

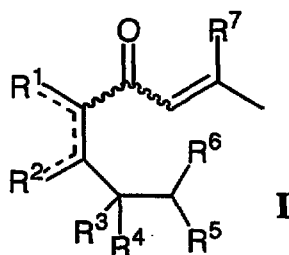
2-,5-,6-,7-,8-Substituted oct-2-en-4-ones

The invention relates to 2-,5-,6-,7-,8-substituted oct-2-en-4-ones, to the use of
5 these compounds as fragrances or flavorings, and to the fragrance or aroma compositions prepared therewith.

Until the discovery of the 1-(2,2,6-trimethylcyclohexyl)but-2-en-1-ones, called
damascones, a perfumistic reconstitution of rose oil was virtually impossible [D.
10 Kastner, *Parfuem. Kosmet.* 1985, 66, 5-16; D. Kastner, *Parfuem. Kosmet.*
1994, 75, 170-181]. With the discovery of the damascones [G. Ohloff, E.
Demole, *J. Chromatogr.* 1987, 406, 181-183], however, not only did this
change, but the substance class also gave many other floral or fruity accords
volume, freshness and naturalness. Moreover, excessive amounts set entirely
15 new trends [M. Gras, *Perfum. Flavor.* 1990, 15, 25-28; M. Gras, *Perfum.*
Flavor. 1992, 17, 1-12]. There has therefore also been no lack of attempts to
find substances with similar odor properties, some of which have even actually
become established in perfumery [G. Fráter, J. A. Bajgrowicz, R. Kräft,
Tetrahedron 1998, 54, 7633-7703]. However, these compounds are
20 structurally very similar to the damascones and, apart from a few exceptions,
are even constitutionally isomeric thereto. In addition, the Japanese laid-open
specification JP 55027135 describes 3(4),4(5)-diseco- and 2(3),4(5)-diseco-
damascones. From a perfumery viewpoint, all of these compounds offer very
little which is new, i.e. they broaden the odor spectrum around the parent
25 compounds only insignificantly and thus do not satisfy the need for novel
innovative scent building-blocks of this odor direction. As a result of the
structural similarities and the similar molecular weight, the known compounds
having damascone-like odor properties established in perfumery have very

similar application properties, i.e. a comparable diffusivity, substantivity and radiative power in compositions. They do not in fact satisfy the need for innovative novel scent building-blocks with other areas of application. To rectify this deficit and to extend the odiferous spectrum of the damascones by novel facets in order thus to open up new composition possibilities for the perfumer and flavorist is an object of the invention.

Surprisingly, we have now found a group of branched acyclic alkenones of the general formula I



in which $R^1, R^2 = \text{CH}_2, \text{CH}_3, \text{CHCH}_3, \text{CH}_2\text{CH}_3,$

$R^3 = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3,$

$R^4, R^5, R^6, R^7 = \text{H}, \text{CH}_3,$

with the condition that the radicals R^4, R^5, R^6, R^7 are not all hydrogen at the same time, and where the dashed line represents an optional double bond, which enrich the typical odor properties of the damascones with novel, characteristic aspects, and have completely different application properties, primarily with regard to a much greater diffusivity and radiative power. Surprisingly, some of these compounds are even much more odor-intensive than the damascones themselves.

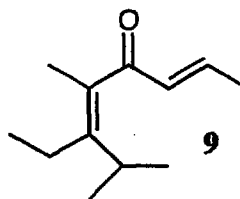
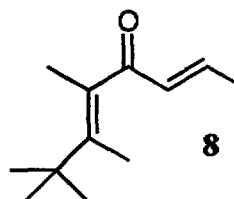
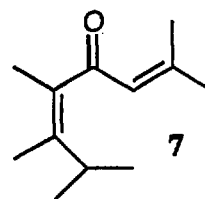
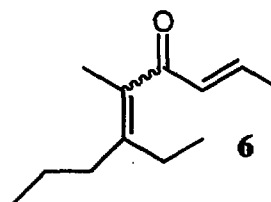
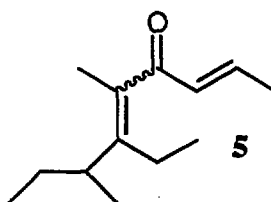
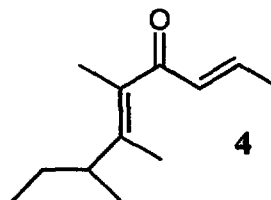
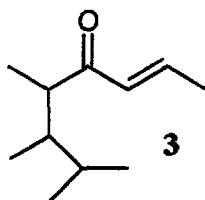
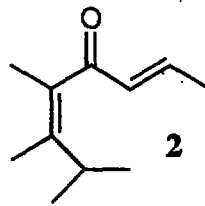
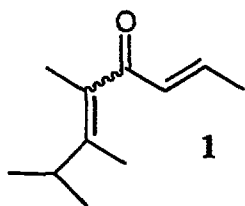
According to the general formula I a double bond does not thus have to be present at positions $R^1(C-5)$, $C-5(C-6)$ and $R^2(C-6)$. (*E/Z*)-Isomers of all double bonds (at most two) present in a molecule and all possible stereoisomers are covered by the general formula I, which is shown in the formula by waved lines.

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The compounds according to the invention are therefore characterized by an oct-2-en-4-one skeleton. Due to the specific odor and/or aroma properties, compounds with a 7-methyloct-2-en-4-one skeleton are preferred, and compounds with a (5*Z*)-7-methylocta-2,5-dien-4-one skeleton are particularly preferred.

