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(54) Benævnelse: **Nye bicycliske dioxaner, deres fremstilling og deres anvendelse som duftforbindelser**

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D. H. BROWN ET AL: "Stereoselectivity in the hydroboration of chiral cyclohexane-derived allylic alcohols" TETRAHEDRON LETTERS, vol. 27, 1986, pages 4367-4370, XP002558531
M. P. SIBI AND S. NAD: "Enantioselective Radical Reactions: Stereoselective Aldol Synthesis from Cyclic Ketones" ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 46, 2007, pages 9231-9234, XP002601740 -& Anonymous: "Stereochemical analysis"[Online] 2007, page 12, XP002604471 Angewandt Chemie - Supporting Information- Retrieved from the Internet: URL:http://www.wiley-vch.de/contents/jc_20 02/2007/z702976_s.pdf> [retrieved on 2010-09-22]

Description

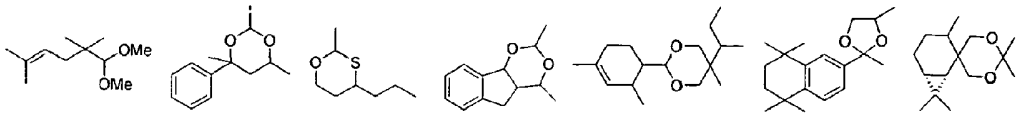
[FIELD OF THE INVENTION]

[0001] The invention relates to the field of fragrances. More particularly, the invention relates to bicyclic dioxanes, their method of preparation, and their use in the fields of perfumery.

[BACKGROUND]

[0002] Acetals form an important class of compounds in the field of aromatic chemistry, especially for use in basic media. The most important acetals are cyclic and are known for their fruity, floral or ambery fragrance (Kraft, P., Bajgrowicz, J. A., Angew. Chem. Int. Ed. 2000, 39, 2980-3010).

[0003] In the fruity notes, examples of commercially available acetals comprise Methyl Pamplemousse® (1), Floropal® (2), and Oxane® (3). These compounds are widely used in the field of perfumery. In the floral notes, rosy notes are quite important. One example of a cyclic dioxane having a floral note is Magnolan®. It is interestingly used to bring freshness, in particular to lily of the valley accords. Examples of cyclic dioxanes having ambery notes include Okoumal (6), Karanal (5), and Spirambrene (7). Okoumal possesses a powerful ambery fragrance which blends very well to woody accords. Karanal and Spirambrene also have a tenacious odour.



1 2 3 4 5 6 7

[0004] US6303798 discloses a dioxin compound and its use in fragrancy

[PROBLEM TO BE SOLVED]

[0005] The need for new compounds is of great importance for the development of the fragrance industry, which recently had to face stricter international regulatory requirements about the use of certain materials, as well as environmental concerns and customer demands for improved performance. Moreover, a phenomenon that is more and more frequently observed in the fields of perfumery are allergies to fragrant com-

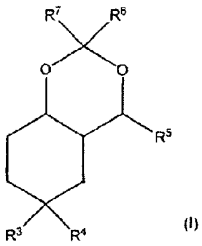
pounds. One way of minimizing the risk of allergies is regularly replacing fragrant compounds in perfumes. There is thus a constant need for new fragrant compounds that may be used to replace existing ones due to their similar fragrance.

[0006] Providing new fragrant compounds as well as means of selectively manufacturing such compounds is therefore an object of the invention.

[0007] The Applicant thus focused on the synthesis of new bicyclic acetals, more precisely bicyclic 1,3-dioxanes. Surprisingly and unexpectedly, the new 1,3-dioxane derivatives did not present the expected ambery notes, but mainly unexpected green notes.

[SUMMARY OF THE INVENTION]

[0008] The invention is directed to the use of compounds of formula:



(I)

as fragrant agents. In this formula:

- R^3 and R^4 are independently a hydrogen atom, a C1-C6 alkyl group or a C2-C6 alkenyl group,
- R^5 is a methyl, ethyl, i-butyl, t-butyl, n-pentyl a C2-C6 alkenyl group or a $(CH_2)_{0-2}$-aryl group,
- R^6 is a C1-C6 alkyl group, a C2-C6 alkenyl group, a $(CH_2)_{0-2}$-aryl group or a C5-C6 cycloalkyl or cycloalkenyl group, and
- R^7 is a hydrogen atom, a C1-C6 alkyl group or a C2-C6 alkenyl group;

or

- R^3, R^4 and R^5 are as above defined, and
- R^6 and R^7 together with the carbon atom to which they are attached form a C5-C6 cycloalkyl or cycloalkenyl group.

[0009] Among the compounds defined by the formula (I) and used according to the invention as fragrant agents, to the inventors' knowledge, some are novel. In this context, the invention is also directed to compounds of formula (I), as defined above, with the proviso that said compound are not:

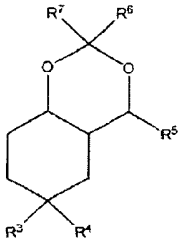
- 2,2-dimethyl-4-ethylhexahydrobenzo[1,3]dioxine
- 2,2-dimethyl-4-n-penthylhexahydrobenzo[1,3]dioxine
- 2,2-dimethyl-4-phenylhexahydrobenzo[1,3]dioxine
- 2,4-dimethy]hexahydrobenzo[1,3]dioxine
- 2,4-diphenylhexahydrobenzo[1,3]dioxine
- 4-ethyl-2-methylhexahydrobenzo[1,3]dioxine
- 4-methyl-2-pheny]hexahydrobenzo[1,3]dioxine
- 2,2,4-trimethylhexahydrobenzo[1,3]dioxine.

[0010] This invention relates to the compounds of formula (I), as described above, as well as to any of their various stereoisomers.

[0011] The invention is also directed to a method of preparation of compounds of formula (I) as defined above.

[DETAILED DESCRIPTION OF THE INVENTION]

[0012] As set forth above, the invention is directed to compounds of formula:



(I),

as previously defined, and to the use of this type of compounds as fragrant agents.

[0013] Preferably, R^3 and R^4 are independently selected from the group consisting of a hydrogen atom, methyl, ethyl, *i*-propyl, *i*-butyl, and *t*-butyl, more preferably from the group consisting of a hydrogen atom, methyl and *t*-butyl.

[0014] R^5 is preferably selected from the group consisting of methyl, ethyl, *i*-butyl, *t*-butyl, *n*-pentyl, 1-propen-1-yl, allyl, vinyl, and phenyl, more preferably from the group consisting of methyl, ethyl, *i*-butyl and phenyl.

[0015] R^6 is preferably selected from the group consisting of methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, *n*-pentyl, 1-propen-1-yl, phenyl, benzyl and 2,4-dimethylcyclohexen-3-yl, more preferably from the group consisting of methyl, ethyl, *i*-propyl, *n*-pentyl, 1-propen-1-yl, phenyl, benzyl and 2,4-dimethylcyclohexen-3-yl. R^7 is then preferably selected from the group consisting of a hydrogen atom, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, *n*-pentyl and 1-propen-1-yl, more preferably from the group consisting of hydrogen atom, methyl and *n*-butyl.

[0016] Alternatively, R^6 and R^7, together with the carbon atom to which they are attached form a cyclopentyl or cyclohexyl group, preferably a cyclopentyl group.

[0017] According to a first preferred embodiment, R^3 and R^4 are hydrogen atoms. In this first embodiment, advantageously:

- R^5 is selected from the group consisting of methyl, ethyl, *i*-butyl and phenyl, and more preferably methyl,
- R^6 is selected from the group consisting of methyl, ethyl, *i*-propyl, phenyl, benzyl and 2,4-dimethylcyclohexen-3-yl, and more preferably ethyl or benzyl,
- R^7 is selected from the group consisting of a hydrogen atom, methyl and *n*-butyl, and more preferably a hydrogen atom.

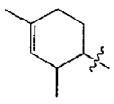
[0018] According to a second preferred embodiment, R^3 and R^7 are hydrogen atoms, and R^4 is *t*-butyl. In this second embodiment, advantageously:

- R^5 is methyl, ethyl or phenyl, and
- R^6 is methyl or *i*-propyl.

[0019] In a third preferred embodiment, R^3 and R^4 are methyls, and R^7 is a hydrogen atom. In this third embodiment, advantageously:

- R^5 is methyl or ethyl, and
- R^6 is selected from the group consisting of methyl, *i*-propyl and 1-propen-1-yl.

