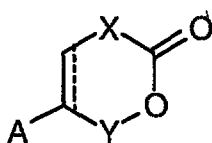


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REPLACED SHEETS		SG
☒	Description	: paged 01 to paged
☒	Claim(s)	: paged 41 to paged
☒	Drawing(s)	: paged to paged
☒	Abstract	: paged to paged

- 5 The invention is concerned with odorant compositions containing macrocycles, namely 15- to 17-membered compounds of the formula



- 10 wherein the dotted line signifies an optional additional bond, X and Y stand for methylene or C₂-12-polymethylene, optionally substituted with an additional methyl group, and A signifies hydrogen or methyl in the case of the unsaturated compound and methyl in the case of the saturated compounds, with the proviso that the unsaturated compounds

- 15 are present to more than 80% in the cis form when A signifies hydrogen and are present to more than 50% in the cis form when A signifies methyl

- with the exception of Z-oxacyclopentadec-6-en-2-one (15-membered ring), Z-oxacycloheptadec-8-en-2-one (17-membered ring) and Z-oxacycloheptadec-11-en-2-one (17-membered ring), and a process for the manufacture of the compounds of formula I.
- 20

- The compounds of formula I or mixtures of compounds of formula I are partially novel and partially known. The compounds I' or the defined mixtures I' with the substituents previously defined for formula I are novel with the exception of Z-oxacyclopentadec-3-(or 6-or 13-)en-2-one, Z-oxacyclohexadec-3-(or 6-, 11-, 12- or 13)en-2-one and Z-oxacycloheptadec-8-(or 10-, 11-, 12-, 13- or 15-)en-2-one.
- 25

- The compounds I and I' thus embrace oxacyclopenta(or -hexa or -hepta)decen-2-ones and the respective corresponding decan-2-ones.
- 30

Formula I is intended to include all possible isomers. Thus, in the case of saturated and unsaturated compounds the racemates and the optically active compounds, that is to



say the R- and S-forms, are included. In the case of the unsaturated compounds the cis/trans ratio is that according to the above definition. Further, diastereoisomeric forms are also possible having regard to multi-methyl substitution.

5 In 1927 Kerschbaum isolated a ambrettolide (Z-oxacycloheptadec-8-en-2-one) from ambrette seed oil (musk seed oil) (Ber. 60,902,(1927). Maurer isolated Z-oxacyclopentadec-6-en-2-one from the same oil (B. Maurer, A. Grieder, Helv. Chim. Acta, 60, 1155, (1977). The company IFF has protected the synthesis of E-oxacycloheptadec-10-en-2-one in a patent (USP 4 064 144).

10

Mookherjee has described the synthesis of a mixture of oxacycloheptadec-8-en-2-one, oxacycloheptadec-9-en-2-one, oxacycloheptadec-10-en-2-one and oxacycloheptadec-11-en-2-one, with the third compound being present to 80% in the aforementioned mixture. A stereochemistry of the compounds is not given. (B.D. Mookherjee, R.W. Trenkle, R.R. Patel, J. Org. Chem. 37, 24, 3846, (1972)). As the
15 aforementioned synthesis is a pyrolysis of an ester, a selective formation of a cis-olefin would not be expected (see in this respect Houben-Weyl, volume V/1b, 105, 1972).

Firmenich has protected a mixture of mainly E-oxacyclohexadec-12-en-2-one and E-oxacyclohexadec-13-en-2-one, with the Z-isomers being present only
20 in a small percentage (EP 0 424 787).

The company IFF has protected the use of oxacyclohexadec-11-en-2-one (USP 4 541 950), but the cis/trans ratio of the product obtained is not given. Since, however, the
25 product was obtained by metathesis, it is doubtful whether the trans content is higher than the cis content, see in this respect A. Fürstner, K. Langemann, J. Org. Chem. 61, 3942, 1996.

The French company Mane et Fils in F-06620 Bar s/Loup sells a compound under the
30 name cis-iso-ambrettolide. This is Z-oxacycloheptadec-11-en-2-one (Parfums, Cosmétiques, Actualiées, No 128, avril/mai 63, 1996).

C. Collaud (Helv. Chim. Acta 25, 965, 1942) describes the production of a mixture of oxacycloheptadec-6-en-2-one and oxacycloheptadec-7-en-2-one, with the stereochemistry of the products not being given. As the aforementioned synthesis is, moreover, a pyrolysis of an ester, a selective formation of a cis-olefin would not be
 5 expected.

In addition to extremely low threshold values the compounds I have a very good adhesion. All have intensive musk notes, which are often also accompanied by powdery, fruity, flowery side-notes. The compounds also have amber-like, earthy notes smelling like
 10 ambrette seeds. Z-13-methyl-oxacyclopentadec-10-en-2-one has and especially fine perfumistic effect with a dominant musk note. The musk note is rounded off by a powdery, fruity component.

Preferred compounds in accordance with the invention are set forth hereinafter
 15

- Z-13-Methyl-oxacyclopentadec-10-en-2-one:

This compound is characterized by a very low threshold value. The olfactometric threshold value is 0.578 ng/l. The GC threshold value is 0.1 ng/l. This gives an "odour value" of 18038 [see N. Neuner-Jehle, F. Etzweiler, in *Perfumes: Art Science and Technology*, Edited by P.M. Müller, D. Lamparsky]. This is the highest "odour value"
 20 which has become known for a macrocyclic musk. For example, Musk R1 (1,7-dioxacycloheptadecan-8-one) has a threshold value of 0.33 ng/l; a vapour pressure of 3.24 µg/l and an "odour value" of 3074. Thibetolide has a threshold value of 2.16 ng/l, a vapour pressure of 6.64 µg/l and an "odour value" of 3074. All other macrocyclic musk odorants
 25 have even lower values. Z-13-Methyl-oxacyclopentadec-10-en-2-one is distinguished by a powdery, musk-like, lactone-like, fruity odour;

- Z-Oxacycloheptadec-12-en-2-one:

Strong, thibetolide-like odour after ambrette seeds;
 30

- Z-oxacyclohexadec-5-en-2-one:

Musk-like, powdery, lactonic odour;

- Z-oxacyclohepadec-9-en-2-one:

The compound has never been produced in the purity achieved here; the spectral data and olfactory properties were not known; strong nitromusk note, with a lactonic, woody, animalic impact;

5 - Z-oxacycloheptadec-10-en-2-one:

The compound has a musk-like odour, after ambrettolide, after ambrette seeds, powdery, fruity, green;

 - 10-methyl-oxacyclopentadecan-2-one:

10 The compound has a nitromusk-like, powdery, lactonic, woody, earthy odour;

 - 8-methyl-oxacyclopentadecan-2-one:

The compound has a nitromusk-like, powdery, amber-like, fruity odour;

15 - 9,13-dimethyloxacyclopentadecan-2-one:

The compound has a musk-like, fruity, powdery, flowery, lactone-like odour;

 - oxacycloheptadec-7-en-2-one:

Fruity, musk-like, flowery, odour similar to ambrette seeds;

20

 - Z-oxacycloheptadec-13-en-2-one:

Very desirable, musk ketone-like, powdery, lactonic, flowery odour;

 - 7-methyl-oxacyclohexadecan-2-one:

25 The compound has a musk-like, flowery, fruity, powdery, lactone-like odour.

 - 8,15-dimethyl-oxacyclopent-7-en-2-one:

Nitromusk, powdery, animalic;

30 - 15-methyl-oxacyclohepadec-12-en-2-one:

The compound is distinguished by a musk-like, woody, animalic, sweet earthy, fruity odour.

35 The macrocycles I can be used generally in the same manner as the known musk odorants. Thus, they harmonize with a large number of natural and also synthetic products which are frequently used in odorant compositions. In particular, in the base note they

produce interesting effects in combination with woody and amber accords, patchouli oil as well as cedarwood and sandalwood odorants. Flowery middle notes confer elegance and radiance to the compounds. Some examples of classes of substances which harmonize well are:

5

- Natural products, such as tree moss absolute, geranium oil, jasmin absolute, patchouli oil, rose oil, sandalwood oil, vetiver oil and ylang-ylang oil, etc,

- alcohols , such as citronellol, Ebanol®, geraniol, linalool, phenylethyl alcohol and Sandalore®, etc,

10

- aldehydes and ketones, such as Florozone® (3-(4-ethylphenyl)-2,2-dimethyl-propional), hydroxycitronellal, Iso-E-Super® (1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-octanaphthalene), Isoraldein®, maltol, methyl edryl ketone, methylionone and vanillin, etc;

15

- ethers and acetals, such as ambrox, geranyl methyl ether, rose oxide and Spirambrene® (2',2',3,7,7-pentamethyl-spiro[bicyclo[4.1.0]heptane-2,5'-[1,3]dioxan]), etc;

- esters and lactones, such as Berryflor®, γ ecalactone and γ -undecalactone, etc.

20

Their versatility permits a broad use of the macrocycles or formula I not only in sweet oriental creations, but also in "fougère", "chypre" and "floral" olfactory directions. By virtue of the low threshold values and the good adhesion, composition for cosmetic products, washing agents and similar mass produced products are also contemplated in addition to luxury perfumes.

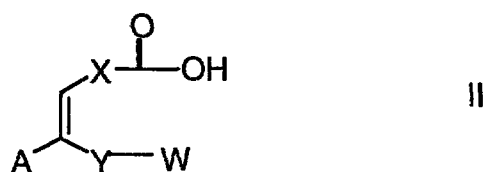
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The compounds of formula I can be used in wide limits which can extend in compositions, for example, from about 0.1 wt.%(detergents) to about 40 wt.%(alcoholic solutions), without these values being, however, limiting values, since the experienced perfumer can also produce effects with even lower concentrations or can synthesize novel complexes with even higher amounts. The preferred concentrations range between about 3% and about 20%. The compositions manufactured with compounds or formula I can be used for all kinds of perfumistic consumer goods (eaux de Cologne, toilet water, extracts, lotions, creams, shampoos, soaps, salves, powders, deodorants, detergents, etc.).