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The general formula I thus covers the compounds 1–9:



The compounds of the general formula I are particularly suitable for the composition of rosy accords, and generally floral bouquets. Particular mention is to be made also of the use in fruity notes and musk-accentuated compositions. However, the use is neither limited to these accords, nor to specific fragrances, classes of substance or odor notes. Examples of further classes of substance which harmonize well which may therefore be listed are:

– Essential oils and extracts, e.g.

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ambrette resinoid, bergamot oil,
geranium oil, grapefruit oil,
mandarin oil, patchouli oil,
rose absolute, sandalwood oil,
ylang-ylang oil, lemon oil.

– Alkanes, alkenes, halogen compounds, e.g.

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farnesene,
alpha-trichloromethylbenzyl acetate.

– Alcohols, ethers, acetals, e.g.

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citronellol, dihydromyrcenol, Ebanol®,
eugenol, Florol®, geraniol, Helional®,
cis-hex-3-enol, Mayol®, nerol,
2-phenylethyl alcohol, rose oxide,
Sandalor®, Spirambren®.

– Aldehydes and ketones, e.g.

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Adoxal®, Bourgeonal®, cepionate,
Cyclohexal®, damascenone,
beta-dihydroionone, Florhydral®,
Hedion®, raspberry ketone (N-112),
hydroxycitronellal, Iso E Super®,
Lemarom®, Lillial®, methylionone,
2-methylundecanal, Myralden®,
10-undecen-1-al, undecanal, vanillin,
Vertofix®.

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- Esters, lactones, nitriles, e.g. Allyl amyl glycolate, benzyl salicylate, citronellyl acetate, citronellyl formate, Cyclogalbanat[®], decalactone *gamma*, Gardenol[®], geranyl acetate, *cis*-hex-3-enyl acetate, hexyl acetate, linalyl acetate, phenylethyl acetate, Peonil[®], *gamma*-undecalactone, Verdox[®].
- Macro-, poly-, heterocycles, e.g. Ambroxan[®], Cashmeran[®], Galaxolid[®], Habanolid[®], Thibetolid[®].

The examples below illustrate the invention:

Example 1

(2E,5E/Z)-5,6,7-Trimethylocta-2,5-dien-4-one (1)

Ethyl (2E/Z)-2,3,4-trimethylpent-2-enoate was prepared in accordance with the procedure of H. Vieregge, H. M. Schmidt, J. Renema, H. J. T. Bos and J. F. Arends [*Recl. Trav. Chim. Pays-Bas* **1966**, 85(9-10), 929-951] in 58 percent yield by boron trifluoride-catalyzed addition of methyl isopropyl ketone to 1-ethoxypropyne. The portionwise addition of a solution of 6.3 ml (73.9 mmol) of 1-bromoprop-1-ene in 60 ml of dry tetrahydrofuran to 1.80 g (73.9 mmol) of magnesium turnings with sporadic heating using a hot-air pistol under an inert-gas atmosphere gave a Grignard solution. In a further reaction vessel, a lithium diisopropylamide solution was prepared under nitrogen at

-70 °C by the dropwise addition of 4.3 ml (42.7 mmol) of 10 M butyllithium solution to a solution of 6.1 ml (42.7 mmol) of diisopropylamine in 22 ml of dry tetrahydrofuran and subsequent stirring for 10 min at this temperature. Then, at room temperature over the course of 20 min, the previously prepared Grignard solution was added dropwise, followed, at 35°C, again over the course of 20 minutes, by a solution of ethyl (2E/Z)-2,3,4-trimethylpent-2-enoate dissolved in 90 ml of dry tetrahydrofuran. After the mixture had been stirred for 2 hours at 35°C and heated under reflux for 1 hour, it was poured onto water, and the product was extracted with ether. The combined ethereal extracts were washed with water and saturated sodium chloride solution, dried over sodium sulfate and evaporated on a rotary evaporator. Flash chromatography (pentane / ether, 19:1, R_f = 0.22) gave 1.8 g (25%) of (2E,5E/Z)-5,6,7-trimethylocta-2,5-dien-4-one (1) as a colorless liquid with a characteristic odor.

Odor: linear, very intensive and very diffusive, fruity-rosy, resembling dried apples, plums, raisins and other dried fruit; in the top note slightly rum- and caramel-like. – IR (film): ν = 1653 cm^{-1} (ν C=O, unsat.), 1620 (ν C=C), 973 (δ C=C–H oop.), 1377 (δ CH₃). – ¹H-NMR (CDCl₃): δ = 0.94 (d, J = 6.6 Hz, 6H, 7-Me₂, 5E), 1.01 (d, J = 6.8 Hz, 6H, 7-Me₂, 5Z), 1.54 (q, 5J = 1.3 Hz, 3H, 6-Me, 2E, 5Z), 1.61 (q, 5J = 0.97 Hz, 3H, 6-Me, 2E, 5E), 1.74 (q, 5J = 0.97 Hz, 3H, 5-Me, 2E, 5E), 1.79 (q, 5J = 1.3 Hz, 3H, 5-Me, 2E, 5Z), 1.91-1.94 (m, 6H, 1-H₃, 5E+5Z), 2.57 (sept, J = 6.6 Hz, 1H, 7-H, 5E), 2.86 (sept, J = 6.8 Hz, 1H, 7-H, 5Z), 6.11 (dq, J = 15.9, 2.0 Hz, 1H, 3-H, 2E, 5Z), 6.12 (dq, J = 15.6, 1.6 Hz, 1H, 3-H, 2E, 5E), 6.74 (dq, J = 15.9, 9.2 Hz, 1H, 2-H, 2E, 5Z), 6.77 (dq, J = 15.6, 6.8 Hz, 1H, 2-H, 2E, 5E). – ¹³C-NMR (CDCl₃): δ = 11.21 / 13.77 (2q, 5-Me), 15.02 / 15.91 (2q, 6-Me), 18.10 / 18.21 (2q, C-1), 19.97 / 20.39 (4q, 7-Me₂), 29.52 / 32.35 (2d, C-7), 128.69 / 128.81 (2s, C-5), 132.03 / 132.41 (2d, C-3),

