vinylcyclopropane compound with a dienophile in the presence of a catalyst to give
30 regioselectively or Z-diastereoselectively the required compounds of formula I'.



11. A process according to claim 10, wherein the vinylcyclopropane compound is 4-methylenespiro[2.6]nonane.

12. A process according to claim 10, wherein the vinylcyclopropane compound is 4-methylenespiro[2.7]decane.

13. A process according to any one of claims 10 to 12, wherein the dienophile is 3-methyl-3-buten-2-one.

14. A process according to any one of claims 10 to 13, wherein the catalyst is $(\text{Ph}_3\text{P})\text{RhCl}$.

15. 4-Methylenespiro[2.6]nonane.

16. 4-Methylenespiro[2.7]decane.

17. The use of the compound set forth in claim 15 or 16 as an odorant.

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