[0020] Particular preferred compounds of formula (I) are those of table hereafter:

	R_3	R_4	R_5	R_6	R_7	Olfactive profile
Iaa	H	H	Me	Me	H	- green, earthy, roasted nuts, coffee
Iab	H	H	Me	*n*-C_5H_{11}	H	- green, fatty
Iac	H	H	Me		H	- green, ripe fruit
Iad	H	H	Me	Ph	H	- green
Iae	H	H	Me	Bz	H	- floral (mimosa, carnation), spicy (eugenol), honey
Iaf	H	H	Me	Et	H	- powerful, spicy (curry, eugenol), hazelnut, fenugrec, coffee beans, celery, tagete, immortelle, fruity (pear, apple, carrot)
Iah	H	H	Me	Me	Me	- green, minty, fresh
Iai	H	H	Me	Me	*n*-Bu	- camphoraceous, pharmaceuticals, caoutchouc
Iaj	H	H	Me	-$(CH_2)_4$-		- peanut, animal, clean
Iak	H	H	Me		H	- green, floral, a bit animalic
Ial	H	H	Me	-[CH=CH-$(CH_2)_3$]-		- herbaceous, earthy, spicy
Ibg	H	H	Et	*i*-Pr	H	- herbaceous, camomile
Ica	H	H	Ph	Me	H	- spicy, exotic fruits

	R_3	R_4	R_5	R_6	R_7	Olfactive profile
Ida	H	H	*i*-Bu	Me	H	- leathery, cresol
I'aa	H	*t*-Bu	Me	Me	H	- sulfur, fatty
I'bg	H	*t*-Bu	Et	*i*-Pr	H	- herbaceous, camomile, woody
I'ca	H	*t*-Bu	Ph	Me	H	- green, chemicals
I"aa	Me	Me	Me	Me	H	- aromatic, woody, powerful.
I"ac	Me	Me	Me		H	- herbal, minty, fruity
I"bg	Me	Me	Et	*i*-Pr	H	- herbaceous

[0021] The compounds of formula (I) as defined above exhibit interesting olfactive properties. Very unexpectedly and surprisingly, they do not show the typical floral, ambery or fruity notes that the skilled person would have expected, but rather green and/or spicy notes.

[0022] In another aspect, the invention therefore relates to the use of the compounds of formula (I) as described above as fragrant agents. This invention also relates to a fragrant composition containing at least one compound of formula (I) according to the invention.

[0023] This invention includes any fragrant composition comprising, as a fragrant or flavouring agent, at least a compound of formula (I). The compounds of the invention may be used alone or in combination with other perfuming ingredients, solvents, additives or fixatives, commonly used and that the person skilled in the art is able to choose in regard of the desired effect and the nature of the product to perfume.

[0024] In a first embodiment, the invention relates to the use of a compound of formula (I) according to the invention or a composition containing at least one of such a com-

pound in the perfumery field for the preparation of perfumed bases and concentrates, fragrances, perfumes and similar products (e.g. topic compositions, cosmetic compositions such as for example face and body creams, cleansers, facial treatments, talc powders, hair oils, shampoos, hair lotions, bath oils and salts, shower and bath gels, soaps, body anti-perspirants and deodorizers, pre-shave, shaving and post-shave creams and lotions, creams, toothpastes, mouth baths, pomades, cleaning products, such as for example softeners, detergents, air deodorizers and household cleaning supplies. Therefore, the invention also relates to a fragrant composition including at least one compound of formula (I).

[0025] In a second embodiment, the invention relates to the use of the compounds or composition as described above, as masking agents of odours, and to any pharmaceutical or cosmetic composition containing at least one compound of formula (I) or one or more isomers of a compound of formula (I). Therefore, this invention also relates to any composition comprising at least one compound of formula (I), as herein described, in combination with any suitable excipient, especially pharmaceutical or cosmetic excipient.

[0026] In another aspect, the invention also relates to a method of fragrancing a composition by adding an olfactory effective amount of a compound of formula (I) of the invention to said composition. Suitable compositions comprise perfumed bases and concentrates, fragrances, perfumes and similar products; topic compositions; cosmetic compositions such as for example face and body creams, cleansers, facial treatments, talc powders, hair oils, shampoos, hair lotions, bath oils and salts, shower and bath gels, soaps, body anti-perspirants and deodorizers, pre-shave, shaving and post-shave creams and lotions, creams, toothpastes, mouth baths, pomades; cleaning products, such as for example softeners, detergents, air deodorizers and household cleaning supplies.

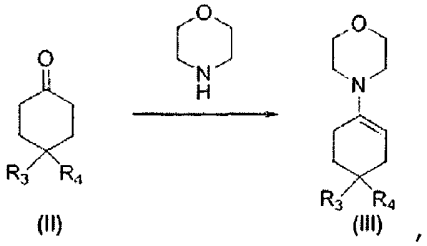
[0027] In yet another aspect, the invention also relates to a method of masking odours comprising adding an olfactory effective amount of at least a compound of formula (I) of the invention to a composition. Suitable compositions comprise particularly pharmaceutical, and cosmetic compositions. Suitable cosmetic composition include face and body creams, cleansers, facial treatments, talc powders, hair oils, shampoos, hair lotions, bath oils and salts, shower and bath gels, soaps, body anti-perspirants and deodoriz-

ers, pre-shave, shaving and post-shave creams and lotions, creams, toothpastes, mouth baths, and pomades.

[0028] The compounds of the invention may be used in a concentration comprised in a range from 0.001% to 99% in weight, preferably from 0.1% to 50% in weight, more preferably from 0.1% to 30% in weight. It is known by the man skilled in the art that these values depend of the nature of the composition/article to be perfumed, the desired intensity of the perfume, and of the nature of the other ingredients present in said composition or article.

[0029] The invention also relates to a process of preparing a compound according formula (I) as defined above, the process comprising the following steps of:

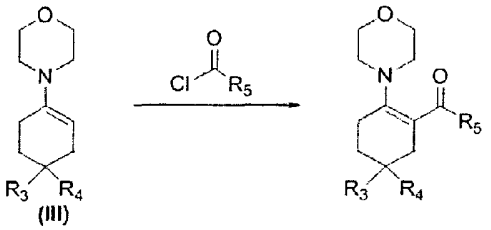
a) reacting a compound of formula (II) with morpholine so as to obtain an enamine of formula (III)



(II) (III) ,

wherein R^3 and R^4 are as defined above,

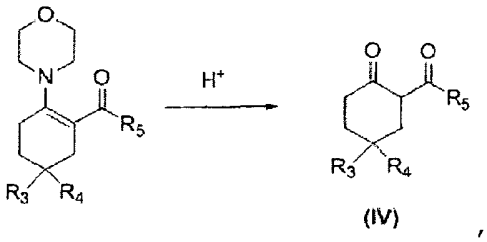
b) acylating the enamine of formula (III) with R^5-COCl, wherein R^5 is as defined above, so as to obtain the corresponding acylated enamine



(III) ,

c) hydrolysing the acylated enamine obtained in the previous step in the presence of an acid, such as for example hydrochloric acid so as to obtain a diketone of for-

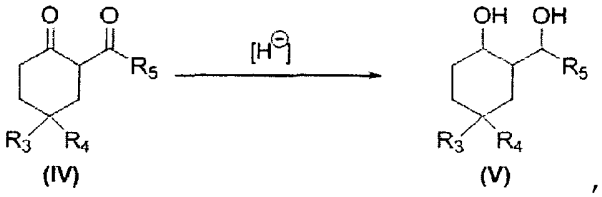
mula (IV)



(IV)

,

d) reducing the diketone (IV) so as to obtain the corresponding diol (V)

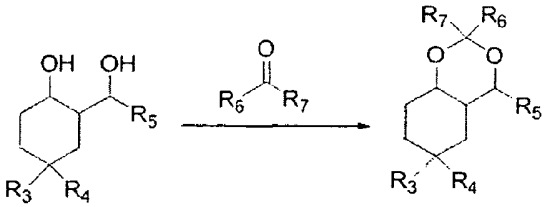


(IV) (V)

,

and

e) reacting the diol (V) with R^6-CO-R^7, wherein R^6 and R^7 are as defined above, so as to obtain the compound of formula (I)



(V) (I)

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[0030] Step a) of the process of the invention is carried out in an organic solvent, which may be selected from the group comprising toluene, xylene, trimethylbenzene, cyclohexane, and methylcyclohexane. According to a preferred embodiment, the organic solvent is cyclohexane or toluene.

[0031] The reaction of step a) is advantageously carried out at refluxing temperature.

[0032] Step b) is carried out in an organic solvent, which may be selected from the group comprising toluene, xylene, trimethylbenzene, cyclohexane and methylcyclohexane, in the presence of an amine, preferably triethylamine. According to a preferred embodiment, the organic solvent is toluene.

[0033] Step c) is advantageously carried out in the same solvent as step b). Preferably, the diketone is directly reacted with the acid without previous purification.

[0034] The reduction of the diketone to the diol in step d) is carried out according to conventional reduction methods well known to the person skilled in the art, e.g. using $NaBH_4$, Dibal-H, $LiAlH_4$ or H_2. Particularly good results were obtained with $NaBH_4$.