35

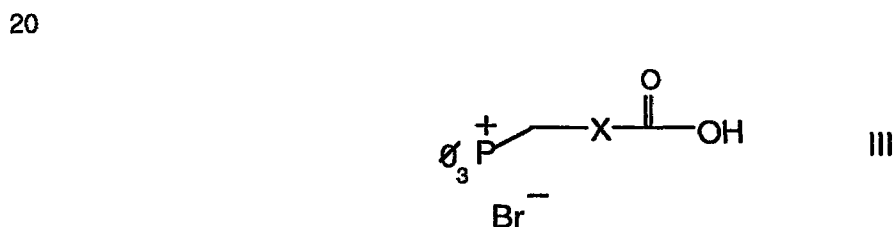
The compounds of formula I can accordingly be used for the production of compositions and, as will be evident from the above compilation, a wide range of known odorants or odorant mixtures can be employed. In the production of such compositions the odorants or odorant mixture set forth above can be used in a manner known to the perfumer such as e.g. from W.A. Poucher, *Perfumes, Cosmetics, Soaps*, 2nd vol., 7th edition, Chapman and Hall, London 1974.

The process for the manufacture of the compounds of formula I or mixtures thereof comprises lactonizing a compound of the formula

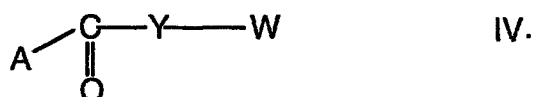


wherein A, X and Y have the above significance and W represents OH, alkanoate, for example acetate, or a leaving group, such as mesylate, tosylate, I, Br, Cl etc., in a manner known per se, namely at elevated temperature and under basic conditions, and, if desired, hydrogenating a thus-obtained unsaturated compound of formula I.

The compounds of formula II can be obtained by subjecting a compound of the formula



to a Wittig reaction with a compound of the formula



The lactonization of a compound of formula II to a compound of formula I can be effected, for example, according to the method of Collaud (BP No. 490 044, 4th January 1937, C. Collaud, *Helv. Chim. Acta*, 1965, 1942).

5 Here, the preparation of an ω -hydroxycarboxylic acid 2,3-dihydroxy-propyl ester is effected first by treatment of the sodium salt of the corresponding ω -hydroxycarboxylic acid or formula II with chloropropane-1,2-diol, followed by an internal trans-esterification in the presence of a methanolate, especially sodium methanolate. The resulting monomer is distilled from the reaction mixture in the presence of a high-boiling solvent or entraining
10 agent, for example glycerol.

A second possibility for the lactonization of a compound of formula II to a compound of formula I is described, for example, in Patent CH 344 712. The ω -hydroxycarboxylic acid is heated at a high temperature in the presence of a base (KOH,
15 NaOH, etc.) and glycerol, with a polyester being obtained. Subsequently, an internal trans-esterification is effected in the presence of sodium methylate. The resulting monomer is distilled from the reactor in a high-boiling solvent, for example glycerol.

When W signifies I, Br or Cl, the lactonization of a compound of formula II to
20 formula I can also be effected according to the method of Mandolini et al. (G. Galli, G. Giannelli, G. Illuminati, L. Mandolini, *J. Org. Chem.*, Vol. 44, No. 8, 1258, 1979). Here, the ω -bromoalkanoate of formula II is added dropwise to a well-stirred suspension of potassium carbonate in dimethyl sulphoxide.

25 The use of these known methods is, however, not suitable for the manufacture of odorants, since sulphur notes which are difficult to remove form in the product. It has now been found that dimethyl sulphoxide can be replaced surprisingly by a sulphur-free solvent, especially N-methylpyrrolidone, and that an olfactorily perfect product can be obtained in this manner.

30 The hydrogenation of an unsaturated compound of formula I can be effected according to methods known per se, namely catalytically. Suitable catalysts are Pd-on-carbon or on potassium carbonate, Pt or Raney-nickel etc. It is conveniently carried out in a solvent such as an alkanol, for example methanol, ethanol etc., in ethyl acetate or acetic
35 acid etc. The suitable temperature range extends from about room temperature to about

100°C. The hydrogenation can be carried out under normal pressure or under elevated pressure. Thus, for example, a pressure up to about 60 atm. or even more is possible.

The preparation of the compounds of formula II can be effected according to methods known per se for Wittig reaction. Accordingly, a phosphonium salt of formula III is conveniently treated firstly with (about 2 equivalents) of a strong base to give an ylid. Potassium t-butyrate, potassium t-amylate, methyllithium, butyllithium, phenyllithium, potassium hydride, sodium hydride, hexamethyldisilazane (as the potassium or sodium salt), lithium diisopropylamide etc. can be used, for example, as bases. An aprotic solvent such as diethyl ether, tetrahydrofuran, benzene, toluene, hexane, dimethylformamide, HMPA (hexamethylphosphoric acid triamide) etc. is preferably used as the medium for the further reaction with a compound of formula IV. The temperatures are not critical, and the convenient temperature range can be broad (about -78 to about 100°C).

The Wittig reaction has been used sporadically for the synthesis of precursors of macrocyclic compounds (Nicolaou et al., J. Org. Chem. 44, 4011, 1979). Büchi and Wuest (Helv. Chim. Acta, 62, 2661, 1979) have used the Horner-Emmons condensation including a Wittig reaction for the synthesis of the cyclic C₁₅-ketones exaltone and muscone. However, the usability for the synthesis of macrocyclic lactones, in addition to various ring sizes, further also with double bonds in various positions, has been unknown until now.

The process in accordance with the invention permits for the first time the manufacture of substituted or unsubstituted macrocyclic lactones with ring sizes 15, 16, 17 having an optional double bond, which are mainly present in the cis form.

Example 1

100 g (0.846 mol), of 3-methyl-1,5-pentanediol, 108 ml of ethyl acetate and 21 g of Amberlyst[®] 15 dissolved in 420 ml of toluene were heated at 94°C to reflux temperature for 3 hours. Then, the mixture was cooled, filtered over Celite and concentrated on a rotary evaporator. There were obtained 104.5 g of crude product as a mixture of 3-methyl-1,5-pentanediol (25%), 3-methyl-1,5-pentanediol monoacetate (50%) and 3-methyl-1,5-pentanediol diacetate (25%).

Example 2

189 g of crude product (from the preceding Example) and 9 g (76 mol) of potassium bromide were placed in 377 ml of methylene chloride and treated at -10°C with 1.18 g (7.55 mmol) of 2,6,6-tetramethylpiperidin-1-oxyl radical. 780 ml of 12-15 percent hypochlorite solution (adjusted to pH 9 with 19 g/l NaHCO₃) were added dropwise at 0-5°C within 50 minutes. After 40 minutes the temperature rose to 18°C in spite of cooling. The mixture was stirred at 2-8°C for 1 hour. Subsequently, a further 195 ml of 12-15 percent hypochlorite solution (adjusted to pH 9 with 19 g/l NaHCO₃) were added dropwise at 0-5°C within 15 minutes. The mixture was stirred for 30 minutes, with the temp. rising to 10°C. A further 195 ml of 12-15 percent hypochlorite solution (adjusted to pH 9 with 19 g/l NaHCO₃) were added dropwise within 10 minutes, with the temp. rising to 6°C. The mixture was stirred at 0-5°C for a further 1 hour and 30 minutes. The reaction mixture was poured into water and extracted twice with methylene chloride. The organic phase was washed (peroxide test negative) with 2N HCl + 5 g KI and with water + 9 g Na₂S₂O₃ · 5H₂O. Thereafter it was dried over Na₂SO₄ and concentrated. 177 g of crude product were obtained. This crude product was distilled and gave 114 g of product (b.p. 75-76°C, 0.2 bar) (content ~70% of 3-methyl-5-oxopentanol acetate according to ¹H-NMR).

Example 3

156 g (0.312 mol) of (8-carboxyoctyl)-triphenylphosphonium bromide were pulverized and placed in 330 ml of tetrahydrofuran. After stirring for 10 minutes the mixture was cooled to -20°C and treated rapidly with 69.9 g (0.622 mol) of potassium t-butyrate in 90 ml of tetrahydrofuran. The temperature rose to 6°C and the reaction mixture became dark red in colour. It was diluted with 50 ml of tetrahydrofuran and stirred at 5-10°C for 1 hour. Then, it was cooled to -20°C and treated with 70 g (0.30 ml, 70%) of 3-methyl-5-oxopentanoyl acetate in 50 ml of tetrahydrofuran. The temperature thereby rose to 15°C. The mixture was stirred at -10°C to -8°C for 1 hour and thereafter at room temperature for 1 hour. It was warmed to 35°C and stirred for a further 30 minutes. The reaction mixture was poured into water, adjusted to pH 12 with 2N NaOH and extracted twice with ether. The organic phase was washed with 2N NaOH and

the aqueous phase was acidified with 85 percent ortho-phosphoric acid and extracted twice with ether. The organic phase was washed with saturated sodium chloride solution, dried over sodium sulphate and concentrated. There were obtained 106 g of crude product which was purified by chromatography. The impurities (~36 g) were mainly triphenyl-
 5 phosphine oxide. The product consisted of a mixture of 9Z-14-acetoxy-12-methyltetradec-9-enoic acid and 9Z-14-hydroxy-12-methyltetradec-9-enoic acid in the ratio 2:1.

Spectra of 9Z-14-hydroxy-12-methyltetradec-9-enoic acid Z/E = 94/6.

10 IR (film): 3336; 3005; 2928; 2855; 1711; 1458; 1246; 1057.

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.4 (2H) m; 3.7 (2H) m; 2.32 (2H) t $J = 7 \text{ Hz}$; 0.9 (3H) d $J = 6.2$.

15 MS 238 (2); 150 (4); 136 (5); 109 (16); 95 (32); 81 (100); 67 (48); 55 (76); 41 (48).

Example 4

Apparatus:

20

350 ml 3-necked sulphonation flask, special headpiece (see Fig. 1), reflux condenser, thermostat, 2 cooling traps, HV pump with constantly maintained vacuum.

53.5 g of crude product (~65 percent) from the preceding Example, 230 ml of
 25 glycerol and 1 g of potassium hydroxide (85 percent) in 1 ml of water were placed in a 350 ml sulphonation flask having a distillation headpiece. The resulting water, acetic acid and 4-5 ml of glycerol were distilled off in a high vacuum. Thereupon, the distillation headpiece was removed and the flask was fitted with the described special headpiece. This was filled with 150 ml of glycerol. The mixture was left to cool and 1 g of sodium
 30 methyrate was added. The methanol formed was removed in a vacuum. The mixture was heated to 170-180°C under reflux (internal initial temperature 155°C) in a high vacuum. (3-4 mbar) for 18 hours. After this time a 15 mm thick layer of lactone had formed in the special headpiece. It was left to cool, 1 g of sodium methyrate was added and the methanol formed was distilled off in vacuum. After distillation for 42 hrs. the addition was repeated.
 35 After a total of 66 hrs. at reflux it was left to cool. The content of the headpiece was diluted

with water and extracted four times with ether. The organic phase was washed with water, dried over sodium sulphate and concentrated. There were obtained 28 g of crude product which was distilled (diffusion pump) over a Widmer column. There were obtained 20 g (69%) of 13-methyloxacyclopentadec-10-en-2-one, $Z/E = 94/6$.