140.32 / 140.47 (2s, C-6), 145.11 / 145.32 (2d, C-2), 201.57 / 201.77 (2s, C-4).
 – MS (EI): m/e (%) = 41 (43) [C₃H₅], 55 (30) [C₄H₇], 69 (32) [C₄H₅O], 123 (20) [M⁺–C₃H₇], 136 (31) [M⁺–2CH₃], 151 (100) [M⁺–CH₃], 166 (11) [M⁺].

5 Example 2

(2E,5Z)-5,6,7-Trimethylocta-2,5-dien-4-one (2)

Using flash chromatography (pentane / ether, 9:1, R_f = 0.53) of the (2E,5E/Z) mixture 1, it was possible to isolate a sample of uniformly (2E,5Z)-configured
 10 5,6,7-trimethylocta-2,5-dien-4-one (2) as a colorless liquid having an extremely intensive odor which exhibited the following olfactory and spectroscopic data.

Odor: Corresponds to compound 1, but is much more intensive and radiative; threshold value: 0.5 ng/l of air whereas the (5E)-isomer shows a threshold
 15 value of 500 ng/l. – IR (film): ν = 1653 cm⁻¹ (ν C=O, unsat.), 1620 (ν C=C), 973 (δ C=C–H oop.), 1377 (δ CH₃). – ¹H-NMR (CDCl₃): δ = 0.94 (d, J = 6.6 Hz, 6H, 7-Me₂), 1.61 (q, ⁵ J = 1.0 Hz, 3H, 6-Me, hence 5Z, the 5E-isomer is at 1.5 Hz), 1.74 (q, ⁵ J = 1.0 Hz, 3H, 5-Me, hence 5Z, the 5E-isomer is at 1.5 Hz), 1.92 (dd, J = 6.8, 1.6 Hz, 3H, 1-H₃), 2.57 (sept, J = 6.6 Hz, 1H, 7-H), 6.12 (dq, J = 15.6,
 20 1.6 Hz, 1H, 3-H, hence 2E), 6.77 (dq, J = 15.6, 6.8 Hz, 1H, 2-H, hence 2E). – NOESY (¹H/¹H): 3-H/7-Me, 5-Me/6-Me. – ¹³C-NMR (CDCl₃): δ = 11.29 (q, 5-Me), 15.99 (q, 6-Me), 18.18 (q, C-1), 20.45 (2q, 7-Me₂), 32.41 (d, C-7), 128.85 (s, C-5), 132.47 (d, C-3), 140.45 (s, C-6), 145.41 (d, C-2), 201.94 (s, C-4). – MS (EI): m/e (%) = 41 (41) [C₃H₅], 55 (30) [C₄H₇], 69 (31) [C₄H₅O], 123 (20) [M⁺–C₃H₇], 136 (33) [M⁺–2CH₃], 151 (100) [M⁺–CH₃], 166 (11) [M⁺].
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Example 3

(2E)-5,6,7-Trimethyloct-2-en-4-one (3)

20.0 g (117 mmol) of a double-bond isomer mixture of ethyl 2,3,4-trimethylpent-2-enoate [synthesis: see *example 1*] were dissolved in 200 ml of ethyl acetate, treated with 0.50 g (0.26 mmol, 0.2 mol%) of 10 percent platinum on activated carbon, and hydrogenated at room temperature for 4 h in an autoclave at a hydrogen atmosphere of 25 bar with vigorous stirring. The catalyst was separated off by filtering the reaction mixture with suction over Celite. After the solvent had been removed on a rotary evaporator, the mixture was distilled under reduced pressure over a 10 cm Widmer column, giving 16.9 g (83%) of colourless ethyl 2,3,4-trimethylvalerate at a boiling point of 105–108°C / 100 mbar. These 16.9 g (98.1 mmol) were dissolved in 150 ml of ethanol / water (1:1) and 9.60 g (147 mmol) of 86 percent potassium hydroxide were added. The reaction mixture was refluxed for 2 h and, after cooling, diluted with 500 ml of water and adjusted to pH 1 with hydrochloric acid. The aqueous phase was extracted three times with ether, and the combined organic phases were dried over sodium sulfate and evaporated on a rotary evaporator. This gave 14.3 g of crude 2,3,4-trimethylvaleric acid which was dissolved in 250 ml of dry tetrahydrofuran. At –10°C, 9.8 ml (98 mmol) of 10 M butyllithium solution in hexane were added dropwise. After the mixture had been stirred for 40 min at –10°C, 123 ml (98 mmol) of 0.8 M propenyllithium solution in ether were slowly added dropwise at this temperature. After stirring for 4 hours at 30°C, the mixture was cooled to –10°C, and 16 ml (218 mmol) of acetone were added dropwise at this temperature. After the mixture had been stirred for a further 10 min at –10°C, 200 ml of saturated ammonium chloride solution were added dropwise at this temperature. The cooling was removed and the reaction mixture was diluted with 200 ml of water. The aqueous phase was extracted

three times with ether, and the combined organic extracts were dried over magnesium sulfate and evaporated on a rotatory evaporator. Flash chromatography (pentane / ether, 19:1, $R_f = 0.24$) over silica gel gave 6.50 g (39%) of (2*E*)-5,6,7-trimethyloct-2-en-4-one as a colorless liquid with a pleasant
 5 odor.