[DEFINITIONS]

[0035] The terms "fragrance" and "fragrant" are used interchangeably whenever a compound or a mixture of compounds is referred to, which is intended to pleasantly stimulate the sense of smell.

[0036] The term "olfactory effective amount" means a level or amount of fragrant compound present in a material at which the incorporated compound exhibits a sensory effect.

[0037] By the term "masking" is meant reducing or eliminating malodour perception generated by one or more molecules entering in the composition of a product.

[0038] The term "isomer" means molecules having the same chemical formula, which means same number and types of atoms, but in which the atoms are arranged differently. The term "isomer" includes structural isomers, geometric isomers, optical isomers and stereoisomers. It particularly includes the *cis*/*trans* isomers, the *cis* isomers being the ones where the bicyclic junction is *cis,* i.e. the substituents forming the acetal cycle are on the same side of the cyclohexyl cycle in (I). The *trans* configuration is the one where the substituents forming the acetal cycle are on two different sides of the cyclohexyl cycle in (I) - the bicyclic junction is *trans.*

[0039] The term "C1-C6 alkyl" or "C1-C6 alkyl group", means any linear or branched saturated hydrocarbon chain having 1, 2, 3, 4, 5 or 6 carbon atoms, such as for example methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *sec*-butyl, *iso*-butyl, *tert*-butyl, and *n*-pentyl.

[0040] The term "C2-C6 alkenyl" or "C2-C6 alkenyl group", means any linear or branched mono or poly unsaturated hydrocarbon chain, having 2, 3, 4, 5 or 6 carbon

atoms, such as for example ethenyl, prop-1-enyl, allyl, but-1-enyl, but-2-enyl or pentenyl.

[0041] The term "C5-C6 cycloalkyl" or "C5-C6 cycloalkyl group", means any cyclic saturated hydrocarbon chain having 5 or 6 carbon atoms (namely, a cyclopentyl or cyclohexyl), substituted or not by one or several alkyl and/or alkenyl groups as described above -preferably methyl and ethyl-.

[0042] The term "C5-C6 cycloalkenyl" or "C5-C6 cycloalkenyl group", means any cyclic mono or poly unsaturated hydrocarbon chain having preferably 5, 6 or 7 carbon atoms, such as for example cyclopentenyl, cyclohexenyl and cycloheptenyl, substituted or not by one or several alkyl and/or alkenyl groups as described above -preferably methyl and ethyl-.

[0043] The term "aryl" refers to a polyunsaturated, aromatic hydrocarbyl group having a single ring (i.e. phenyl) or multiple aromatic rings fused together (e.g. naphtyl) or linked covalently, typically containing 5 to 12 atoms; preferably 6 to 10, wherein at least one ring is aromatic. A preferred aryl group is phenyl. The term "$(CH_2)_{0-2}$-aryl" thus includes any aryl group as defined above as well as any -CH_2-aryl group and any -$(CH_2)_2$-aryl group, wherein the aryl moiety is as defined above. A preferred -CH_2-aryl group is the benzyl group and a preferred -$(CH_2)_2$-aryl group is -$(CH_2)_2$-phenyl.

[0044] The invention will be better understood with reference to the following examples. These examples are intended to be representative of specific embodiments of the invention, and are not intended as limiting the scope of the invention.

[EXAMPLES]

Example 1: Preparation of 4-cyclohex-1-enyl-morpholine (III)

[0045] Cyclohexanone (98.14 g, 1.00 mol) is added dropwise to a 12M solution of morpholine (118.48 g, 1.36 mol) in cyclohexane (120 ml) at 65-70°C. The reaction mixture is then heated under reflux and the completion of the reaction is followed by GC. The formed water is removed using a Dean-Stark apparatus.

[0046] After cooling down, the solvent is removed under vacuum and the crude 4-

cyclohex-1-enyl-morpholine (orange liquid, quantitative yield) is used directly in the following step.

Example 2: Preparation of 4-(4-tert-butyl-cyclohex-1-enyl)-morpholine (III')

[0047] Compound **III'** (white solid) is obtained quantitatively according to Example 1, from 4-tert-butylcyclohexanone (77.12 g, 0.50 mol), morpholine (54.01 g, 0.62 mol) and cyclohexane (60 mL).

Example 3: Preparation of 4-(4,4-dimethyl-cyclohex-1-enyl)-morpholine (III")

[0048] Compound **III"** (brown liquid) is obtained quantitatively according to Example 1, from 4,4-dimethylcyclohexanone (350.03 g, 2.76 mol), morpholine (327.01 g, 3.75 mol) and cyclohexane (330 mL).

Example 4: Preparation of 2-acetyl-cyclohexanone (IVa)

[0049] To a 0.65 M solution of 4-cyclohex-1-enyl-morpholine (82.64 g, 0.50 mol, 1 eq.), obtained in Example 1, in toluene (770 ml) is added triethylamine (71.33 g, 0.70 mol, 1.41 eq). Acetyl chloride (55.34 g, 0.70 mol, 1.41 eq)) is then added dropwise and the reaction mixture is further stirred at 35°C for 20 hours and then at room temperature overnight.

[0050] After completion of the reaction (followed by GC), a 20% HCl aqueous solution (250 mL) is added and the mixture is stirred under reflux for 1 hour.

[0051] After cooling down, the organic phase is washed twice with water, once with saturated aqueous $NaHCO_3$ solution and with brine. The organic phase is then dried over magnesium sulphate and the solvents are evaporated. The crude oil is then purified by distillation to give compound **IVa** as a colourless oil (49.95 g, 0.36 mol, 72% yield).
Bp: 48°C/0.6 torr

Example 5: Preparation of 2-propionyl-cyclohexanone (IVb)

[0052] Compound IVb is obtained in 49% yield as a colourless oil, according to Example 4, from 4-cyclohex-1-enyl-morpholine (82.64g, 0.50 mol, obtained in Example 1),

triethylamine (71.33g, 1.41 mol), propionyl chloride (64.76 g, 1.41 mol), toluene (770 mL) and 20% aqueous HCl (250 mL).
Bp: 98°C/5.4 torr

Example 6: Preparation of 2-benzoyl-cyclohexanone (IVc)

[0053] Compound **IVc** is obtained in 50% yield as a yellow powder, according to Example 4, from 4-cyclohex-1-enyl-morpholine (40.96 g, 0.25 mol, obtained in Example 1), triethylamine (35.35 g, 0.35 mol), benzoyl chloride (49.19g, 0.35 mol), toluene (380 mL) and 20% aqueous HCl (125 mL).
Bp: 110°C/0.3 torr

Example 7: Preparation of 2-(3-methylbutanoyl)cyclohexanone (IVd)

[0054] Compound **IVd** is obtained in 90% yield as a pale yellow liquid, according to Example 4, from 4-cyclohex-1-enyl-morpholine (82.64 g, 0.5 mol, obtained in Example 1), triethylamine (71.34 g, 0.71 mol), isovaleryl chloride (85.01 g, 0.71 mol), toluene (760 mL) and 20% aqueous HCl (166 mL).
Bp: 76°C / 0.68 torr

Example 8: Preparation of 2-acetyl-4-*tert*-butyl-cyclohexanone (IV'a)

[0055] Compound **IV'a** is obtained in 53% yield as a yellow oil, according to Example 4, from morpholino-enamine **III'** (36.89 g, 0.17 mol, obtained in Example 2), triethylamine (24.25 g, 0.24 mol), acetyl chloride (18.84 g, 0.24 mol), toluene (260 mL) and 20% aqueous HCl (85 mL).
Bp: 74°C / 0.5 torr

Example 9: Preparation of 4-*tert*-butyl-2-propionyl-cyclohexanone (IV'b)

[0056] Compound **IV'b** is obtained in 58% yield as a yellow oil, according to Example 4, from morpholino-enamine **III'** (36.89 g, 0.17 mol, obtained in Example 2), triethylamine (24.25 g, 0.24 mol), propionyl chloride (22.2 g, 0.24 mol), toluene (260 mL) and 20% aqueous HCl (85 mL).
Bp: 98°C / 0.7 torr

Example 10: Preparation of 2-benzoyl-4-*tert*-butyl-cyclohexanone (IV'c)

[0057] Compound **IV'c** is obtained in 35% yield as a yellow powder, according to Example 4, from morpholino-enamine **III'** (36.89 g, 0.17 mol, obtained in Example 2), triethylamine (24.25 g, 0.24 mol), benzoyl chloride (33.73 g, 0.24 mol), toluene (260 mL) and 20% aqueous HCl (85 mL).
Bp: 110°C / 0.2 torr

Example 11: Preparation of 2-((*E*)-but-2-enoyl)-4-*tert*-butyl-cyclohexanone (IV'e)