5

IR (film): 3008; 2927; 2857; 1734; 1459; 1378; 1245; 1180; 1146; 1055.

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.45 (2H) m; 4.2 (2H) m; 0.95 (3H) d $J = 6.2$ Hz.

10 $^{13}\text{C-NMR}$ (CDCl_3) 173.9 (s); 131.3 (d); 127.8 (d); 61.9 (t); 36.2 (t); 34.0 (t); 33.9 (t); 31.2 (d); 27.62 (t); 27.60 (t); 27.1 (t); 26.8 (t); 25.6 (t); 24.8 (t) 18.6 (9).

MS 238 (2); 196 (2); 150 (5); 136 (5); 123 (5); 109 (14); 95 (30); 81 (100); 67 (49); 55 (53); 41 (48); 27 (15).

15 Odour: musk-like, fatty, fruity, powdery, lactone-like.

Example 5

527 g (1 mol) of 10-carboxydecyltriphenylphosphonium bromide were suspended
 20 in 1.4 l of tetrahydrofuran. 248 g (2.2 mol) of potassium t-butyrate dissolved in 1 l of tetrahydrofuran were added at 0°. After stirring at 5°C for 30 minutes 120 g (1.18 mol) of tetrahydropyran-2-ol were added at 0-10°C. The reaction mixture was stirred at room temperature for 90 minutes, poured into water and extracted with t-butyl methyl ether. The aqueous phase was adjusted to pH 2 with 4N sulphuric acid and extracted with t-butyl
 25 methyl ether. 274 g of crude product were obtained. For the purification of the aforementioned crude product, 552 g were esterified with 700 ml of methanol and 10 ml of sulphuric acid as the catalyst (3 hours, reflux temperature). After usual working up there were obtained 620 g of crude ester which was distilled. There were obtained 301 g (53%) of methyl 16-hydroxyhexadec-11-enoate, $Z/E = 94/6$.

30

Example 6

240 g (0.84 mol) of methyl Z-16-hydroxyhexadec-11-enoate and 50 g of potassium hydroxide were dissolved in 500 ml of methanol in a 3 litre flask. The mixture was heated

to reflux temperature for 2 hours. Then, the methanol was distilled off and 800 ml of glycerol were added to the residue. 250 ml of glycerol were distilled off (150°C, 3 mmHg). 160 g (1.45 mol) of 3-chloropropane-1,2-diol were added slowly at 150°C and the mixture was stirred at this temperature for 1 hour. Then, 200 ml of a mixture of 3-chloropropane-
 5 1,2-diol and glycerol were distilled off (120-148°C 3 mmHg, internal temperature 160-170°C). The mixture was cooled to 60°C and treated at this temperature with 25 ml of 5.4M ethanolic sodium methanolate solution. The mixture was distilled further (3 mmHg, 180-200°C) and glycerol was replaced continuously. After 950 ml of a two-phase mixture had been distilled off the residue was extracted with hexane. After distillation there were
 10 obtained 167 g (78%) of 12Z-oxacycloheptadec-12-en-2-one, Z/E = 91/9.

IR (film) 2928; 2857; 1736; 1461; 1245; 1174.

¹H-NMR (CDCl₃, 200 MHz) 5.35 (2H) m; 4.1 (2H) t J = 6.5 Hz; 2.32 (2H) t J = 7.5 Hz.

15 ¹³C-NMR (CDCl₃) 173.35 (s); 130.04 (d); 129.06 (d); 63.83 (t); 34.09 (t); 28.43 (t); 28.27 (t); 28.15 (t); 27.34 (t); 27.10 (t); 26.85 (t); 26.85 (t); 26.08 (t); 5.63 (t); 24.41 (t).

MS: 252 (s); 224 (5); 195 (6); 164 (7); 150 (8); 135 (24); 123 (12); 107 (26); 96 (47); 82 (97); 67 (100); 55 (60); 41 (53); 29 (8).

20

Odour: musk-like, after ambrette musk, Musk 174 and thibetolide.

Example 7

25 The procedure was effected analogously to Example 3.

27.4 g of (3-carboxypropyl)triphenylphosphonium bromide (63.8 mmol) were placed in 100 ml of THF and treated with 17.2 g (153 mmol) of potassium t-butyrate in 25 ml of THF. 28.5 g (60%, 69 mmol) of 11-bromoundecanal were added to this mixture.
 30 After the usual working up there were obtained 20 g of crude product and after chromatography there were obtained 14 g (66%) of 9Z-15-bromopentadec-4-enoic acid, Z/E = 91/9.

IR (liquid): 3008; 2926; 2854; 1711; 7436; 1281; 1252; 1211.

$^1\text{H-NMR}$ (CDCl_3) 5.4 (2H) m; 3.4 (2H) t $J = 7$ Hz; 2.4 (4H) m.

5 MS 300 (2); 258 (9); 238 (35); 150 (17); 137 (25); 123 (32); 110 (38); 96 (88); 82 (91); 69 (98); 55 (100); 41 (86); 29 (32).

Example 8

10 17 g of potassium carbonate were placed under a nitrogen atmosphere and suspended in 200 ml of N-methylpyrrolidone. A solution of 13 g (41 mol) of Z-15-bromopentadec-4-enoic in 120 ml of N-methylpyrrolidone was added dropwise using a fine dosing dropping funnel during 7 hrs while stirring at 110-115°C. The mixture was stirred for 1 hour while cooling slowly. The reaction mixture was poured into water,
15 extracted with ether, washed with water and saturated sodium chloride solution, dried over sodium sulphate and concentrated. The crude product (9.7 g) was chromatographed and distilled in a bulb-tube. There were obtained 5.8 g (60%) of Z-oxacyclohexadec-5-en-2-one, Z/E = 91/9.

20 IR (film) 3008; 2928; 2857; 1737; 1459; 1350; 1254; 1166; 1041.

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.41 (2H) m; 4.15 (2H) t $J = 6.2$.

$^{13}\text{C-NMR}$ (CDCl_3) 172.9 (s); 131.15 (d); 127.6 (d); 64.15 (t); 35.25 (t); 27.52 (t); 27.47 (t);
25 27.16 (t); 27.10 (t); 26.95 (t); 26.64 (t); 26.60 (t); 25.58 (t); 24.48 (t); 23.54 (t).

MS 238 (5); 220 (2); 178 (3); 163 (2); 149 (7); 135 (9); 126 (14); 112 (22); 96 (69); 82 (90); 67 (100); 55 (94); 41 (85).

30 Odour: musk-like, fatty, powdery, lactone-like.

Example 9

The procedure was effected analogously to Example 3.

5 48.5g (0.1 mol) of (7-carboxyheptyl)triphenylphosphonium bromide were
suspended in 150 ml of tetrahydrofuran. After the addition of 24.7 g (0.22 mol) of
potassium t-butyrate in 50 ml of tetrahydrofuran 26.4 g (0.12 mol) of 8-bromooctanal were
added dropwise. After the usual working up there were obtained 35.4 g of crude 8Z-16-
bromohexadec-8-enoic acid, Z/E = 93/6.

10

IR: 3004; 2928; 2855; 1709; 1438; 1160; 1121.

$^1\text{H-NMR}$ (CDCl_3) 5.35 (2H) m; 3.4 (2H) t $J = 6,25$; 2.35 (2H) t $J = 7.5$.

15

Example 10

The procedure was effected analogously to Example 8.

41.5 g of potassium carbonate were placed in 400 ml of N-methylpyrrolidone and
20 treated with a solution of 34 g (0.1 mol) of 8Z-16-bromohexadec-8-enoic acid in N-
methylpyrrolidone. After the usual working up there were obtained 8 g of crude product.
After chromatography and bulb-tube distillation there were isolated 11.2 g (44%) of 2-
oxacycloheptadec-9-en-2-one, Z/E = 93/6.

25 IR (film): 3003; 2929; 2856; 1735; 1461; 1346; 1247; 1182; 1076.

$^1\text{H-NMR}$ (CDCl_3 , 200 Mhz) 5.39 (2H) m; 4.12 (2H) t $J = 5.5$ Hz; 2.33 (2H) t $J = 7.5$.

$^{13}\text{C-NMR}$ (CDCl_3) 173.8 (s) 130.0 (d); 129.8 (d); 64.0 (t); 34.6 (t); 29.1 (t); 28.7 (t); 28.3
30 (t); 28.0 (t); 27.95 (t); 27.86 (t); 27.83 (t); 26.3 (t); 26.1 (t); 25.9 (t); 24.9 (t).

Odour: intensive musk-like, lactone-like, after nitromusk, ambrette musk and ambretone
(limonene aldehyde), woody, animalic.

Example 11

The procedure was effected analogously to Example 3.

5

97 g (0.2 mol) of (7-carboxyheptyl)-triphenylphosphonium bromide were dissolved in 500 ml of tetrahydrofuran. 45 g (0.4 mol) of potassium t-butyrate (0.4 mol) in 200 ml of tetrahydrofuran were then added. Thereafter, 26 g (0.2 mol) of 7-hydroxyheptan-2-one were added. After the usual working up there were obtained 49 g of crude
10 product. After chromatographic purification there were isolated 27.6 g (60%) of 14-hydroxy-9-methyltetradec-8-enoic acid, $Z/E = 80/20$.

$^1\text{H-NMR}$ (CDCl_3 200 MHz) 5.1 (1H) d $J = 6.5$ Hz; 3.65 (2H) t $J = 6.25$ Hz; 2.3(2H) t = 7.5 Hz.

15

Example 12

The procedure was effected analogously to Example 4.

20 24.5 g (95.5 mol) of 14-hydroxy-9-methyltetradec-8-enoic acid, ($Z/E = 80/20$) were placed in 50 ml of glycerol and treated with 0.54 g of potassium hydroxide (50 percent). The resulting water was distilled off. Thereupon, the distillation headpiece was removed and the special headpiece (see Figure) was fitted and filled with glycerol. After the addition of 1 g of sodium methylate the mixture was heated to 152°C , 6 mbar. After 24 hours the
25 addition of 1 g of MeONa was again effected. After 48 hours extraction of the content of the special headpiece yielded 19 g of crude product. By chromatography there were obtained 19 g (82%) of 10-methyloxacyclopentadec-9-en-2-one, $Z/E = 80/20$.