Odor: Weaker than 1 and 2, but also very diffusive, fruity-rosy, reminiscent of raspberries and dried fruit. – IR (film): $\nu = 1629 \text{ cm}^{-1}$ ($\nu \text{ C=C}$), 1695 / 1668 ($\nu \text{ C=O}$, unsat.), 970 ($\delta \text{ C=C-H oop.}$), 1378 ($\delta \text{ CH}_3$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.70 / 0.74 / 0.76 / 0.84$ (4d, $J = 6.8 \text{ Hz}$, 6H, 7-Me₂), 0.92 / 0.93 (2d, $J = 6.5 \text{ Hz}$, 3H, 6-Me), 0.98 / 1.05 (2d, $J = 6.8 \text{ Hz}$, 3H, 5-Me), 1.49–1.71 (m, 1H, 7-H), 1.85–1.93 (m, 4H, 1-H₃, 6-H), 2.78 (quint, $J = 6.8 \text{ Hz}$) / 2.61 (dq, $J = 9.6, 6.8 \text{ Hz}$) [1H, 5-H], 6.21 (dq, $J = 15.4, 1.6 \text{ Hz}$, 1H, 3-H), 6.85–6.94 (m, 1H, 2-H). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 11.03 / 11.69$ (4q, 7-Me₂), 14.97 / 15.19 (2q, 5-Me), 18.08 / 18.22 (2q, C-1), 21.35 / 21.42 (2q, 6-Me), 27.10 / 30.30 (2d, C-7), 40.33 / 40.50 (2d, C-6), 46.73 / 47.70 (2d, C-5), 130.19 / 130.87 (2d, C-3), 141.83 / 142.19 (2d, C-2), 203.83 / 204.47 (2s, C-4). – MS (EI): m/e (%) = 69 (100) [$\text{C}_4\text{H}_5\text{O}^+$], 83 (16) [$\text{M}^+ - \text{C}_5\text{H}_{10} - \text{CH}_3$], 98 (58) [$\text{M}^+ - \text{C}_5\text{H}_{10}$, McLafferty fragmentation], 125 (2) [$\text{M}^+ - \text{C}_3\text{H}_7$], 168 (1) [M^+].
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Example 4

(2*E*,5*E*)-5,6,7-Trimethylnona-2,5-dien-4-one (4)

Analogously to example 1 and the general procedure of H. Vieregge, H. M. Schmidt, J. Renema, H. J. T. Bos and J. F. Arends [*Recl. Trav. Chim. Pays-Bas* 1966, 85(9-10), 929-951], ethyl 2,3,4-trimethylhex-2-enoate was prepared by the addition of 3-methylpentan-2-one to 1-ethoxypropyne in 46 percent yield.
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5.83 g (31.7 mmol) of this ethyl 2,3,4-trimethylhex-2-enoate were dissolved in 100 ml of ethanol / water (1:1) and then 2.93 g (44.4 mmol) of 86 percent strength potassium hydroxide were added. After the mixture had been refluxed for 3 hours, a further 2.93 g (44.4 mmol) of 86 percent strength potassium hydroxide were added, and the reaction mixture was then refluxed for a further 3 h. After cooling, 300 ml of water were added and the mixture was acidified with concentrated phosphoric acid. The aqueous phase was extracted with 400 ml of ether, and the organic phases were dried and evaporated to dryness on a rotary evaporator. After flash chromatography (pentane / ether, 4:1) over silica gel, 3.77 g (76%) of 2,3,4-trimethylhex-2-enoic acid were isolated, which were taken up in 50 ml of dry tetrahydrofuran. At -10°C , 15.1 ml (24.2 mmol) of 1.6 M butyllithium solution in tetrahydrofuran were added dropwise under nitrogen. After the mixture had been stirred for 15 min at this temperature, 30.0 ml (24.2 mmol) of propenyllithium solution in ether were added dropwise over the course of 10 min. The cooling was removed and the reaction mixture was heated to 30°C . It was stirred for 1 h at this temperature, then cooled to 0°C , and 4 ml of acetone, followed by 50 ml of saturated ammonium chloride solution, were added dropwise. After the reaction mixture had been heated to room temperature, it was diluted with 200 ml of water, and the product was extracted by washing with 3 x 400 ml of ether. The organic extracts were combined, dried and evaporated on a rotary evaporator, and the crude product was subjected to flash chromatography over silica gel with 4 l of pentane / ether (49:1) and 2 l of pentane / ether (19:1). As a result, 0.67 g (15%) of (2*E*,5*E*)-5,6,7-trimethylnona-2,5-dien-4-one (**4**) was isolated as a colorless liquid having an intensive and characteristic odor.