[0058] Compound **IV'e** is obtained as white crystals, according to Example 4, from morpholino-enamine **III'** (55.33 g, 0.25 mol, obtained in Example 2), triethylamine (35.66 g, 0.35 mol), crotonyl chloride (36.85 g, 0.35 mol), toluene (380 mL) and 20% aqueous HCl (125 mL).
Bp: 115°C/0.76 torr
Mp: 73.6°C

Example 12: Preparation of 2-acetyl-4,4-dimethyl-cyclohexanone (IV"a)

[0059] Compound **IV"a** is obtained in 33% yield as a pale yellow oil, according to Example 4, from morpholino-enamine **III"** (266.36 g, 1.36 mol, obtained in Example 3), triethylamine (194.04 g, 1.91 mol), acetyl chloride (149.93 g, 1.91 mol), toluene (2.09 L) and 20% aqueous HCl (685 mL).
Bp: 98°C / 6.1 torr

Example 13: Preparation of 4,4-dimethyl-2-propionyl-cyclohexanone (IV"b)

[0060] Compound **IV"b** is obtained in 26% yield as a orange oil, according to Example 4, from morpholino-enamine **III"** (131.88 g, 0.67 mol, obtained in Example 3), triethylamine (95.59 g, 0.94 mol), propionyl chloride (86.96 g, 0.94 mol), toluene (1.03 L) and 20% aqueous HCl (340 mL).
Bp: 64°C/1.1 torr

Example 14: Preparation of 2-(1-hydroxy-ethyl)-cyclohexanol (Va)

[0061] Diketone **IVa** (49.95 g, 0.36 mol, 1 eq., obtained in Example 4) is added dropwise to a 10-15°C molar suspension of $NaBH_4$ (13.47 g, 0.36 mol, 1 eq.) in EtOH (360 ml). After completion of the reaction (followed by tlc), acetone (65 ml) is added to the

reaction mixture. Half of the solvents is then evaporated and the mixture is diluted in water and MTBE. 10% aqueous HCl is added and the aqueous phase is extracted three times with MTBE. The combined organic phases are then washed with saturated aqueous $NaHCO_3$ and with brine. After drying over magnesium sulphate, the organic phase is filtered and the solvents are evaporated to give crude diol **Va** as a pale yellow oil in quantitative yield. Compound **Va** is used in the next step without further purification.

Example 15: Preparation of 2-(1-hydroxy-propyl)-cyclohexanol (Vb)

[0062] Compound **Vb** is obtained in 93% yield as a yellow oil, according to Example 4 from diketone **IVb** (37.73 g, 0.24 mol, obtained in Example 5), $NaBH_4$ (9.14 g, 0.24 mol), ethanol (240 mL) and acetone (40 mL).

Example 16: Preparation of 2-(hydroxy-phenyl-methyl)-cyclohexanol (Vc)

[0063] Compound **Vc** is obtained in quantitative yield as a pale yellow oil, according to Example 14, from diketone **IVc** (25.03 g, 0.12 mol, obtained in Example 6), $NaBH_4$ (4.67 g, 0.12 mol), ethanol (120 mL) and acetone (20 mL).

Example 17: Preparation of 2-(1-hydroxy-3-methylbutyl)cyclohexanol (Vd)

[0064] Compound **Vd** is obtained in quantitative yield as a colourless oil, according to Example 14, from diketone **IVd** (46.02 g, 0.25 mol, obtained in Example 7), $NaBH_4$ (9.45 g, 0.25 mol), ethanol (240 mL) and acetone (45 mL).

Example 18: Preparation of 4-*tert*-butyl-2-(1-hydroxy-ethyl)-cyclohexanol (V'a)

[0065] Compound **V'a** is obtained in quantitative yield as a yellow oil, according to Example 14, from diketone **IV'a** (15.5 g, 0.08 mol, obtained in Example 8), $NaBH_4$ (3.02 g, 0.08 mol), ethanol (80 mL) and acetone (15 mL).

Example 19: Preparation of 4-*tert*-butyl-2-(hydroxy-propyl-methyl)-cyclohexanol (V'b)

[0066] Compound **V'b** is obtained in quantitative yield as a yellow oil, according to Example 14, from diketone **IV'b** (16.7 g, 0.08 mol, obtained in Example 9), $NaBH_4$ (3.02 g, 0.08 mol), ethanol (80 mL) and acetone (15 mL).

Example 20: Preparation of 4-*tert*-butyl-2-(hydroxy-phenyl-methyl)-cyclohexanol (V'c)

[0067] Compound **V'c** is obtained in 78% yield as a white powder, according to Example 14, from diketone **IV'c** (14.56 g, 0.06 mol, obtained in Example 10), $NaBH_4$ (2.27 g, 0.06 mol), ethanol (60 mL) and acetone (10 mL).

Example 21: Preparation of 2-(1-hydroxy-ethyl)-4,4-dimethyl-cyclohexanol (V"a)

[0068] Compound **V"a** is obtained in quantitative yield as a pale yellow oil, according to Example 14, from diketone **IV"a** (72.17 g, 0.43 mol, obtained in Example 12), $NaBH_4$ (16.25 g, 0.43 mol), ethanol (430 mL) and acetone (85 mL).

Example 22: Preparation of 2-(1-hydroxy-propyl)-4,4-dimethyl-cyclohexanol (V"b)

[0069] Compound **V"b** is obtained in quantitative yield as a pale yellow oil, according to Example 14, from diketone **IV"b** (29.99 g, 0.16 mol, obtained in Example 13), $NaBH_4$ (6.05 g, 0.16 mol), ethanol (160 mL) and acetone (30 mL).

Example 23: Preparation of 2,4-dimethyl-hexahydro-benzo[1,3]dioxine (Iaa)

[0070] Acetaldehyde (28.81 g, 0.40 mol) is added dropwise to a 2.3M solution of diol **Va** (28.63 g, 0.20 mol, obtained in Example 14) in refluxing cyclohexane (85 ml). The reaction is catalysed with PTSA. The reaction mixture is refluxed for a further 2 hours and the formed water is removed with a Dean-Stark apparatus.

[0071] After completion of the reaction (followed by GC), the reaction mixture is cooled down and poured into a half-saturated aqueous $NaHCO_3$ solution. The aqueous phase is extracted twice with MTBE and the combined organic layers are washed with a saturated aqueous $NaHCO_3$ solution and with brine and then dried over magnesium sulphate. The solvents are evaporated and the crude product is purified by distillation to give compound **Iaa** as a colourless oil in 25% yield. It consists in a mixture of 5 isomers with 2 major isomers (83%) as *cis* and *trans* isomers in a 70:30 ratio.

Bp: 65°C / 6.5 torr

Olfactory profile: Green, earthy, roasted nuts, coffee

Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.70-1.80 (m, 8H); 1.12 (d, 3H, *J*= 6.5 Hz,); 1.32 (d, 3H, *J* = 5.1 Hz,); 1.88 (m, 1H); 3.76 (m, 2H); 4.72 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.8; 19.4; 20.5; 21.2; 25.2; 31.7; 39.1; 75.3; 75.5; 98.7.

MS [e/m (%)]: 169 (M^+, 5); 155 (10); 127 (3); 109 (39); 98 (9); 93 (11); 89 (29); 82 (100); 67 (75); 55 (16); 43 (18); 41 (15).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.17 (d, 3H, *J* = 6.3 Hz); 1.32 (d, 3H, J = 5,1 Hz); 3.21 (dt, 1H, *J* = 4.0 Hz, J = 10.2 Hz); 3.38 (dq, 1H, *J* = 6.3 Hz, *J* = 9.5 Hz); 4.78 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.5; 21.2; 24.6; 25.3; 25.8; 31.6; 47.2; 76.9; 80.5; 98.4. **MS** [e/m (%)]: 169 (M^+ , 16); 155 (92); 127 (7); 109 (74); 98 (12); 93 (15); 89 (17); 82 (100); 67 (96); 55 (26); 43 (27); 41 (21).

Minor *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 5.00 (q, 1H, *J* = 5.0 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 91.4.

MS [e/m (%)]: *idem* major *cis*-isomers.

Example 24: Preparation of 4-methyl-2-pentyl-hexahydro-benzo[1,3]dioxine (Iab)

[0072] Compound **Iab** is obtained as a colourless oil in 20% yield, according to Example 23, from diol **Va** (28.63 g, 0.2 mol, obtained in Example 14), hexanal (24.03 g, 0.24 mol) and cyclohexane (85 ml). It consists in a mixture of 3 isomers with 2 major isomers (98%) in a 50:50 ratio.