IR: (film) 2930; 2857; 1735; 1459; 1382; 1251; 1161; 1085.

30

$^1\text{H-NMR}$ (CDCl_3 200 MHz) 5.03 (1H) m ; 4.15 (2H) t $J = 5.6$ Hz (Z isomer) 4.11 (2H) t $J = 6.5$ (E isomer) 2.35 (2H) m .

MS 238 (3); 210 (2); 149 (3); 135 (3); 123 (13); 109 (26); 95 (53); 81 (88); 67 (89); 55 (90); 41 (100).

^{13}C -NMR (CDCl_3) 173.8 (s); 134.8 (s); 126.2 (d); 64.4 (t); 34.3 (t); 31.3 (t); 28.5 (t); 28.3 (t); 27.5 (t); 26.9 (t); 26.6 (t); 26.1 (t); 25.5 (t); 24.8 (t); *Z* isomer.

^{13}C -NMR (CDCl_3) 173.7 (s); 133.9 (s); 126.0 (d); 63.5 (t); 38.8 (t); 33.4 (t); 28.9 (t); 28.4 (t); 27.1 (t); 26.8 (t); 25.5 (t); 24.4 (t); 23.9 (t); *E* isomer.

10 Odour: musk-like, powdery, slightly fruity, waxy.

Example 13

1.14 g of 10 percent palladium-on-carbon were added to 13.5 g (57 mol) of 10-methyloxacyclopentadec-9-en 2-one in 60 ml of ethanol and the mixture was subsequently hydrogenated under normal pressure for 6.5 hours. Then, it was suction filtered over Celite and the solution was concentrated, chromatographed and distilled in a bulb-tube. There were obtained 8.4 g (62%) of 10-methyloxacyclopentadecan-2-one.

20 IR (film) 2928; 2859; 1735; 1459; 1377; 1343; 1247; 1113; 1047.

^1H -NMR (CDCl_3 200 MHz) 4.14 (2H) m; 2.35 (2H) m; 0.86 (3H) d $J = 7$ Hz.

MS 240 (0.8); 169 (4); 151 (10); 141 (11); 135 (7); 123 (8); 112 (19); 97 (69); 83 (31); 69 (54); 55 (100); 41 (81); 29 (33).

Odour: musk-like, lactone-like, woody, nitromusk, powdery, earthy.

Example 14

30

The procedure was effected analogously to Example 3.

45.7 g (0.1 mol) of (5-carboxypentyl)triphenylphosphonium bromide were placed in 200 ml of tetrahydrofuran and 25 g (0.22 ol) of potassium *t*-butylate in 100 l of

tetrahydrofuran were added dropwise at 0°C. Then, 15.8 g (0.1 mol) of 9-hydroxy-2-nonanone were added. After stirring for 30 minutes and usual working up there were obtained 28.5 g of crude 14-hydroxy-7-methyltetradec-6-enoic acid.

5

Example 15

138.5 g of crude 14-hydroxy-7-methyltetradec-6-enoic acid, prepared according to the preceding Example, were dissolved in 400 ml of methanol, treated with 3 ml of sulphuric acid and heated to reflux temperature for 1 hour. After usual working up and
10 distillation there were obtained 93 g (90%) of methyl 14-hydroxy-7-methyltetradec-6-enoate, *Z/E* = 60/40.

IR (film) 3380; 2930; 2856; 1742; 1437; 1173; 1059.

15 ¹H-NMR (CDCl₃; 200 MHz) 5.1 (1H) t *J* = 7 Hz; 3.68 (3H) s; 3.65 (2H) t *J* = 6.25 Hz; 2.31 (2H) t *J* = 7.5.

MS: 270 (1); 220 (2); 171 (7,8); 138 (16); 123 (31); 109 (19); 95 (61); 81 (87); 67 (65); 55 (100); 41 (63); 29 (19).

20

Example 16

84.5g (0.31 mol) of methyl 14-hydroxy-7-methyl-tetradec-6-enoate, 21 g of 86 percent potassium hydroxide in 220 ml of methanol, 72 g of chloropropane-1,2-diol
25 and 9 ml of 5.4M methanolic sodium methylate solution were mixed analogously to Example 6. The product was distilled (b.p. 114°C) in a high vacuum (0.1 Torr) and subsequently chromatographed. There were obtained 29 g (38%) of 8-methyloxacyclopentadec-7-en-2-one, *Z/E* = 60/40.

30 IR (film) 2931; 2858; 1736; 1459; 1234; 1153; 1058.

¹H-NMR (CDCl₃ 200 MHz) 5.06-5.22 (1H) m; 4.05-4.2 (2H) m; 2.22-2.4 (2H) m.

^{13}C -NMR (CDCl_3) 173.6 (s); 173.5 (s); 135.8 (s), 134.9 (s); 125.1 (d); 124.3 (d); 63.6 (t); 63.5 (t); 38.5 (t); 35.1 (t); 33.9 (t); 29.8 (t); 29.5 (t); 28.8 (t); 28.1 (t); 27.63 (t); 27.62 (t); 27.36 (t); 27.2 (t); 26.8 (t); 26.5 (t); 26.0 (t); 25.93 (t); 25.8 (t); 25.1 (t); 24.7 (t); 24.5 (t); 23.2 (9); 15.4 (9).

5

Odour: weak after musk.

Example 17

10 25 g (0.10 mol) of *Z*-8-methyloxacyclopentadec-7-en-2-one were dissolved in 150 ml of methanol and hydrogenated (1.5 hours) with 2 g of 5% palladium-on-carbon with 100 mbar over-pressure. Then, the mixture was filtered over Celite, and the solution was concentrated, distilled in a bulb-tube and chromatographed. There were obtained 20 g (83%) of 8-methyloxacyclopentadecan-1-one.

15

IR (CDCl_3) 2930; 2859; 1736; 1460; 1246; 1167.

^1H -NMR (CDCl_3 200 MHz) 4.3-4.0 (2H) m; 2.5-2.2 (2H) m; 0.85 (3H) d $J = 7.0\text{Hz}$.

20 ^{13}C -NMR (CDCl_3) 173.9 (s); 63.8 (t); 34.9 (t); 33.9 (t); 32.2 (t); 30.5 (d); 28.4 (t); 28.2 (t); 26.9 (t); 26.2 (t); 24.8 (t); 24.8 (t); 24.5 (t); 23.3 (t); 20.8 (q).
MS 240 (1); 138 (12); 125 (15); 110 (11); 97 (21); 83 (35); 69 (57); 55 (100); 41 (84); 27 (39).

25 Odour: musk, after ambrette musk and ambrettolide, powdery, flowery, nitromusk, amber-like, fruity.

Example 18

30 The procedure was effected analogously to Example 3.

95 g (0.2 mol) of (6-carboxyhexyl)triphenylphosphonium bromide in 600 ml of tetrahydrofuran were added to 48 g (0.42 mol) of potassium *t*-butylate in 200 ml of tetrahydrofuran. Thereafter, 29 g (0.18 mol) of 8-hydroxy-6-methyl-2-octanone were

added. After working up and chromatography there were obtained 26 g (48%) of 14-hydroxy-8,12-dimethyltetradec-7-enoic acid, *Z/E* = 58/42.

IR (film) 2930; 2857; 1710; 1461; 1202; 1062.

5

$^1\text{H-NMR}$ (CDCl_3 ; 200 MHz) 5.1 (1H) t $J = 7.5$; 3.7 (2H) m; 2.33 (2H) t $J = 7$ Hz; 0.9 (3H) d $J = 6.3$.

10

MS 270 (2); 252 (7); 137 (15); 123 (77); 109 (26); 95 (62); 81 (100); 69 (55); 55 (88); 41 (55); 29 (19).

Example 19

24.5 g (0.09 mol) of 14-hydroxy-8,12-dimethyltetradec-7-enoic acid were dissolved
 15 in 50 ml of methanol and treated with phenolphthalein. 6 g of 85 percent potassium hydroxide were dissolved in 50 ml of methanol and titrated until a colour change took place. Subsequently, the methanol was distilled off and 80 ml of glycerol were added. 30 ml thereof were distilled off. Thereafter, 20 g (0.18 mol) of chloropropane-1,2-diol were added at 130°C and the mixture was stirred at 130°C for 1 hour. The excess
 20 chloropropane-1,2-diol was distilled off and treated at 70°C with 4 ml of 5.4M methanolic sodium methylate solution. Heating to reflux temperature was carried out for 48 hours with the special headpiece (see Figure). The product-glycerol mixture was poured into 1 litre of water and extracted three times with hexane. The organic phase was washed with saturated potassium bicarbonate solution, dried, concentrated and distilled in a bulb-tube
 25 in a high vacuum. There were obtained 19 g (83%) of 9,13-dimethyloxacyclopent-8-en-2-one, *Z/E* = 58/42.

IR (film) 2928; 2858; 1734; 1457; 1378; 1249; 1152; 1068.

30 $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.1 (1H) m; 4.3-3.92 (2H) m; 2.31 (2H) t $J = 6.5$ Hz; 0.9 (3H) t $J = 6$ Hz.

¹³C-NMR (CDCl₃) 174.1 (s); 174.0 (s); 134.9 (s); 134.2 (s); 125.7 (d); 125.6 (d); 62.5 (t); 62.1 (t); 38.5 (t); 37.0 (t); 35.9 (t); 34.38 (t); 34.35 (t); 34.2 (t); 33.6 (t); 30.1 (t); 29.8 (d); 29.4 (d); 28.8 (t); 28.5 (t); 27.9 (t); 27.3 (t); 27.2 (t); 26.9 (t); 25.2 (t); 24.8 (t); 24.5 (t); 23.1 (t); 22.9 (q); 19.5 (q); 18.6 (q); 15.2 (q).

5

MS 252 (11); 245 (45); 137 (15); 123 (93); 108 (29); 95 (60); 81 (100); 67 (53); 55 (79); 41 (59); 29 (23).

Odour: musk-like, fruity, powdery, lactone-like, earthy, good adhesion.

10

Example 20

9 g (0.035 mol) of 9,13-dimethyloxacyclopent-8-en-2-one were dissolved in 100 ml of ethyl acetate, 1 g of 5% palladium on active charcoal was added and the mixture was hydrogenated under normal pressure. Then, it was filtered over Celite, concentrated and distilled in a bulb-tube. There were obtained 9 g (99%) of 9, 13-dimethyloxacyclopentan-2-one.