Odor: Linear, very intensive and long-lasting, fruity-rosy, reminiscent of apples and dried fruit. – IR (film): $\nu = 1652\text{ cm}^{-1}$ ($\nu\text{ C=O}$, unsat.), 972 ($\delta\text{ C=C-H oop.}$), 1620 ($\nu\text{ C=C}$), 1376 ($\delta\text{ CH}_3$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.87$ (t, $J = 7.4\text{ Hz}$, 3H, 9- H_3), 0.99 (d, $J = 7.2\text{ Hz}$, 3H, 7-Me), 1.38 (qd, $J = 7.4, 7.2\text{ Hz}$, 2H, 8- H_2), 1.50 (q, $^5J = 1.5\text{ Hz}$, 3H, 6-Me), 1.79 (q, $^5J = 1.5\text{ Hz}$, 3H, 5E-Me), 1.92 (dd, $J = 6.8, 1.6\text{ Hz}$, 3H, 1- H_3), 2.60 (sext, $J = 7.2\text{ Hz}$, 1H, 7-H), 6.11 (dq, $J = 15.6, 1.6\text{ Hz}$, 1H, 3-H), 6.80 (dq, $J = 15.6, 6.8\text{ Hz}$, 1H, 2E-H). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 12.17$ (q, C-9), 13.63 (q, 5-Me), 15.35 (q, 6-Me), 18.16 / 18.23 (2q, C-1, 7-Me), 27.26 (t, C-8), 36.74 (d, C-7), 130.09 (s, C-5), 132.14 (d, C-3), 139.09 (s, C-6), 145.06 (d, C-2), 201.77 (s, C-4). – MS (EI): m/e (%) = 41 (73) [C_3H_5], 55 (33) [C_4H_7], 69 (62) [$\text{C}_4\text{H}_5\text{O}$], 109 (43) [$\text{M}^+ - \text{C}_5\text{H}_{11}$], 123 (43) [$\text{M}^+ - \text{C}_4\text{H}_9$], 136 (17) [$\text{M}^+ - \text{C}_3\text{H}_8$], 151 (100) [$\text{M}^+ - \text{C}_2\text{H}_5$], 165 (26) [$\text{M}^+ - \text{CH}_3$], 180 (13) [M^+].

Example 5

15 (2E,5E/Z)-6-Ethyl-5,7-dimethylnona-2,5-dien-4-one (5)

Analogously to example 4, 3-ethyl-2,4-dimethylhex-2-enoic acid was prepared from ethoxypropyne and 4-methylhexan-3-one. 0.60 g (3.52 mmol) of 3-ethyl-2,4-dimethylhex-2-enoic acid was initially introduced into 10 ml of dry tetrahydrofuran at -10°C . At this temperature, 0.35 ml (3.5 mmol) of 10M butyllithium solution was slowly injected using a syringe over the course of 15 min, and, after stirring for a further 45 min, 3.52 ml (3.52 mmol) of 1M propenyllithium solution in ether were added and the mixture was stirred for 15 h at room temperature. It was then cooled again to -10°C , and the reaction mixture was treated at this temperature with 0.6 ml of acetone and, after stirring for 10 min, with 7 ml of saturated ammonium chloride solution. The reaction mixture was then poured onto 50 ml of water, and the product was extracted

with 2 x 50 ml of ether. The extracts were combined, washed in each case with 50 ml of water and 25 ml of saturated sodium chloride solution, dried over sodium sulfate and evaporated to dryness on a rotary evaporator. After flash chromatography (pentane / ether, 98:2, R_f = 0.37) on silica gel, 200 mg (29%) of colorless (2*E*,5*E*/*Z*)-6-ethyl-5,7-dimethylnona-2,5-dien-4-one (5) with a pleasant odor were isolated.

Odor. Fruity-rosy, reminiscent of dried fruits, but with a significant caramel- and icing-like nuance. – IR (film): ν = 1652 cm^{-1} (ν C=O, unsat.), 973 (δ C=C–H oop.), 1623 (ν C=C), 1376 (δ CH₃). – ¹H-NMR (CDCl₃): δ = 0.76 / 0.90 (t, J = 7.4 Hz, 3H, 9-H₃), 0.95 / 0.96 (2t, J = 7.2 Hz, 3H, CH₃, 6-Et), 1.06 / 1.08 (2d, J = 7.2 Hz, 3H, 7-Me), 1.26–1.50 (m, 2H, 8-H₂), 1.78 / 1.79 (2 br. s, 3H, 5-Me), 1.91 / 1.93 (2t, J = 1.6 Hz, 3H, 1-H₃), 1.98 / 2.05 (2 br. q, J = 7.2 Hz, 2H, CH₂, 6-Et), 2.24 / 2.55 (sext, J = 7.1 Hz, 1H, 7-H), 6.10 / 6.12 (2dq, J = 15.6, 1.6 Hz, 1H, 3-H), 6.78 (br. dq, J = 15.6, 6.8 Hz, 1H, 2*E*-H). – ¹³C-NMR (CDCl₃): δ = 12.22 / 12.48 (2q, C-9), 13.95 / 15.25 (2q, 5-Me), 15.73 / 15.79 (2q, CH₃, 6-Et), 18.12 / 18.18 / 18.64 / 18.77 (4q, C-1, 7-Me), 19.50 / 22.35 (2t, CH₂, 6-Et), 27.72 / 27.96 (2t, C-8), 37.49 / 40.24 (2d, C-7), 130.69 (2s, C-5), 132.08 / 132.64 (2d, C-3), 144.51 / 144.80 (2s, C-6), 144.91 / 145.17 (2d, C-2), 201.66 / 202.11 (2s, C-4). – MS (EI): m/e (%) = 41 (65) [C₃H₅], 55 (28) [C₄H₇], 69 (49) [C₄H₅O], 123 (35) [M⁺–C₅H₁₁], 137 (76) [M⁺–C₄H₉], 165 (100) [M⁺–C₂H₅], 179 (25) [M⁺–CH₃], 194 (5) [M⁺].