Bp: 80°C / 0.6 torr

Olfactory profile: green, fatty

1st isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.87 (t, 3H, *J* = 6.6 Hz); 1.05-1.20 (m, 3H); 1.06-1.81 (m, 16H); 1.91 (m, 1H); 3.75 (m, 2H); 4.56 (t, 1H, *J* = 4.8 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 14.1; 17.8; 19.4; 20.5; 22.6; 23.6; 25.2; 31.7; 31.8; 35.1; 39.3; 75.2; 75.5; 101.9.

MS [e/m (%)]: 225 (M^+, 8); 155 (64); 145 (8); 127 (4); 109 (100); 83 (20); 82 (59); 67 (46); 55 (20); 43 (13); 41 (15).

2nd isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.20 (dt, 1H, *J* = 4.0 Hz, *J* = 10.3 Hz); 3.37 (dq, 1H, *J* = 6.2 Hz, *J* = 9.5 Hz); 4.60 (t, 1H, *J* = 5.2 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 14.0; 18.6; 22.5; 24.0; 24.6; 25.4; 25.9; 31.7; 31.8; 35.1; 39.3; 77.0; 80.6; 101.8.

MS [e/m (%)]: 225 (M^+, 13); 155 (100); 145 (3); 127 (5); 109 (64); 83 (15); 82 (36); 67 (35); 55 (18); 43 (11); 41 (13).

Example 25: Preparation of 4-methyl-2-propenyl-hexahydro-benzo[1,3]dioxine (Iac)

[0073] Compound **Iac** is obtained as a colourless oil in 20% yield, according to Example 23, from diol **Va** (25.96 g, 0.18 mol, obtained in Example 14), crotonaldehyde (15.14 g, 0.21 mol) and cyclohexane (75 ml). It consists in a mixture of 5 isomers with 2 major isomers (85%) as *cis* and *trans* isomers in a 62:38 ratio.

Bp: 62°C / 0.6 torr

Olfactory profile: green, ripe fruit

Major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.75-1.85 (m, 8H); 1.16 (d, 3H, *J*= 6.5 Hz); 1.73 (d, 3H, *J*= 6.4 Hz); 1.95 (m, 1H); 3.85 (m, 2H); 4.98 (d, 1H, *J* = 6.0 Hz); 5.61 (m, 1H); 5.90 (dq, 1H, *J* = 0.5 Hz, *J* = 6.4 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.4; 17.5; 19.0; 20.1; 24.8; 31.4; 38.9; 75.1; 75.3; 101.0; 128.4; 130.5.

MS [e/m (%)]: 195 (M^+, 6); 181 (10); 155 (1); 127 (3); 109 (68); 82 (14); 71 (100); 69 (18); 67 (44); 55 (17); 41 (19).

Major trans-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.22 (d, 3H, *J*= 6.2 Hz,); 1.74 (d, 3H, *J* = 6.5 Hz); 3.29 (m, 1H); 3.48 (dq, 1H, *J*= 6.2 Hz, *J*= 9.5 Hz); 5.06 (d, 1H, *J* = 5.7 Hz); 5.97 (dq, 1H, *J* = 0.5 Hz, *J* = 6.5 Hz).

^{13}**C-NMR** (50 MHz, $CDCl_3$): δ (ppm) 17.3; 18.3; 24.3; 25.0; 25.6; 31.3; 47.0; 80.2; 80.3; 101.4; 128.1; 130.4.

MS [e/m (%)]: 195 (M^+, 13); 181 (59); 155 (4); 127 (2); 109 (50); 82 (18); 71 (100); 69 (25); 67 (48); 55 (25); 41 (23).

Example 26: Preparation of 4-methyl-2-phenyl-hexahydro-benzo[1,3]dioxine (Iad)

[0074] Compound **Iad** is obtained as a pale yellow oil in 44% yield, according to Example 23, from diol **Va** (14.98 g, 0.1 mol, obtained in 14), benzaldehyde (21.22 g, 0.2 mol) and cyclohexane (50 ml). It consists in a mixture of 5 isomers with 2 major isomers (84%) as *cis*/*trans* isomers in a 60:40 ratio.

Bp: 102°C / 0.5 torr

Olfactory profile: green

Major *cis*-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$): δ (ppm) 0.82-1.43 (m, 2H); 1.23 (d, 3H, *J*= 6.5 Hz); 1.44-1.95 (m , 6H); 2.03 (m, 1H); 4.02 (m, 2H); 5.57 (s, 1H); 7.37 (m, 3H); 7.55 (m, 2H).

^{13}**C-NMR** (50 MHz, $CDCl_3$): δ (ppm) 17.9; 20.5; 24.6; 25.2; 31.7; 39.2; 75.9; 76.2; 101.7; 126.4; 128.2; 128.7; 139.2.

MS [e/m (%)]: 231 (M^+, 80); 155 (2); 109 (43); 107 (100); 105 (36); 81 (20); 79 (23); 77 (23); 67 (32); 51 (5); 39 (6).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.30 (d, 3H, *J* = 6.2 Hz); 3.48 (m, 1H); 3.65 (dq, 1H, *J* = 6.2 Hz, *J* = 9.5 Hz); 5.65 (s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.6; 19.5; 25.4; 25.9; 31.7; 47.4; 77.6; 81.1; 101.0; 126.2; 128.2; 128.6; 138.8.

MS [e/m (%)]: 231 (M^+, 100); 155 (8); 109 (21); 107 (75); 105 (44); 81 (14); 79 (21); 77 (21); 67 (36); 51 (5); 39 (6).

Minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 5.89 (s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 32.1.

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 5.84 (s, 1H).

^{13}C-NMR (50 MHz, $GDCl_3$, selected data): δ (ppm) 31.7.

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 5.94 (s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 31.4.

Example 27: Preparation of 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxine (Iae)

[0075] Compound Iae is obtained as colourless oil in 30% yield, according to Example 23, from diol **Va** (25.96 g, 0.18 mol, obtained in Example 14), phenylacetaldehyde (25.23 g, 0.21 mol) and cyclohexane (75 ml). It consists in a mixture of 4 isomers with 2 major isomers (93%) as *cis*/*trans* isomers in a 75:25 ratio.
Bp: 90°C / 0.2 torr
Olfactory profile: Floral (mimosa, carnation), spicy (eugenol), honey.
Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 1.10 (d, 3H, *J* = 6.6 Hz); 1.20-1.83 (m, 8H); 1.88 (m, 1H); 2.91 (d, 2H, *J* = 5.0 Hz); 3.69 (m, 2H); 4.70 (t, 1H, *J*= 5.0 Hz); 7.23 (m, 5H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.8; 19.4; 20.5; 25.2; 31.7; 39.2; 41.7; 75.3; 75.5; 101.9; 126.1; 127.9; 129.9; 137.2.

MS [e/m (%)]: 245 (M^+, 1); 155 (52); 121 (3); 109 (100); 91 (31); 67 (25); 55 (8); 43 (5); 41 (8).

Major trans-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.16 (d, 3H, *J* = 6.3 Hz); 2.91 (d, 2H, *J* = 5.0 Hz); 3.16 (dt, 1H, *J* = 4.0 Hz, *J* = 10.3 Hz); 3.34 (dq, 1H, *J* = 6.3 Hz, *J* = 9.5 Hz); 4.74 (t, 1H, *J* = 5.0 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.6; 24.5; 25.4; 25.9; 31.6; 41.8; 47.6; 77.1; 80.6; 102.0; 126.2; 128.0; 129.7; 137.1.

MS [e/m (%)]: 245 (M^+, 4); 155 (83); 121 (2); 109 (100); 91 (33); 67 (28); 55 (12); 43 (9); 41 (11).

Example 28: Preparation of 2-ethyl-4-methylhexahydro-4*H*-benzo[d][1,3]dioxine (Iaf)

[0076] Compound **Iaf** is obtained as colourless oil in 60% yield, according to Example 23, from diol **Va** (25.96 g, 0.18 mol, obtained in Example 14), propionaldehyde (51 g, 0.88 mol) and cyclohexane (450 ml). It consists principally in a mixture of 5 isomers with 3 major isomers (78%) in a 47:31:22 ratio.

Bp: 80-83 °C / 5.7 torr

Olfactory profile: powerful, spicy (curry, eugenol), hazelnut, fenugrec, coffee beans, celery, tagete, immortelle, fruity (pear, apple, carrot).

1st major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.70-1.05 (m, 1H); 0.92 (t, *J* = 7.5 Hz, 3H); 1.05-1.53 (m, 5H); 1.17 (d, *J* = 6.2 Hz, 3H); 1.53-1.73 (m, 3H); 1.73-2.05 (m, 2H); 3.19 (dt, *J* = 10.1, 4.00 Hz, 1H); 3.38 (tt, *J* = 9.5, 5.3 Hz, 1H); 4.54 (t, *J* = 5.2 Hz, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 8.62, 18.56; 24.59; 25.38; 25.88; 28.13; 31.66; 47.54; 76.94; 80.49; 102.70.