15

IR (film) 2928; 2859; 1736; 1459; 1378; 1245; 1156; 1116; 1056.

20

¹H-NMR (CDCl₃) 4.4-3.92 (2H) m; 2.5-2.2 (2H) m.

25

¹³C-NMR 174.1 (s); 174.0 (s); 62.19 (t); 62.15 (t); 36.5 (t); 35.9 (t); 35.27 (t); 35.26 (t); 34.9 (t); 33.9 (t); 33.8 (t); 33.4 (t); 33.2 (t); 30.6 (d); 29.4 (d); 27.8 (t); 27.4 (d); 27.32 (d); 27.31 (t); 26.7 (t); 26.5 (t); 25.0 (t); 24.7 (t); 24.5 (t); 22.7 (t); 22.2 (t); 20.5 (q); 20.3 (q); 19.6 (q); 19.1 (q).

MS 245 (45); 170 (30); 152 (35); 140 (55); 125 (47); 111 (33); 97 (62); 83 (66); 69 (87); 55 (100); 41 (85); 29 (43).

30

Odour: musk-like, fruity, powdery, flowery, lactonic, earthy, fatty.

Example 21

The procedure was effected analogously to Example 3.

5 60 g (0.13 mol) of (5-carboxypentyl)triphenylphosphonium bromide were suspended in 250 ml of tetrahydrofuran. 30 g (0.26 mol) of potassium t-butyrate in 20 ml of tetrahydrofuran were then added. Subsequently, 26 g (0.11 mol) of 10-bromodecanal were added. After usual working up there were obtained 28 g (65%) of crude 6Z-16-bromohexadec-6-enoic acid, $Z/E = 93/7$.

10

IR (film) 2927; 2854; 1709; 1438; 1162; 1121; 723.

$^1\text{H-NMR}$ (CDCl_3 200 MHz) 5.36 (2H) m; 3.4 (2H) t $J = 6.3$ Hz; 2.4 t $J = 7.5$ Hz.

15 MS 252 (15); 183 (9); 152 (14); 137 (11); 123 (15); 110 (17); 96 (39); 81 (51); 69 (66); 55 (100); 41 (70).

Example 22

20 The procedure was effected analogously to Example 8.

25g of potassium carbonate were suspended in 300 ml of N-methyl pyrrolidone. 30 g (0.09 mol) of crude 6Z-16-bromohexadec-6-enoic acid in 200 ml of N-methyl-pyrrolidone were added dropwise while stirring at 110-115°C within 10 hours. After usual
25 working up there were obtained 18 g of crude product and after chromatography there were obtained 12 g (53%) of Z-oxacycloheptadec-7-en-2-one, $Z/E = 93/7$.

IR: (film) 3002; 2928; 2856; 1735; 1461; 1233; 1147.

30 $^1\text{H-NMR}$ (CDCl_3 200 MHz) 5.32 (2H) m; 4.12 (2H) t $J = 5.5$ Hz; 2.31 (2H) t $J = 7.5$ Hz.

$^{13}\text{C-NMR}$ (CDCl_3) 173.4 (s); 130.3 (d); 129.4 (d); 64.4 (t); 34.8 (t); 29.0 (t); 28.5 (t); 28.2 (t); 27.9 (t); 27.6 (t); 27.3 (t); 27.2 (t); 26.8 (t); 26.0 (t); 25.8 (t); 24.7 (t).

MS 252 (2); 109 (11); 95 (29); 81 (53); 67 (69); 55 (74); 41 (100); 27(53).

Odour: ambrette seeds, fruity, musk-like, fatty, flowery.

5

Example 23

The procedure was effected analogously to Example 3.

10 130 g (0.24 mol) of (11-carboxyundecyl)triphenylphosphonium bromide were placed in 800 ml of tetrahydrofuran. 58 g (0.51 mol) of potassium t-butyrate in 200 ml of tetrahydrofuran were added and then 28 g (0.26 mol) of 4-chlorobutanyl were added. After usual working up there were obtained 60 g (86%) of crude 12Z-16-chlorohexadec-12-enoic acid, *Z/E* = 97/3.

15

IR (film) 3005; 2926; 2854; 1709; 1438; 1285; 1167; 723; 694.

¹H-NMR (CDCl₃ 200 MHz) 5.5 - 5.2 (2H) m; 3.51 (2H) t *J* = 6.5; 2.32 (2H) t *J* = 7.5 Hz.

20 MS 252 (9); 123 (11); 109 (19); 95 (45); 81 (92); 68 (100); 55 (100); 41 (82); 29 (19).

Example 24

The procedure was effected analogously to Example 8.

25

45 g of potassium carbonate were placed in 700 ml of N-methylpyrrolidone. A solution of 57.6 g (0.2 mol) of 16-chlorohexadec-12-enoic acid in 300 ml of N-methylpyrrolidone was added dropwise at 100-110°C within 5 hours. After working up and chromatography there were obtained 28 g (55%) of 13Z-oxacyclohept-13-en-2-one, *Z/E* = 97/3.

30

IR (film) 3004; 2928; 2856; 1737; 1459; 1343; 1248; 1169.

¹H-NMR 5.45-5.27 (2H) m; 4.12 (2H) t; 2.34 (3H) t.

^{13}C -NMR 173.7(s); 130.9 (d); 128.4(d); 63.6 (t); 34.1 (t); 28.8 (t); 27.8 (t); 27.5 (t); 27.5 (t); 27.2 (t); 27.1 (t); 26.8 (t); 26.7 (t); 26.1 (t); 24.6 (t); 23.8 (t).

5 MS: 252 (1); 109 (9); 95 (27); 81 (67); 67 (100); 55 (70); 41 (88); 27 (23).

Odour: musk-like, after musk ketone, powdery, less fruity than ambrettolide, ambrette-like, lactonic, fatty, flowery.

10

Example 25

The procedure was effected analogously to Example 3.

15 164.6 g (0.37 mol) of (4-carboxybutyl)triphenylphosphonium bromide were suspended in 700 ml of tetrahydrofuran. 101 g (0.9 mol) of potassium t-butyrate in 150 ml of tetrahydrofuran were added and then 68 g (0.36 mol) of 11-hydroxy-2-undecanone in 50 ml of tetrahydrofuran were added. After usual working up there were obtained 98 g of crude 5Z-6-methylpentadec-5-enoic acid.

20

Example 26

25 98 g of crude 6-methylpentadec-5-enoic acid acid (from the proceeding Example) were dissolved in 305 ml of methanol, treated with 2 ml of sulphuric acid and heated to reflux temperature 2 hours. Then, the mixture was poured into water, made basic with saturated potassium bicarbonate solution, extracted twice with t-butyl methyl ether, concentrated and distilled in a high vacuum (0.1 Torr, 162-170°C). There were obtained 75 g (85%) of methyl 6-methylpentadec-5-enoate Z/E = 56/46.

IR (film) 3365; 2928; 2855; 1741; 1437; 1369.

30

^1H -NMR (CDCl_3) 5.1 (1H) t $J = 7.5$ Hz; 3.65 (3H)s; 3.62 (2H) t $J = 6.25$ Hz; 2.3 (2H) t $J = 7.5$ Hz.

MS 284 (2); 201 (2); 173 (6); 151 (8); 137 (23); 124 (26); 109 (31); 95 (77); 82 (91); 67 (79); 55 (100); 41 (76); 27 (26).

Example 27

5

The procedure was effected analogously to Example 6.

87 g (0.3 mol) of methyl 5Z-6-methylpentadec-5-enoate and 19.5 g of 86 percent potassium hydroxide were dissolved in 200 ml of methanol. 66 g of 3-chloropropane-1,2-diol and 200 ml of glycerol as well as 5 ml of 5.4M methanolic sodium methylate solution were added. After usual working up the product were distilled in a high vacuum over a Vigreux column. There were obtained 59 g (78%) of 7-methyloxacyclohexadec-6-en-2-one, Z/E = 56/46.

15 IR (film) 2928; 2856; 1737; 1456; 1309; 1241; 1153.

^1H -NMR (CDCl_3 200 MHz) 5.1 (1H) m; 4.15 (2H) m; 2.32 (2H) m.

^{13}C -NMR 173.7(s); 173.5 (s); 136.0 (s); 135.5 (s); 124.4 (d); 124.2 (d); 64.8 (t); 64.0 (t); 38.9 (t); 34.3 (t); 32.5 (t); 30.4 (t); 28.2 (t); 27.67 (t); 27.66 (t); 27.34 (t); 27.31 (t); 27.29 (t); 27.23 (t); 26.84 (t); 26.79 (t); 26.72 (t); 26.69 (t); 26.2 (t); 25.9 (t); 25.8 (t); 25.7 (t); 25.5 (t); 24.3 (t); 22.8 (q); 14.9 (q).

MS 252 (13); 210 (12); 151 (13); 140 (15); 124 (22); 110 (33); 95 (100); 81 (90); 67 (66); 55 (85); 41 (68); 29 (21).

Odour: musk-like, fruity, green.

Example 28

30

28 g (0.11 mol) of 7-methyloxacyclohexadec-6-en-2-one were dissolved in 200 ml of ethyl acetate and hydrogenated in the presence of 2 g of 5% palladium-on-carbon under 150 mbar of hydrogen. The mixture was filtered over Celite, concentrated and distilled in a bulb-tube. There were obtained 26 g (92%) of 7-methyloxacyclohexadecan-2-one.

IR (film) 2929; 2858; 2858; 1737; 1461; 1377; 1237; 1167; 1111.

^1H -NMR (CDCl_3 200 MHz) 4.3-4.1 (2H) m; 2.33 (2H) m; 0.86 (3H) d $J = 6.5$ Hz.

5

^{13}C -NMR (CDCl_3) 173.8 (s); 63.7 (t); 35.39 (t); 34.49 (t); 33.31 (t); 30.49 (d); 28.23 (t); 27.07 (t); 26.77 (t); 26.16 (t); 26.06 (t); 26.01 (t); 25.38 (t); 25.02 (t); 24.07 (t); 20.57 (q).

MS 254 (0.4); 210 (4); 137 (6); 124 (41); 111 (32); 97 (42); 83 (67); 69 (72); 55 (100); 41 (63); 29 (17).

10

Odour: musk-like, flowery, fruity, lactonic, powdery.

Example 29

15

The procedure was effected analogously to Example 3.