All further compounds were prepared analogously to these procedures. For these, therefore, only the olfactory characterization and the spectroscopic data are listed.

Example 6**(2E,5E/Z)-6-Ethyl-5-methylnona-2,5-dien-4-one (6)**

Odor: Fruity-rosy, reminiscent of dried fruits, with a slightly green hint. – IR
 5 (film): $\nu = 1652 \text{ cm}^{-1}$ ($\nu \text{ C=O}$, unsat.), 972 ($\delta \text{ C=C-H}$ oop.), 1376 ($\delta \text{ CH}_3$). – $^1\text{H-NMR}$ (CDCl_3): $\delta = 0.84 / 0.96$ (2t, $J = 7.4 \text{ Hz}$, 3H, 9- H_3), 0.95 / 1.03 (2t, $J = 7.6$,
 3H, CH_3 , 6-Et), 1.26–1.49 (m, 2H, 8- H_2), 1.78 / 1.79 (2 br. s, 3H, 5-Me), 1.91 /
 1.93 (2dd, $J = 1.6, 0.8 \text{ Hz}$, 3H, 1- H_3), 1.91–2.12 (m, 4H, C-7, CH_2 , 6-Et), 6.12 /
 6.14 (2dq, $J = 15.8, 1.6 \text{ Hz}$, 1H, 3-H), 6.76 / 6.77 (2dq, $J = 15.8, 7.0 \text{ Hz}$, 1H,
 10 2E-H). – $^{13}\text{C-NMR}$ (CDCl_3): $\delta = 12.33 / 13.03$ (2q, C-9), 14.08 / 14.19 (2q, CH_3 ,
 6-Et), 15.52 / 15.77 (2q, 5-Me), 18.19 (2q, C-1), 21.13 / 21.59 (2t, C-8), 23.91 /
 26.34 (2t, CH_2 , 6-Et), 32.44 / 35.23 (2t, C-7), 129.95 / 130.10 (2s, C-5), 132.17
 / 132.21 (2d, C-3), 141.66 / 142.03 (2s, C-6), 145.04 / 145.15 (2d, C-2), 201.26
 / 201.44 (2s, C-4). – MS (EI): m/e (%) = 41 (80) [C_3H_5], 55 (38) [C_4H_7], 69 (64)
 15 [$\text{C}_4\text{H}_5\text{O}$], 123 (100) [$\text{M}^+ - \text{C}_4\text{H}_9$], 137 (31) [$\text{M}^+ - \text{C}_3\text{H}_7$], 151 (93) [$\text{M}^+ - \text{C}_2\text{H}_5$], 165
 (41) [$\text{M}^+ - \text{CH}_3$], 180 (11) [M^+].

Example 7**(5Z)-2,5,6,7-Tetramethylocta-2,5-dien-4-one (7)**

20

Odor: Fruity-rosy, reminiscent of dried fruits, weaker than compound 2, but
 more intensive than the corresponding (5E)-isomer [(5E)-7]. – IR (film): $\nu =$
 1612 cm^{-1} ($\nu \text{ C=C}$), 1667 ($\nu \text{ C=O}$, unsat.), 1378 ($\delta \text{ CH}_3$). – $^1\text{H-NMR}$ (CDCl_3): δ
 = 0.96 (d, $J = 6.8 \text{ Hz}$, 6H, 7- Me_2), 1.58 (q, $^5J = 0.8 \text{ Hz}$, 3H, 6-Me), 1.75 (q, $^5J =$
 25 0.8 Hz, 3H, 5-Me), 1.91 (d, $J = 1.4 \text{ Hz}$, 3H, 2E-Me), 2.15 (d, $J = 1.1 \text{ Hz}$, 3H, 2Z-
 Me), 2.82 (sept, $J = 6.8 \text{ Hz}$, 1H, 7-H), 6.09 (s, 1H, 3-H). – NOESY ($^1\text{H}/^1\text{H}$): 3-
 H/8- H_3 , 1-H/3-H, 3-H/5-Me, 5-Me/6-Me, 6-Me/8- H_3 . – $^{13}\text{C-NMR}$ (CDCl_3): $\delta =$

11.78 (q, 5-Me), 15.39 (q, 6-Me), 20.47 (2q, C-1, 2-Me), 27.58 / 27.63 (2q, 7-Me₂), 31.78 (d, C-7), 125.00 (d, C-3), 132.08 (s, C-5), 141.14 (s, C-6), 154.37 (s, C-2), 199.88 (s, C-4). – MS (EI): *m/e* (%) = 43 (26) [C₃H₇], 55 (52) [C₄H₇], 83 (59) [C₅H₇O], 123 (32) [M⁺–C₄H₉], 137 (43) [M⁺–C₃H₇], 150 (27) [M⁺–2CH₃],
 5 165 (100) [M⁺–CH₃], 180 (20) [M⁺].