MS [e/m (%)]: 184 (M+, 1); 183 (10); 155 (63); 109 (82); 93 (11); 83 (14); 82 (79); 81 (17); 79 (13); 67 (100); 59 (19); 57 (27); 55 (37); 54 (21); 53 (13); 43 (21); 41 (34); 39 (18).

2nd major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.93 (t, *J* = 7.61 Hz, 3H); 1.12 (d, *J* = 6.54 Hz, 3H); 3.67-3.85 (m, 2H); 4.51 (t, *J* = 4.65 Hz, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 8.19; 17.8; 19.39; 20.53; 26.63; 28.06; 31.76; 39.32; 75.17; 75.41; 102.50.

MS [e/m (%)]: 184 (M+, <1); 183 (4); 155 (29); 109 (80); 103 (14); 93 (11); 83 (14); 82 (100); 81 (14); 79 (13); 67 (100); 59 (17); 57 (20); 55 (29); 54 (20); 43 (19); 41 (30); 39 (15).

3rd major trans-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.90 (t, *J* = 7.64 Hz, 3H); 1.23 (d, *J* = 6.96 Hz, 3H); 3.45-3.57 (m, 1H); 4.0-4.15 (m, 1H); 4.78 (t, *J* = 5.01 Hz, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 8.45; 13.08; 25.23; 25.67; 28.23, 32.14; 43.89; 71.67; 74.18, 95.27.

MS [e/m (%)]: 184 (M+, 1); 183 (9); 155 (66); 127 (10); 109 (100); 93 (13); 83 (12); 82 (40); 81 (15); 79 (11); 67 (90); 59 (15); 57 (33); 55 (37); 54 (17); 53 (12); 43 (19); 41 (32); 39 (17).

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.32 (d, *J* = 7.0 Hz, 3H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 7.99; 16.18; 20.32; 24.59; 25.62; 28.23; 31.58; 38.94; 69.14; 73.86; 95.07.

MS [e/m (%)]: 184 (M+, <1); 183 (4); 155 (40); 109 (100); 93 (11); 83 (10); 82 (30); 81 (11); 79 (9); 67 (70); 59 (10); 57 (19); 55 (26); 54 (11); 43 (14); 41 (23); 39 (11).

2nd minor isomers:

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 44.2; 74.9; 79.6; 97.6.

MS [e/m (%)]: 184 (M+, <1); 183 (2); 155 (40); 109 (100); 93 (5); 83 (10); 82 (38); 81 (12); 79 (10); 67 (73); 59 (17); 57 (21); 55 (29); 54 (15); 43 (16); 41 (26); 39 (13).

Example 29: Preparation of 2,2,4-trimethylhexahydro-*4H*-benzo[*d*][1,3]dioxine (Iah)

[0077] Compound **Iah** is obtained as colourless oil in 14% yield, according to Example 23, from diol **Va** (40.57 g, 0.28 mol, obtained in Example 14), acetone (32.52 g, 0.56 mol) and cyclohexane (110 ml). It consists in a mixture of 4 isomers with 2 major isomers (96%) as *cis*/*trans* enantiomers in a 53:47 ratio.

Bp: 44°C / 0.6 torr

Olfactory profile: green, minty, fresh.

Major *cis*-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$): δ (ppm) 0.70-1.30 (m, 4H), 1.06 (d, *J* = 6.46 Hz, 3H), 1.30-1.65 (m, 2H), 1.40 (s, 3H), 1.41 (s, 3H), 3.45 (dt, *J* = 9.8 Hz, *J* = 3.6 Hz, 1H), 1.65-1.90 (m, 3H), 3.63 (qd, *J* = 9.64 Hz, *J* = 6.09 Hz, 1H).

^{13}**C-NMR** (50 MHz, $CDCl_3$): δ (ppm) 18.14, 19.63, 20.18, 25.14, 25.44, 30.06, 31.75, 39.33, 37.97, 68.17, 98.31.

MS [e/m (%)]: 184 (M+, <1); 169 (54); 127 (11); 109 (100); 93 (6); 82 (18); 81 (11); 67 (68); 59 (77); 55 (23); 54 (11); 43 (62); 41 (25); 39 (14).

Major *trans*-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.11 (d, *J* = 6.09 Hz, 3H), 1.38 (s, 3H), 1.45 (s, 3H), 3.90-4.09 (m, 2H).

^{13}**C-NMR** (50 MHz, $CDCl_3$): δ (ppm) 18.41, 19.02, 19.95, 24.64, 25.80, 30.29, 32.12, 47.76, 69.85, 73.14, 98.29.

MS [e/m (%)]: 184 (M+, <1); 169 (100); 127 (19); 109 (94); 93 (10); 82 (26); 81 (15); 67 (83); 59 (95); 55 (35); 54 (15); 43 (89); 41 (34); 39 (21).

Example 30: Preparation of 2-butyl-2,4-dimethylhexahydro-4*H*-benzo[d]-[1,3]dioxine (Iai)

[0078] Compound Iai is obtained as colourless oil in 10% yield, according to Example 23, from diol **Va** (40.57 g, 0.28 mol, obtained in Example 14), 2-hexanone (33.65 g, 0.34 mol) and cyclohexane (110 ml). It consists in a mixture of 2 isomers (94%) as *cis* and *trans* enantiomers in a 56:44 ratio.

Bp: 60°C / 0.47 torr

Olfactory profile: Camphoraceous, pharmaceuticals, caoutchouc.

Major cis-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$): δ (ppm) 0.80-0.95 (m, 3H); 1.02-1.20 (m, 5H); 1.20-1.50 (m, 10H); 1.50-1.87 (m, 6H); 3.92-4.13 (m, 2H).

^{13}**C-NMR** (50 MHz, $CDCl_3$, selected data): δ (ppm) 39.07 & 39.38; 67.45 & 67.63; 67.71 & 67.93; 99.35 & 99.41.

MS [e/m (%)]: 226 (M+, <1); 211 (29); 169 (29); 127 (7); 109 (100); 101 (30); 85 (17); 67 (42); 57 (13); 55 (20); 43 (44); 41 (18).

Major *trans*-isomers:

^{1}**H-NMR** (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.32-3.52 (m, 1H); 3.61 (ddd, *J* = 10.2 Hz, *J* = 6.1 Hz, *J* = 4.0 Hz, 1H).

^{13}**C-NMR** (50 MHz, $CDCl_3$, selected data): δ (ppm) 47.47 & 47.96; 69.34 & 69.58; 72.61 & 72.86; 100.19 & 100.26.

MS [e/m (%)]: 226 (M+, <1); 211 (92); 169 (88); 127 (15); 109 (100); 101 (53); 85 (44); 81 (14); 67 (61); 57 (26); 55 (40); 43 (86); 41 (34).

Example 31: Preparation of 4-methylhexahydro-*4H*-spiro[benzo[*d*][1,3]dioxine-2,1'-cyclopentane) (Iaj)

[0079] Compound **Iaj** is obtained as colourless oil in 16% yield, according to Example 23, from diol **Va** (40.57 g, 0.28 mol, obtained in Example 14), cyclopentanone (28.26 g, 0.34 mol) and cyclohexane (110 ml). It consists in a mixture of 2 isomers (97%) as *cis*/*trans* enantiomers in a 57:43 ratio.

Bp: 64-68°C / 0.57 torr

Olfactory profile: Peanut, animal, clean.

Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 1.06 (d, *J* = 6.6 Hz); 1.05-1.5 (m, 4H); 1.50-2.0 (m, 9H); 3.83-3.97 (m, 2H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.12; 20.31; 22.61; 24.61; 24.64; 25.15; 31.49; 31.81; 39.40; 40.46; 69.49; 69.75; 110.36.

MS [e/m (%)]: 210 (M+, 9); 181 (48); 109 (100); 85 (32); 81 (11); 67 (61); 56 (17); 55 (63); 43 (13); 41 (25); 39 (11).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.70-0.95 (m, 1H); 1.12 (d, *J* = 6.0 Hz, 3H); 3.34 (dt, *J*= 10.2 Hz, *J*= 3.8 Hz, I H); 3.52 (qd, *J* = 9.8 Hz, *J* = 6.1 Hz, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.53; 18.91; 22.53; 24.48; 25.40; 25.86; 31.65; 32.0; 40.55; 47.75; 71.41; 74.80; 110.25.

MS [e/m (%)]: 210 (M+, 8); 182 (16); 181 (100); 109 (67); 85 (32); 81 (10); 67 (52); 56 (21); 55 (77); 43 (13); 41 (27); 39 (12).