100 g (0.2 mol) of (8-carboxyoctyl)triphenylphosphium bromide were placed in 500 ml of tetrahydrofuran and treated with 47 g (0.42 mol) of potassium *t*-butylate in 300 ml of tetrahydrofuran and then with 33 g (0.17 mol) of 7-bromoheptanal. After usual working up and chromatography there were obtained 49 g (74%) of 9*Z*-16-bromohexadec-9-enoic acid, *Z/E* = 98/2.

20

IR (film) 3004; 2928; 2854; 1709; 1463; 1285; 937.

25

^1H -NMR (CDCl_3 , 200 MHz) 5.35 (2H) m; 3.4 (2H) t $J = 6.5$ Hz; 2.35 (2H) t $J = 7.5$ Hz.

MS 232 (0.39); 316 (3); 272 (7.8); 252 (49); 234 (6); 182 (5); 164 (10); 150 (17); 137 (24); 123 (29); 110 (33); 96 (57); 83 (68); 69 (96); 55 (100); 41 (96); 29 (35).

30

Example 30

The procedure was effected analogously to Example 8.

5 40 g (0.29 mol) of potassium carbonate were suspended in finely pulverized form in 600 mg of N-methylpyrrolidone. 49 g (0.147 mol) of Z-16-bromohexadec-9-enoic acid in 300 ml of N-methylpyrrolidone were added dropwise within 6 hours. A standard working up was effected; bulb-tube distillation and recrystallization gave 19 g (51%) of 10Z-oxacycloheptadec-10-en-2-one, Z/E = 98/2.

10

IR (film) 3002; 2929; 2856; 1736; 1460; 1343; 1242; 1177; 1059; 722.

$^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.36 (2H) m; 4.15 (2H) t $J = 5.5$ Hz; 2.34 (2H) t $J = 6.5$ Hz.

15 $^{13}\text{C-NMR}$ (CDCl_3) 173.61 (s); 130.12 (d); 129.88 (d); 64.11 (t); 34.51 (t); 29.05 (t); 28.46 (t); 28.32 (t); 27.98 (t); 27.68 (t); 27.57 (t); 26.31 (t); 25.77 (t); 25.64 (t); 25.00 (t).

MS 284 (2); 201 (2); 173 (6); 151 (8); 137 (23); 124 (26); 109 (31); 95 (77); 82 (91); 67 (79); 55 (100); 41 (76); 27 (26).

20

Odour: musk-like, after ambrette musk and ambrettolide, powdery, strong, fruity, green, earthy, mossy.

Example 31

25

The procedure was effected analogously to Example 3.

94 g (0.2 mol) of (6-carboxyhexyl)triphenylphosphonium bromide were suspended in 500 ml of tetrahydrofuran. 47 g (0.42 mol) of potassium t-butyrate in 200 ml
30 of tetrahydrofuran were added, followed by 50 g (0.22 mol) of 9-bromononanal. After working up and chromatography there were obtained 52 g (78%) of 7Z-16-bromohexadec-7-enoic acid, Z/E = 90/10.

IR (film) 3004; 2927; 2854; 1709; 1462; 1277; 1239; 939.

H-NMR (CDCl₃, 200 MHz) 5.36 (2H) m; 3.4 (2H) t $J = 7$ Hz; 2.35 (2H) t $J = 7.5$ Hz.

MS 252 (13); 150 (7); 123 (13); 110 (18); 96 (36); 83 (43); 69 (60); 55 (100); 41 (67); 29
5 (20).

Example 32

The procedure was effected analogously to Example 8.

10 41 g of potassium carbonate were suspended in 600 ml of N-methylpyrrolidone. A
solution of 51 g (0.15 mol) of 7Z-16-bromohexadec-7-enoic acid in 400 ml of N-
methylpyrrolidone was added dropwise at 90°C within 8 hours. After usual working up
and chromatography there were obtained 30 g (77%) of 8Z-oxacycloheptadec-8-en-2-one,
Z/E = 90/10.

15

IR (film) 3000; 2927; 2855; 1736; 1460; 1385; 1257; 1184; 1069.

¹H-NMR (CDCl₃, 200 MHz) 5.3 (2H) m; 4.13 (2H) t $J = 6$ Hz; 2.32 (2H) t $J = 7$ Hz.

20 ¹³C-NMR (CDCl₃) 173.71 (s); 130.04 (d); 129.88 (d); 63.51 (t); 34.37 (t); 29.29 (t); 28.66
(t); 28.58 (t); 28.38 (t); 28.32 (t); 28.22 (t); 27.51 (t); 26.81 (t); 26.66 (t); 25.19 (t); 25.13 (t).

MS 252 (4); 149 (8); 137 (8.6); 123 (13); 109 (23); 96 (62); 81 (100); 67 (97); 54 (64).

25 Odour: musk-like, dry, after ambrette seed oil, powdery, flowery, fruity, lactone-like,
animalic.

Example 33

30 The procedure was effected analogously to Example 3.

325 g (0.7 mol) of (5-carboxypentyl)triphenylphosphonium bromide were
dissolved in 1500 ml of tetrahydrofuran. After the addition of 180 g (1.6 mol) of
potassium t-butyrate in 700 ml of tetrahydrofuran the mixture was treated with 175 g

(0.71 mol) of 9-hydroxy-2-decanone (70% purity). After usual working up there were obtained 186 g of crude 14-hydroxy-7-methyl-pentadec-6-enoic acid. This product was dissolved in 400 ml of methanol and, after the addition of 5 ml of concentrated sulphuric acid, heated to reflux for 2 hours. After working up, bulb-tube distillation and
 5 chromatography there were obtained 102 g (50%) of methyl 14-hydroxy-7-methyl-pentadec-6-enoate.

IR (film) 3419; 2929; 2856; 1741; 1437; 1374; 1201; 1172.

10 $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.1 (1H) t $J = 7.5$ Hz; 3.8 (2H) m; 3.68 (3H) s; 2.3 (2H) t $J = 7.5$ Hz; 1.19 (3H) d $J = 6.3$ Hz.

MS 284 (3); 266 (4); 168 (2); 149 (10); 137 (28); 123 (14); 108 (35); 95 (74); 81 (100); 67 (57); 55 (78); 41 (41); 29 (11).

15

Example 34

The procedure was effected analogously to Example 19.

20 105 g (0.37 mol) of methyl 14-hydroxy-7-methylpentadec-6-enoate and 26 g (0.388 mol) of 86 percent potassium hydroxide were dissolved in 200 ml of methanol and treated with 90 g (0.8 mol) of 3-chloropropane-1,2-diol in 300 ml of glycerol as well as 15 ml of 30 percent methanolic potassium methylate solution. After the addition of the methylate solution the distillation headpiece was replaced by a special headpiece (see
 25 Figure 1) and heated under reflux at 180°C under 2-4 mbar for 4 hours. After extraction there were obtained 69.5 g (74%) of 8,15-dimethyloxacyclopent-7-en-2-one, $Z/E = 6/4$.

IR (film) 2920; 2857; 1731; 1459; 1376; 1237; 1130; 1056.

30 $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) 5.11 (1H) m; 4.94 (1H) m; 1.56 (3H) s; 1.21 (3H) d $J = 6.25$ Hz.

$^{13}\text{C-NMR}$ (CDCl_3) 173.44 (s); 173.24 (s); 135.98 (s); 134.85 (s); 125.29 (d); 124.41 (d); 70.27 (d); 70.16 (d); 38.32 (t); 35.73 (t); 35.58 (t); 34.71 (t); 34.26 (t); 29.74 (t); 29.55 (t);

28.89 (t); 27.80 (t); 27.69 (t); 27.46 (t); 27.34 (t); 26.88 (t); 25.95 (t); 25.74 (t); 25.11 (t);
24.98 (t); 24.44 (t); 23.98 (t) 23.26 (q); 20.53 (q); 19.61 (q); 15.40 (q).

MS 252 (4); 154 (15); 137 (15); 121 (7); 107 (30); 95 (88); 81 (100); 67 (73); 55 (93); 41
5 (80); 29 (26).

Odour: musk-like, powdery, after nitromusk, animalic, fatty.

Example 35

10

The procedure was effected analogously to Example 5.

422 g (0.8 mol) of 10-carboxydecyl-triphenylphosphonium bromide and 204 g
(1.81 mol) of potassium t-butyrate were reacted in 1.8 litres of THF and treated with 200 g
15 (1.12 mol) of 70% 3-methyl-5-oxo-pentanol acetate from Example 2. Analogous working
up as in Example 5 gave 297 g of crude product. This product was esterified analogously to
Example 5 and, after working up and distillation, gave 168.9 g (70.9%) of 16-hydroxy-14-
methyl-hexadec-11-en-oate (Z/E = 95/5).

20 IR (liquid) 3419; 3005; 2926; 2854; 1741; 1458; 1436; 1375; 1265; 1197 ; 1172; 1058.

H-NMR (CDCl₃) 5.4 (2H) m; 3.7 (3H) s; 2.3 (2H) t ;1.9 (2H) d.

MS 298 (0.39); 185 (7);109 (22); 95 (33); 81 (100); 74 (18); 68 (31); 55 (57); 41 (30); 29(9).

25

Example 36

The procedure was effected analogously to Example 6.

30 42 g (0.14 mmol) of methyl 16-hydroxy-14-methyl-hexadec-11-enoate were reacted
with 9 g of potassium hydroxide in 100 ml of methanol, treated with 150 ml of glycerol and
the methanol and 50 ml of glycerol were distilled off. Then, the mixture was reacted with
30 g of 3-chloropropane-1,2-diol at 150°C for 1 hour and evaporated to 70 ml under
3 mm vacuum. After the addition of 3 ml of 30% potassium methylate solution in
35 methanol the mixture was refluxed for 58 hours at 170-190°C (3-4 mbar) as in Example 6

using the special headpiece. After working up as described in Example 6 there were obtained 35.8 of crude product. After distillation there were obtained 26.3 g (70%) of 15-methyl-oxacycloheptadec-12-en-2-one, Z/E = 95/5.

5 IR(film) 3006; 2927; 2855; 1736; 1460; 1347; 1250; 1174; 1150; 1118; 1052.

H-NMR (CDCl₃) 5.4 (2H) m; 4.18 (1H) m; 4.10 (1H) m; 2.3 (2H) t; 0.96 (3H) d.

13C-NMR (CDCl₃) 173.7 (s); 131 (d); 127.7 (d); 62.4(t); 35.1(t); 34.6(t); 34.2 (t); 30.6 (d);
10 28.4(t); 28.1 (t); 27.9 (t); 27.4 (t); 27.21 (t); 27.15 (t); 26.0 (t); 24.4 (t); 19.2(q).