Example 8

(2E,5E)-5,6,7,7-Tetramethylocta-2,5-dien-4-one (8)

10 Odor: Fruity, intensively reminiscent of apples, but also strongly reminiscent of dried fruits, having a somewhat celery- and jasmone-like side, and agrestic aspects. – IR (film): ν = 1653 cm⁻¹ (ν C=O, unsat.), 972 (δ C=C–H oop.), 1621 (ν C=C), 1377 (δ CH₃). – ¹H-NMR (CDCl₃): δ = 1.21 (s, 9H, 7-Me₃), 1.57 (q, *J* = 1.5 Hz, 3H, 6-Me, 5E), 1.88 (q, *J* = 1.5 Hz, 3H, 5E-Me), 1.93 (dd, *J* = 7.0, 1.6
 15 Hz, 3H, 1-H₃), 6.04 (dq, *J* = 15.7, 1.6 Hz, 1H, 3-H, 2E), 6.74 (dq, *J* = 15.7, 6.8 Hz, 1H, 2E-H). – NOESY (¹H/¹H): 5-Me/7-Me₃, 6-Me/7-Me₃. – ¹³C-NMR (CDCl₃): δ = 17.80 (q, 5-Me), 18.29 (q, C-1), 19.11 (q, 6-Me), 29.82 (3q, 7-Me₃), 35.88 (s, C-7), 130.43 (s, C-5), 131.92 (d, C-3), 140.35 (s, C-6), 145.73 (d, C-2), 203.15 (s, C-4). – MS (EI): *m/e* (%) = 41 (81) [C₃H₅], 57 (76) [C₄H₉], 69 (65) [C₅H₉], 109 (38) [M⁺–C₅H₁₁], 124 (30) [M⁺–C₄H₈], 137 (24) [M⁺–C₃H₇], 150 (9) [M⁺–2CH₃], 165 (100) [M⁺–CH₃], 180 (10) [M⁺].
 20

Example 9

(2E,5Z)-6-Ethyl-5,7-dimethylocta-2,5-dien-4-one (9)

25

Odor: Fruity-rosy, reminiscent of raspberries and dried fruits, more intensive, more diffusive and more agrestic than the corresponding (5E)-isomer [(5E)-9]

which, however, smells more like fresh apples. – IR (film): $\nu = 1651 \text{ cm}^{-1}$ (ν C=O, unsat.), 972 (δ C=C–H oop.), 1621 (ν C=C), 1376 (δ CH₃). – ¹H-NMR (CDCl₃): $\delta = 0.94$ (d, $J = 6.8 \text{ Hz}$, 6H, 7-Me₂), 1.06 (t, $J = 7.6 \text{ Hz}$, 3H, CH₃, 6-Et), 1.77 (s, 3H, 5-Me), 1.93 (dd, $J = 6.8, 1.6 \text{ Hz}$, 3H, 1-H₃), 2.07 (q, $J = 7.6 \text{ Hz}$, 2H, CH₂, 6-Et), 2.54 (sept, $J = 6.8 \text{ Hz}$, 1H, 7-H), 6.11 (dq, $J = 15.7, 1.6 \text{ Hz}$, 1H, 3-H, hence 2E), 6.77 (dq, $J = 15.7, 6.8 \text{ Hz}$, 1H, 2-H, hence 2E). – NOESY (¹H/¹H): 5-Me/CH₂CH₃. – ¹³C-NMR (CDCl₃): $\delta = 14.08$ (q, 5-Me), 15.64 (q, CH₃, 6-Et), 18.15 (q, C-1), 19.32 (t, CH₂, 6-Et), 20.82 (2q, 7-Me₂), 32.94 (d, C-7), 129.41 (s, C-5), 132.55 (d, C-3), 145.37 (d, C-2), 145.55 (s, C-6), 202.26 (s, C-4). – MS (EI): m/e (%) = 41 (80) [C₃H₅], 55 (29) [C₄H₇], 69 (61) [C₅H₉], 81 (17) / 95 (17) / 109 (24) / 123 (40) / 137 (76) / 151 (36) / 165 (100) [M⁺–C_nH_{2n+1}], 180 (14) [M⁺].

Example 10

15 Floral-fruity-green female fragrance containing compound 1

No.	Compound / Constituent	Parts by weight in ‰
	1. Adoxal	3
20	2. Ambrofix, 10 percent in BB	15
	3. Benzyl acetate, extra	6
	4. Bergamot oil	80
	5. Calone 1951	4
	6. Cedryl methyl ether	5
25	7. Citronellyl acetate	15
	8. Citronellol, extra	35
	9. Dimetol	2

	10.	DPG (dipropylene glycol)	94
	11.	Estragol	1
	12.	Ethyl linalool	35
5	13.	Ethyl-3-methyl-3-phenylglycidate (strawberry aldehyde)	1
	14.	Eugenol, very pure	3
	15.	Floralozone [3-(4-ethylphenyl)-2,2-dimethylpropanal], 10 percent in DPG	4
	16.	Floropal (2,4,6-trimethyl-4-phenyl-1,3-dioxane)	3
10	17.	Galaxolide 50 PHT (4,6,6,7,8,8,-hexamethyl-1,3,4,6,7,8-hexahydrocyclopenta[g]benzopyran)	140
	18.	Gardenol (1-phenylethyl acetate)	30
	19.	Hedione (methyl dihydrojasmonate)	120
	20.	cis-3-Hexenyl acetate, 10 percent in DPG	17
15	21.	cis-3-Hexenyl salicylate	9
	22.	Iso E Super	60
	23.	Isoraldein 70 (methylionone)	35
	24.	Lavender oil, French	7
	25.	Lilial [2-methyl-3-(4-tert-butylphenyl)propanal]	90
20	26.	Melonal (2,6-dimethyl-5-hepten-1-al), 10 percent in DPG	12
	27.	3-(4-Methoxyphenyl)-2-methylpropanal	6
	28.	1-Phenyl-2-methylprop-2-yl acetate	9
25	29.	Sandalore [5-(2,2,3-trimethyl-3-cyclopenten-1-yl)-3-methylpentan-2-ol]	15
	30.	Tagette oil, extra	3
	31.	Terpineol	10

	32.	Tropional [2-methyl-3-(3,4-methylenedioxyphenyl) propanal]	48
	33.	Viridine (2-phenylacetaldehyde dimethyl acetal)	1
	34.	Ylang-ylang oil	2
5	35.	Lemon oil, Italian	30
	36.	Compound 1, 10 percent in DPG	50
			<u>1000</u>

10 This composition gives a feminine, floral-aquatic perfume with a hesperidic-green top note of bergamot, citrus and lavender notes, rosy, lily-of-the-valley- and watermelon-accentuated middle notes and fruity-musklike-woody base note.