Example 32: Preparation of 2-(2,4-dimethylcyclohex-3-enyl)-4-methylhexahydro-4*H*-benzo[d][1,3]dioxine (Iak)

[0080] Compound **Iak** is obtained as colourless oil in 28% yield, according to Example 23, from diol **Va** (40 g, 0.278 mol, obtained in Example 14), 2,4-dimethylcyclohex-3-enecarbaldehyde (Triplal™, 46 g, 0.333 mol) and cyclohexane (140 ml). It consists in a mixture of isomers, with 4 main isomers (85%) in a 42:31:16:11 ratio (*cis*/*trans* ratio: 58:42).

Bp: 105°C / 0.4 torr

Olfactory profile: floral, green, a bit animalic.

Major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.86 (d, *J* = 6.8 Hz); 1.05-1.55 (m, 13H); 1.55-2.0 (m, 7H); 1.63 (s, 3H); 2.0-2.3 (m, 1H); 3.65-3.85 (m, 2H); 4.32-4.45 (m, 1H); 5.15 (br s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 101.80 & 101.84; 127.56; 132.65.

MS [e/m (%)]: 264 (M+, 5); 249 (7); 155 (11); 138 (25); 137 (21); 127 (24); 123 (28); 120 (42); 110 (14); 109 (100); 107 (32); 95 (14); 93 (13); 91 (12); 81 (17); 79 (15); 67 (52); 55 (20); 41 (17).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.0 (d, *J* = 7.0 Hz, 3H); 2.32-2.48 (m, 1H); 3.10-3.30 (m, 1H); 3.30-3.45 (m, 1H); 4.60-4.70 (m, 1H);5.33(brs, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 103.63 & 103.55; 127.52; 132.95.

MS [e/m (%)]: 264 (M+, 7); 249 (11); 155 (30); 138 (18); 137 (22); 127 (19); 123 (22); 120 (32); 110(13); 109 (100); 107 (31); 95 (13); 93 (13); 91 (12); 81 (16); 79 (13); 67 (46); 55 (23); 41 (19).

Minor *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.65-3.85 (m, 2H); 4.60-4.70 (m, 1H); 5.33 (br s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 102.02 & 102.12; 127.16; 133.05.

MS [e/m (%)]: 264 (M+, 11); 249 (21); 155 (15); 138 (20); 127 (15); 123 (10); 120 (15); 110 (10); 109 (100); 107 (18); 95 (13); 81 (15); 79 (12); 67 (44); 55 (16); 41 (13).

Minor *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.95-4.15 (m, 2H); 4.85-4.97 (m, 1H); 5.15 (br s, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 103.38; 127.35.

MS [e/m (%)]: 264 (M+, 15); 249 (41); 181 (11); 155 (50); 127 (16); 123 (12); 120 (14); 110 (10); 109 (100); 107 (16); 95 (12); 93 (10); 81 (16); 79 (12); 67 (43); 55 (19); 41 (16).

Example 33: Preparation of 4-methyl-4a,5,6,7,8,8a-hexahydro-4*H*-spiro[benzo[d][1,3]dioxine-2,1'-cyclohex[2]ene] (Ial)

[0081] Compound **Ial** is obtained as colourless oil, according to Example 23, from diol **Va** (40 g, 0.278 mol, obtained in Example 14) and cyclohexenone. It consists in a mixture of isomers in a 25:31:20:24 ratio.

1st isomers:

MS [e/m (%)]: 222 (M+, 15); 168 (97); 109 (100); 97 (12); 81 (13); 79 (16); 77 (12); 68 (22); 67 (55); 55 (24); 54 (24); 43 (10); 41 (26); 39 (19).

2nd isomers:

MS [e/m (%)]: 222 (M+, 44); 168 (12); 109 (100); 97 (14); 96 (47); 81 (28); 79 (18); 68 (18); 67 (59); 55 (15); 54 (22); 53 (11); 43 (13); 41 (25); 39 (17).

3rd isomers

MS [e/m (%)]: 222 (M+, 14); 168 (100); 109 (29); 97 (11); 81 (13); 79 (10); 68 (10); 67 (31); 55 (11); 54 (14).

4th isomers:

MS [e/m (%)]: 222 (M+, 100); 207 (13); 168 (53); 114 (14); 109 (70); 97 (16); 96 (81); 95 (14); 81 (57); 79 (24); 77 (12); 68 (18); 67 (64); 55 (37); 54 (27); 53 (18); 43 (18); 41 (39); 39 (23).

Example 34: Preparation of 4-ethyl-2-isopropyl-hexahydro-benzo[1,3]dioxine (Ibg)

[0082] Compound **Ibg** is obtained as colourless oil in 65% yield, according to Example 23, from diol **Vb** (35.65 g, 0.23 mol, obtained in Example 15), isobutyraldehyde (32.45 g, 0.45 mol) and cyclohexane (100 mL). It consists in a mixture of 6 isomers with 3 major isomers (85%) in a 63:20:17 ratio. The major enantiomers have the *cis* configuration.

Bp: 98°C / 6.8 torr

Olfactory profile: herbaceous, camomile

1st major isomers (*cis*-isomers):

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.85-1.00 (m, 3H); 0.94 (d, 3H, *J*= 6.8 Hz); 0.95 (d, 3H, *J* = 6.8 Hz); 1.01-1.82 (m, 10H); 1.83-1.75 (m, 2H); 3.41 (ddd, 1H, *J*= 2.0 Hz, *J*= 6.9 Hz, *J*= 8.0 Hz); 3.72 (m, 1H); 4.30(d, 1H, *J* = 4.4 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 9.8; 16.7; 17.1; 19.6; 20.3; 24.7; 25.4; 31.9; 32.8; 37.9; 75.0; 81.2; 105.0.

MS [e/m (%)]: 211 (M^+, 6); 169 (51); 141 (3); 131 (18); 111 (5); 123 (100); 93 (11); 82 (77); 81 (59); 73 (28); 67 (64); 55 (21); 41 (24).

2nd major isomers:

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 9.4; 25.4; 31.8; 32.8; 45.4; 80.5; 81.7; 105.5. **MS** [e/m (%)]: *idem* 1st major isomer.

3rd major isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.85-1.00 (m, 3H); 0.90 (d, 3H, *J* = 6.8 Hz); 0.91 (d, 3H, *J*= 6.8 Hz); 1.01-1.82 (m, 10H); 1.83-1.98 (m, 2H); 3.42 (m, 1H); 3.70 (ddd, 1H, *J* = 3.9 Hz, *J* = 5.5 Hz, *J* = 11.9 Hz); 4.38 (d, 1H, *J* = 5.6 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 9.9; 16.9; 17.5; 18.5; 24.5; 25.7; 26.4; 32.2; 32.7; 43.9; 74.8; 76.4; 97.9.

MS [e/m (%)]: 211 (M^+, 6); 169 (75); 141 (5); 123 (100); 111 (38); 93 (21); 82 (17); 81 (66); 73 (11); 67 (46); 55 (22); 41 (20).

1st minor isomers

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 44.2; 74.9; 79.6; 97.6.

MS [e/m (%)]: *idem* 3rd major isomer.

Example 35: Preparation of 2-methyl-4-phenyl-hexahydro-benzo[1,3]dioxine (Ica)

[0083] Compound **Ica** is obtained as white crystals in 25% yield, according to Example 23, from diol **Vc** (24.75 g, 0.12 mol, obtained in Example 16), acetaldehyde (17.29 g, 0.24 mol) and cyclohexane (50 mL). It consists in a mixture of 3 isomers with 1 major enantiomers (84%), as *cis*-isomers.

Bp: 88°C / 0.3 torr

Mp: ***57.4°C***

Olfactory profile: Spicy, exotic fruits

Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.85-1.20 (m, 2H); 1.21-1.51 (m, 2H); 1.47 (d, 3H, *J* = 5.1 Hz); 1.52-1.72 (m, 4H); 1.98 (m, 1H); 4.02 (m, 1H); 4.80 (m, 1H); 4.94 (q, 1H, *J* = 5.1 Hz); 7.29 (m, 5H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 20.1; 20.6; 21.3; 25.4; 31.9; 40.4; 75.4; 81.2; 99.3; 125.5; 126.9; 128.1; 140.4.

MS [e/m (%)]: 189 (1); 188 (1); 171 (1); 151 (15); 129 (4); 117 (6); 107 (100); 91 (16); 82 (41); 67 (52); 54 (16); 41 (8); 39 (6).

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.36 (d, 3H, *J* = 5.0 Hz); 3.90 (m, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 31.7; 47.0; 81.1; 84.3; 93.2; 127.3; 128.3.

2nd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 1.42 (d, 3H, *J* = 5.1 Hz); 3.42 (dt, 1H, *J* = 4.1 Hz, *J* = 10.5 Hz); 4.23 (d, 1H, *J* = 9.8 Hz); 4.97 (q, 1H, *J* = 5.1 Hz).