MS 266 (4); 251 (2); 238 (5); 224 (10); 123 (7); 109 (19); 95 (30); 81 (100); 68 (47); 55 (53); 41(43); 29 (15).

15 Odour: musk, woody, animalic, sweet, earth, fruity, homogeneous.

Example 37

The procedure was effected analogously to Example 3.

20

68.1 g (149 mmol) of (4-carboxy-3-methyl-butyl)-triphenylphosphonium bromide were placed in 150 ml of THF and treated with 33.4 g (298 mmol) of potassium t-butyrate in 50 ml of THF. 35 g (149 mmol) of 10-bromodecanal were added to this mixture. After usual working up there were obtained 111.8 g of crude product and, after chromatography,
25 there were obtained 29 g of 3-methyl-5Z-15-bromopentadec-5-enoic acid.

IR (film) 3005; 2926; 2853; 1707; 1309.

H-NMR (CDCl₃) 1 (3H) d; 3.4 (2H) m; 5.4 (2H) m.

30

MS 272 (31); 252 (14); 230 (4); 192 (6); 151 (10); 123 (12); 110 (18); 95 (43); 81 (67); 68 (100); 55 (70); 41 (50); 29 (15).

Example 38

The procedure was effected analogously to Example 8.

5 17.4 g of potassium carbonate were placed in 320 ml of N-methylpyrrolidone and treated dropwise with a solution of 28 g (84 mmol) of 3-methyl-5Z-15-bromopentadec-5-enoic acid in 240 ml of N-methylpyrrolidone. After usual working up there were obtained 21.2 g of crude product. After chromatography and bulb-tube distillation there were isolated 15.4 g of Z-4-methyloxacyclohexadec-6-en-2-one.

10

IR (film) 3006; 2927; 2855; 1735; 1458; 1379; 1305; 1252; 1172; 1147; 1079.

H-NMR (CDCl₃) 1(3H) d; 4.01 (1H) m; 4.3 (1H) m; 5.4 (2H) m.

15 MS 252 (4); 210 (4); 192 (5); 149 (4); 135 (8); 121 (12); 110 (25); 95 (43); 81 (78); 67 (78); 55 (78); 41 (100); 27 (33).

Odour: musk, fruity, woody, earthy, mossy.

20

Example 39

0.5 g of 10 percent palladium-on-charcoal was added to 5.1 g (20 mmol) of Z-4-methyloxacyclohexadec-6-en-2-one in 20 ml of ethanol and the mixture was subsequently hydrogenated under normal pressure for 2 hours. Then, the mixture was suction filtered
25 over Celite and the solution was concentrated, chromatographed and distilled in a bulb-tube. There were obtained 4 g (78%) of 4-methyloxacyclohexadecan-2-one.

IR (film) 2928; 2857; 1735; 1460; 1380; 1252; 1174; 1113.

30 H-NMR (CDCl₃) 0.95 (3H) d; 2.22 (2H) d; 4.03 (1H) m; 4.21 (1H) m.

13 CNMR (CDCl₃) 173.3 (s); 63.8 (t); 42 (t); 35 (t); 30 (d); 28.2 (t); 26.8 (t); 26.6 (t); 26.3 (t); 26.2 (t); 25.6 (t); 25.5 (t); 25.0 (t); 24.8 (t); 20.1 (q).

MS 254 (0.7); 194 (10); 166 (4); 152 (4); 138 (6); 124 (9); 110 (15); 96 (32); 87 (35); 82 (44); 69 (66); 55 (100); 41 (86); 29 (30).

Odour: musk, fresh, animalic, powdery, woody after pine needles.

5

Example 40: Odorant compositions

a) Accord: Fresh, flowery, rose, violets, suitable e.g. for feminine eau de Cologne.

10		Parts by weight
	Compound of Example 4	10
	BENZYL ACETATE EXTRA	40
	3-CIS-HEXENYL ACETATE	1
15	PHENYLETHYL ALCOHOL	80
	α -HEXYLCINNAMALDEHYDE	100
	BERGAMOT RECONSTITUTION	150
	BERRYFLOR	30
	CITRONELLOL EXTRA	40
20	CYCLAL C	2
	β -DAMASCONE 10 % DPG	2
	DIPROPYLENE GLYCOL	90
	EBANOL	5
	ETHYLLINALOOL	100
25	FLORHYDRAL	6
	CITRONELLYL FORMATE	7
	GARDENOL	4
	GIVESCONE	8
	HEDIONE	50
30	HYDROXYCITRONELLAL	30
	INDOLENE 10 % DPG	5
	ISORALDEINE 95	80
	CIS-JASMONE	2
	KEPHALIS	50
35	LILIAL	50

	ROSE OXIDE	1
	HEXYL SALICYLATE	5
	TANGERINE OIL	2
	TERPINEOL PURE	30
5	TROPIONAL	20
		=====
		1000

In this composition the compound of Example 4 confers volume and musk odour,
 10 rounds off the flowery notes and gives the accord more cosmetic character.

b) Accord: Flowery, green, spicy, suitable e.g. for shampoos, soaps and toilet articles.

		Parts by weight
15	Compound of Example 4	15
	BENZYL ACETATE EXTRA	60
	DIMETHYLBENZYL CARBINOL ACETATE	30
	GERANYL ACETATE	40
20	PHENYLETHYL ALCOHOL	120
	α -HEXYLCINNAMALDEHYDE	120
	10-UNDECEN-1-AL	5
	PHENYLACETALDEHYDE 85 % IN PHENYLETHYL ALCOHOL	2
	BERGAMOT GIVCO 104	140
25	CEDARWOOD OIL VIRGIN.	10
	CYCLOHEXAL	40
	GERANIOL PURE	50
	CLOVE BUD ESS.	5
	HEDIONE	40
30	HELIOTROPIN	10
	ISOEUGENOL	2
	ISORALDEINE 95	50
	LILIAL	50
	LINALOOL SYNT.	60
35	MANDARIN OIL COMMON	20

	PECHE PURE	1
	BENZYL SALICYLATE	80
	3-CIS-HEXENYL SALICYLATE	10
	TROPIONAL	10
5	VERTOFIX COEUR	30
		=====
		1000

10 The compound of Example 4 confers volume to the composition by its musk and lactone-like character, rounds off the green notes and combines the spicy notes with the flowery notes. Moreover, the compound of Example 4 enhances the substantivity of the composition.

c) Fresh, flowery bouquet, e.g. for cosmetics and for soaps.

15

Parts by weight

	Compound of Example 8	20
	BENZYL ACETATE EXTRA	30
20	L-BORNYL ACETATE PURE	6
	LINALYL ACETATE SYNTH.	80
	p-TERT. BUTYLCYCLOHEXYL ACETATE 100	
	VERDYL ACETATE	15
	α -HEXYLCINNAMALDEHYDE	130
25	ALLYL AMYL GLYCOLATE	3
	CEDARWOOD OIL VIRGIN.	10
	DAMASCENONE 10 % DPG	5
	DIHYDROMYRCENOL	80
	DIMETHYLOCTENONE	7
30	DIPROPYLENE GLYCOL	30
	GIVESCONE	10
	HEDIONE	40
	INDOLENE	4
	ISORALDEINE 95	100
35	LEMAROME N	5

	LINALOOL SYNT.	200
	NECTARYL	10
	OKOUMAL	10
	TANGERINE OIL	1
5	VERTOFIX COEUR	100
		=====
		1000

10 This fresh, flowery bouquet for cosmetics and soaps becomes richer by the addition of the compound of Example 8, and has the desired musk note and volume, and confers a cosmetic effect to the composition.

d) Flowery-oriental, feminine accord, e.g. for cosmetics, e.g. Colognes.

15		Parts by weight
	Compound of Example 28	20
	BENZYL ACETATE EXTRA	30
	CITRONELLYL ACETATE	6
20	LINALYL ACETATE SYNTH.	50
	PHENYLETHYL ALCOHOL	50
	α -AMYL CINNAMALDEHYDE	150
	10-UNDECEN-1-AL 10 % DPG	3
	ALLYL AMYL GLYCOLATE	4
25	BERGAMOT GIVCO 104	80
	CARBITOL	30
	CARDAMONE ESS. CEYLON	2
	CASSIONE (FIRMENICH) 10 % DPG	5
	COUMARIN PURE CRYST.	5
30	CYCLAL C 10 % DPG	5
	DIPROPYLENE GLYCOL	100
	EBANOL	10
	ETHYL LINALOOL	80
	GERANIOL EXTRA	20
35	GERANIOL PURE	8

	HEDIONE	100
	INDOLE 10 % DPG	3
	ISO E SUPER	50
	CIS-JASMONE 10 % DPG	6
5	MANDARIN OIL ESS-RECONSTITUTION	50
	PATCHOULI OIL IRON-FREE	20
	BENZYL SALICYLATE	60
	3-CIS-HEXENYL SALICYLATE	30
	STEMON	3
10	VANILLIN	20
		=====
		1000

- 15 This flowery-oriental, feminine accord becomes richer by the addition of the compound of Example 28. With its mild, musk-like character the compound gives to the composition more volume and velvety character which comes into play especially in cosmetics and Cologne.

- 20 e) Flowery accord, e.g. for cosmetics and shampoos.

		Parts by weight
	Compound of Example 8 or 24	30
	BENZYL ACETATE EXTRA	100
25	DIMETHYLBENZYL CARBINOL ACETATE	30
	GERANYL ACETATE	30
	3-CIS-HEXENYL ACETATE	2
	LINALYL ACETATE	50
	p -TERT BUTYLCYCLOHEXYL ACETATE	80
30	VERDYL ACETATE	50
	PHENYLETHYL ALCOHOL	100
	UNDEC-10-EN-1-AL	3
	2-METHYL-UNDECANAL	3
	BERRYFLOR	50
35	CITRONELLOL EXTRA	60

	CYCLAL C	3
	CYCLOHEXYLALLYL PROPIONATE	15
	γ -DECALACTONE	2
	DIHYDROMYRCENOL	40
5	DIPROPYLENE GLYCOL	20
	EUGENOL PURE	20
	FLORHYDRAL (3-(3-ISOPROPYLPHENYL)BUTANOL)	10
	FRUCTONE (2-METHYL-1,3-DIOXOLAN-2-ACETIC ACID ETHYL ESTER)	5
	GARDENOL	20
10	GERANONITRILE	5
	HELIOTROPIN CRYST.	20
	β -IONONE	30
	JASMONYL	50
	LILIAL	80
15	LINALOOL	50
	ROSE OXIDE	2
	TERPINEOL	40
		=====
		1000

20

This flowery bouquet becomes richer by the addition of the compounds of Example 24 or Example 8. The composition takes on a soft musk effect and has more volume.

f) Flowery lime blossom accord, e.g. for detergents.