15 The compound 1 combines harmoniously with the rose accord and emphasizes it, like the fruity aspects of this creation. Moreover, it also integrates harmoniously the lavender-like facets in the initial odor. Compared with damascones and their analogs, the hesperidic elements are much more strongly emphasized, and, moreover, the compound 1 gives the scent a very
20 much greater diffusivity than would be the case if damascones were used.

Example 11

Perfume composition containing compound 1 for a cream soap

25	No.	Compound / Constituent	Parts by weight in 1/1120
	1.	Benzyl acetate, extra	10

	2.	Benzyl salicylate	4
	3.	Citronellol, extra	200
	4.	Dimethyl sulfide, 1% in triethyl citrate	0.1
	5.	Ethylvanillin	0.4
5	6.	Eugenol, pure	2.5
	7.	Geraniol, extra	110
	8.	Geranium, Bourbon RGV	20
	9.	Geranyl acetate, pure	10
	10.	cis-3-Hexenol	1
10	11.	Irisantheme [3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one]	60
	12.	Isopulegol	2
	13.	Camomile oil, Roman	1
	14.	Koavone	3
15	15.	Laurylaldehyde	1
	16.	Nerol	90
	17.	Nonanal	1.5
	18.	Methyl 2-nonynoate	0.5
	19.	2-Phenylacetaldehyde, 85 percent strength	
20		in 2-phenylethyl alcohol	2
	20.	2-Phenylacetic acid, pure, crystalline	0.5
	21.	2-Phenylethyl alcohol	420
	22.	Phenethyl phenylacetate	0.5
	23.	1-Phenyl-2-methyl-2-propanyl acetate	6
25	24.	Rosacetol (alpha-trichloromethylbenzyl acetate)	6
	25.	Cinammon rose, RHS MEF	2
	26.	Rose oxide	1

27.	Cinnamyl alcohol, synthetic	15
28.	Compound 1, 1 percent in DPG	150

1120

5

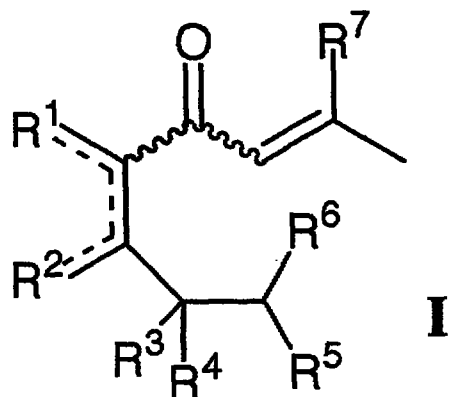
This composition gives a fruity-rosy perfume oil, reminiscent of the typical scent of the Bulgarian rose.

10 The compound 1 represents a scent cornerstone in this markedly rosy composition. It gives the creation a very much more natural character than the damascones which, in direct contrast, shift the overall impression more in the direction of plums, wood and wine notes. Moreover, the compound 1 introduces more apple-like, green aspects to the composition and thus better brings out the mild cleansing, caring product character of the cream soap.

Patent claims



1. A compound of the general formula I



5

in which $R^1, R^2 = \text{CH}_2, \text{CH}_3, \text{CHCH}_3, \text{CH}_2\text{CH}_3,$
 $R^3 = \text{H}, \text{CH}_3, \text{CH}_2\text{CH}_3,$
 $R^4, R^5, R^6, R^7 = \text{H}, \text{CH}_3,$

10

with the condition that the radicals R^4, R^5, R^6, R^7 are not all hydrogen at the same time, and where a dashed line represents an optional double bond, including the (*E/Z*)-isomers of all double bonds and all possible stereoisomers.

15

2. A compound of the general formula I as claimed in claim 1 having an (*E*)-configured double bond in position 5(6).

3. A compound of the general formula I as claimed in claim 1, in which $R^4 = \text{CH}_3$.

20



4. A compound of the general formula I as claimed in claim 1 having an (E)-configured double bond in position 5(6) and in which $R^4 = CH_3$.
5. A compound of the general formula I as claimed in claim 1 from the group (2E,5Z)-5,6,7-trimethylocta-2,5-dien-4-one, (2E)-5,6,7-trimethyloct-2-en-4-one, (2E,5Z)-5,6,7-trimethylnona-2,5-dien-4-one, (2E,5E/Z)-6-ethyl-5,7-dimethylnona-2,5-dien-4-one, (2E,5E/Z)-6-ethyl-5-methylnona-2,5-dien-4-one, (2E,5Z)-2,5,6,7-tetramethylocta-2,5-dien-4-one, (2E,5E)-5,6,7,7-tetramethylocta-2,5-dien-4-one, (2E,5Z)-6-ethyl-5,7-dimethylocta-2,5-dien-4-one and all their double-bond isomers, and (2E,5E/Z)-5,6,7-trimethylocta-2,5-dien-4-one.
6. A fragrance or aroma composition having a content of at least one compound as claimed in any of claims 1 to 5.
7. The use of at least one compound as claimed in any of claims 1 to 5 as fragrance or flavoring.