25

		Parts by weight
	Compound of Example 24 or 28	10
	CITRONELLYL ACETATE	50
30	VERDYL ACETATE	100
	PHENYLETHYL ALCOHOL	60
	HEXYLCINNAMALDEHYDE	150
	4-METHOXY BENZALDEHYDE	25
	METHYL BENZOATE	5
35	COUMARIN	15

	DIHYDROMYRCENOL	60
	DIPROPYLENE GLYCOL	30
	3-CIS-HEXENOL	10
	ISO E SUPER	90
5	ISORALDEINE 70	140
	LILIAL	130
	NECTARYL	20
	OKOUMAL	15
	UNDECAVERTOL (4-METHYL-DEC-3-EN-5-OL)	40
10	VERDANTOL (LILIAL METHYL ANTHRANILATE)	50
		=====
		1000

- 15 The compound of Example 28 or Example 24 gives to this typical flowery lime blossom accord soft, musk-like volume and more substantivity; in particular, the soft musk-like note comes into play on damp and dry washing.

- g) Flowery, fruity accord, e.g. for cosmetics, e.g. Colognes.
- 20

		Parts by weight
	Compound of Example 6	10
	BENZYL ACETATE EXTRA	80
25	VETIVENYL ACETATE	40
	PHENYLETHYL ALCOHOL	150
	α -HEXYLCINNAMALDEHYDE	120
	DECANAL	2
	10-UNDECEN-1-AL	1
30	METHYL ANTHRANILATE EXTRA	1
	BERGAMOT GIVCO 104	120
	DIPROPYLENE GLYCOL	30
	ETHYL LINALOOL	100
	EUGENOL PURE	20
35	GARDENOL	5

	INDOLENE	3
	ISOEUGENOL	3
	ISORALDEINE 70	60
	METHYL CEDRYL KETONE	80
5	NECTARYL	5
	NONADYL	30
	BENZYL SALICYLATE	100
	3-CIS-HEXENYL SALICYLATE	20
	SANDALORE	20
10		=====
		1000

In this flowery, fruity, feminine accord with woody undertones the compound of Example 6 with its musk-like character accompanies the flowery notes and confers more strength to the fruity elements. This accord is especially suitable for Colognes and cosmetics.

h) Fresh, spicy, woody accord, e.g. for cosmetics, e.g. Colognes for men

20		Parts by weight
	Compound of Example 6	10
	BENZYL ACETATE EXTRA	30
	GERANYL ACETATE PURE	50
25	ALLYL AMYL GLYCOLATE	3
	METHYL ANTHRANILATE EXTRA	1
	BASIL ESSENCE	10
	BERGAMOT RGV 2	200
	CARBITOL	60
30	α -ISOMETHYLIONONE (α -KETONE)	50
	LEMON OIL ARGENTINIAN	100
	COUMARIN	20
	DIHYDROMYRCENOL	100
	TARRAGON OIL	5
35	EVERNYL	3

	CLOVE BUD OIL	15
	HEDIONE	50
	ISO E SUPER	50
	ISOEUGENOL	3
5	NUTMEG ESSENCE	20
	PATCHOULI OIL	30
	PETITGRAIN OIL PARAGUAY	7
	SANDALORE	20
	VANILLIN	2
10		=====
		1000

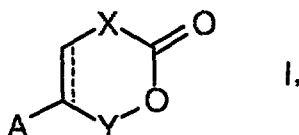
The compound of Example 6 confers to this fruity, spicy, woody accord more volume and a velvety, musk-like impression and rounds off the composition.



Claims

1. An odorant composition, which contains a compound or a mixture of the formula

5



wherein the dotted line signifies an optional additional bond, X and Y stand for methylene or C₂-12-polymethylene, optionally substituted with an additional methyl group, and A signifies hydrogen or methyl in the case of the unsaturated compound and methyl in the case of the saturated compounds, with the proviso that the unsaturated compounds

are present to more than 80% in the cis form when A signifies hydrogen and are present to more than 50% in the cis form when A signifies methyl,

15

with the exception of Z-oxacyclopentadec-6-en-2-one (15-membered ring), Z-oxacycloheptadec-8-en-2-one (17-membered ring) and Z-oxacycloheptadec-11-en-2-one (17-membered ring).

20

2. An odorant composition according to claim 1, containing a compound corresponding to Examples 1 to 39.

3. An odorant composition according to claim 1, containing oxacycloheptadec-12-en-2-one.

25

4. An odorant composition according to claim 1, containing oxacycloheptadec-9-en-2-one.

5. An odorant composition according to claim 1, containing oxacycloheptadec-7-en-2-one.

30

6. An odorant composition according to claim 1, containing oxacycloheptadec-13-en-2-one.

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7. An odorant composition according to claim 1, containing oxacycloheptadec-10-en-2-one.
- 5 8. An odorant composition according to claim 1, containing oxacycloheptadec-14-en-2-one.
9. An odorant composition according to claim 1, containing 15-methyloxacycloheptadec-12-en-2-one.
- 10 10. An odorant composition according to claim 1, containing 13-methyloxacyclopentadec-10-en-2-one.
11. An odorant composition according to claim 1, containing R-Z-13-methyl-oxacyclopentadec-10-en-2-one.
- 15 12. An odorant composition according to claim 1, containing S-Z-13-methyloxacyclopentadec-10-en-2-one.
13. An odorant composition according to claim 1, containing oxacyclohexadec-5-en-2-one.
14. An odorant composition according to claim 1, containing 10-methyloxacyclopentadec-9-en-2-one.
- 25 15. An odorant composition according to claim 1, containing 10-methyloxacyclopentadecan-2-one.
16. An odorant composition according to claim 1, containing 8-methyl-oxacyclopentadec-7-en-2-one.
- 30 17. An odorant composition according to claim 1, containing 8-methyloxacyclopentadecan-2-one.
18. An odorant composition according to claim 1, containing 9,13-dimethyloxacyclopent-8-en-2-one.
- 35

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19. An odorant composition according to claim 1, containing 7-methyl-oxacyclohexadec-6-en-2-one.

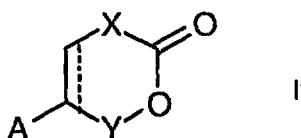
5 20 An odorant composition according to claim 1, containing 4-methyl-oxacyclohexadecan-2-one.

21. An odorant composition according to claim 1, containing 7-methyl-oxacyclohexadecan-2-one.

10

22. An odorant composition according to claim 1, containing 8,15-dimethyl-oxacyclopent-7-en-2-one.

23. Compounds of the formula
15



in which the dotted line signifies an optional additional bond, X and Y stand for methylene or C₂-12-polymethylene optionally substituted with a further methyl group and A signifies
20 hydrogen or methyl in the case of the unsaturated compounds and methyl in the case of the saturated compounds, with the proviso that the unsaturated compounds

are present to more than 80% in the cis form when A signifies hydrogen and are present to more than 50% in the cis form when A signifies methyl,

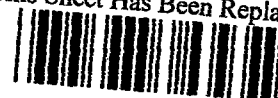
25

with the exception of Z-oxacyclopentadec-3-(or 6- or 13-)en-2-one, Z-oxacyclohexadec-3-(or 6-, 11-, 12- or 13-)en-2-one and Z-oxacycloheptadec-8-(or 10-, 11-, 12-, 13- or 15-)en-2-one.

30 24. The compounds according to claim 23 corresponding to Examples 1 to 39.

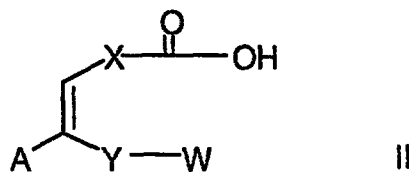
25. 13-Methyl-oxacyclopentadec-10-en-2-one according to claim 23.

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26. R-Z-13-Methyl-oxacyclopentadec-10-en-2-one according to claim 23.
27. S-Z-13-Methyl-oxacyclopentadec-10-en-2-one according to claim 23.
- 5 28. Oxacyclohexadec-5-en-2-one according to claim 23.
29. 10-Methyl-oxacyclopentadec-9-en-2-one according to claim 23.
30. 10-Methyl-oxacyclopentadecan-2-one according to claim 23.
- 10 31. 8-Methyl-oxacyclopentadec-7-en-2-one according to claim 23.
32. 8-Methyl-oxacyclopentadecan-2-one according to claim 23.
- 15 33. 15-Methyl-oxacycloheptadec-12-en-2-one according to claim 23.
34. 9,13-Dimethyl-oxacyclopent-8-en-2-one according to claim 23.
35. 7-Methyl-oxacyclohexadec-6-en-2-one according to claim 23.
- 20 36. 7-Methyl-oxacyclohexadecan-2-one according to claim 23.
37. 4-Methyl-oxacyclohexadecan-2-one according to claim 23.
- 25 38. 8,15-Dimethyl-oxacyclopent-7-en-2-one according to claim 23.
39. A process for the manufacture of the compounds of formula I in accordance with claim 1, which process comprises lactonizing a compound of the formula



wherein A, X and Y have the significance given in claim 1 and W represents OH,

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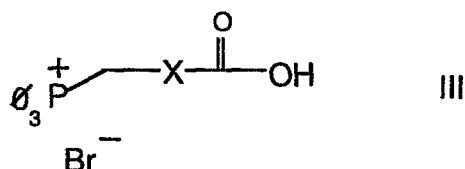




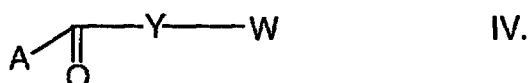
O-alkanoyl or a leaving group, such as mesylate, tosylate, I, Br, Cl etc., in a manner known per se, namely at elevated temperature and under basic conditions, and, if desired, hydrogenating a thus-obtained unsaturated compound of formula I.

5 40. A process according to claim 39, wherein a compound of formula II in which W signifies a leaving group, such as mesylate, tosylate, I, Br, Cl etc., is lactonized using a base, such as e.g. potassium carbonate or sodium carbonate, and with the addition of N-methylpyrrolidone as the solvent.

10 41. A process according to claim 39, wherein a compound of formula II is prepared by subjecting a compound of the formula



15 to a Wittig reaction with a compound of the formula



42. The use of a compound of formula I as defined in claim 1 or of a mixture of
20 compounds of formula I as an odorant.

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