Example 36: Preparation of 4-isobutyl-2-methylhexahydro-4H-benzo[d][1,3]-dioxine (Ida)

[0084] Compound **Ida** is obtained as a colourless oil in 50% yield, according to Example 23, from diol **Vd** (24 g, 0.13 mol, obtained in Example 17), acetaldehyde (11.3 g, 0.26 mol) and cyclohexane (100 mL). It consists in a mixture of 6 isomers with 2 major isomers (75%) as *cis*/*trans* enantiomers in a 60:40 ratio.

Bp: 60°C/0.5 torr

Olfactory profile: Leathery, cresol.

Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.88 (d, *J* = 6.6 Hz, 3H); 0.89 (d, *J* = 6.6 Hz, 3H); 1.05-1.37 (m, 4H); 1.33 (d, *J* = 5.1 Hz, 3H); 1.37-1.55 (m, 3H); 1.55-1.80 (m, 3H); 1.80-2.20 (m, 2H); 3.58-3.71 (m, 1H); 3.74-3.80 (m, 1H); 4.72 (q, *J* = 5.09 Hz, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 19.84; 20.56; 21.21; 22.63; 22.94; 24.0; 25.33; 31.81; 38.16; 40.74; 75.43; 77.94; 98.89.

MS [e/m (%)]: 212 (M+, <0); 211 (2); 197 (1); 151 (3); 150 (3); 131 (14); 111 (4); 95 (13); 87 (16); (100); 69 (17); 67 (52); 55 (16); 43 (21); 41 (24).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.15-3.36 (m, 1H); 3.58-3.71 (m, 1H); 4.95 (m, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 25.72 & 25.79; 32.34 & 34.55; 43.67 & 45.93; 73.48 & 74.71; 78.85 & 80.69; 91.19 & 91.73.

MS [e/m (%)]: 212 (M+, <0); 211 (4); 197 (13); 155 (29); 151 (8); 131 (17); 111 (65); 95 (39); 93 (33); 87 (33); 83 (27); 82 (100); 81 (29); 79 (19); 69 (40); 67 (81); 57 (15); 55 (37); 54 (21); 45 (20); 43 (45); 41 (51); 39 (17).

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.42-3.60 (m, 1H); 3.96-4.05 (m, 1H); 4.76 (q, *J* = 10.2 Hz,1H)

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 25.38; 31.61; 38.07; 98.56.

MS [e/m (%)]: 212 (M+, <0); 211 (3); 197 (27); 155 (26); 151 (10); 131 (7); 111 (100); 95 (53); 93 (45); 83 (18); 82 (61); 81 (31); 79 (17); 69 (40); 67 (72); 55 (36); 54 (18); 45 (15); 43 (40); 41 (46); 39 (15).

2nd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 5.07 (q, *J* = 9.8 Hz, 1H).

MS [e/m (%)]: 212 (M+, <0); 211 (2); 197 (19); 151 (9); 150 (6); 131 (9); 111 (13); 95 (33); 87 (18); 83 (19); 82 (100); 81 (27); 79 (15); 69 (41); 67 (71); 57 (13); 55 (29); 54 (18); 45 (14); 43 (30); 41 (37); 39 (11).

Example 37: Preparation of 6-*tert*-butyl-2,4-dimethyl-hexahydro-benzo[1,3]-dioxine (l'aa)

[0085] Compound **l'aa** is obtained as a yellow oil in 26% yield, according to Example 23, from diol **V'a** (48.74 g, 0.24 mol, obtained in Example 18), acetaldehyde (35.23 g, 0.49 mol) and cyclohexane (100 mL). It consists in a mixture of 6 isomers with 3 major isomers (65%) in a 42:29:29 ratio.

Bp: 58°C / 0.3 torr

Olfactory profile: Sulfur, fatty.

1st major isomers (*cis*-isomers):

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.86 (s, 9H); 0.90-1.92 (m, 7H); 1.16 (d, 3H, *J* = 6.6 Hz); 1.33 (d, 3H, *J* = 5.1 Hz); 1.99 (m, 1H); 3.73 (m, 1H); 3.83 (m, 1H); 4.74 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.9; 21.2; 21.5; 25.6; 27.6; 32.6; 36.0; 39.8; 47.1; 74.9; 75.5; 98.7.

MS [e/m (%)]: 225 (M^+, 10); 211 (40); 165 (21); 149 (8); 138 (66); 125 (5); 109 (61); 108 (14); 95 (37); 83 (25); 82 (35); 81 (32); 80 (47); 79 (23); 67 (25); 57 (100); 55 (25); 43 (26); 41 (28).

2nd major isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.85 (s, 9H); 4.68 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 20.2; 29.4; 36.0.

MS [e/m (%)]: 225 (M^+, 2); 211 (2); 165 (5); 149 (10); 138 (21); 136 (100); 125 (20); 109 (24); 108 (11); 95 (18); 83 (19); 82 (29); 81 (29); 80 (38); 79 (22); 67 (21); 57 (74); 55 (21); 43 (22); 41 (24).

3rd major isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.84 (s, 9H); 0.90-1.85 (m, 7H); 1.19 (d, 3H, *J* = 6.3 Hz); 1.32 (d, 3H, *J* = 5.1 Hz); 1.96 (m, 1H); 3.15 (ddd, 1H, *J* = 4.1 Hz, *J* = 9.8 Hz, *J* = 11.2 Hz); 3.38 (dt, l H, *J* = 6.3 Hz, *J* = 9.7 Hz); 4.78 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 18.6; 21.2; 25.3; 26.5; 27.8; 31.6; 32.3; 46.7; 47.0; 77.1; 80.6; 98.4.

MS [e/m (%)]: *idem* 1st major isomers.

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.83 (s, 9H); 1.24 (d, 1H, *J* = 7.0 Hz); 1.26 (d, ^{3}H, *J* = 5.1 Hz); 1.96 (m, 1H); 3.47 (dt, 1H, *J* = 4.4 Hz, *J* = 10.7 Hz); 4.07 (dq, 1H, *J* = 7.0 Hz, *J* = 12.8 Hz); 5.03 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 13.0; 21.3; 25.3; 27.4; 27.5; 32.1; 32.2; 43.2; 47.5; 72.0; 74.2; 91.1.

MS [e/m (%)]: *idem* 1st major isomers.

2nd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.83 (s, 9H); 3.16 (m, 1H); 3.44 (m, 1H); 4.69 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 18.0; 20.2; 25.6: 27.6; 32.0; 41.1; 47.1; 75.2; 75.7; 98.6.

MS [e/m (%)]: 211 (85); 165 (24); 149 (8); 138 (19); 125 (9); 109 (72); 108 (27); 95 (40); 83 (34); 82 (32); 81 (28); 80 (30); 79 (24); 67 (25); 57 (100); 55 (29); 43 (26); 41 (27).

Example 38: Preparation of 6-*tert*-butyl-4-ethyl-2-isopropyl-hexahydrobenzo-[1,3]dioxine (I'bg)

[0086] Compound **I'bg** is obtained as a pale yellow oil in 21% yield, according to Example 23, from diol **V'b** (17.83 g, 0.08 mol, obtained in Example 19), isobutyraldehyde (7.19 g, 0.1 mol) and cyclohexane (40 mL). It consists in a mixture of 5 isomers with 2 major isomers (76%) as *cis*/*trans* enantiomers in a 63:37 ratio.
Bp: 88°C/0.7 torr
Olfactory profile: herbaceous, camomile, woody.
Major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.84 (s, 9H); 0.87-1.00 (m, 3H); 0.92 (d, 6H, *J* = 7.0 Hz); 1.01-1.70 (m, 9H); 1.77 (m, 1H); 1.19 (m, 1H); 3.42 (ddd, 1H, *J* = 1.6 Hz, *J* = 6.1 Hz, J = 7.7 Hz); 3.64 (m, 1H); 4.28 (d, 1H, *J* = 4.4 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 9.9; 16.7; 17.1; 20.4; 21.4; 24.7; 27.5; 32.1; 32.5; 32.8; 38.6; 47.0; 74.5; 81.2; 104.9.

MS [e/m (%)]: 267 (M^+, 6); 225 (62); 179 (53); 163 (4); 138 (33); 136 (1); 123 (63); 109 (45); 95 (27); 83 (19); 82 (28); 81 (30); 80 (47); 79 (19); 67 (22); 57 (100); 55 (18); 43 (18); 41 (27).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.85 (s, 9H); 0.91 (d, 6H, *J* = 8.7 Hz); 3.42 (m, 1H); 3.75 (m, 1H); 4.22 (d, 1H, *J* = 4.5 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 9.9; 16.8; 17.1; 19.0; 24.8; 28.0; 29.5; 32.4; 32.7; 33.3; 47.0; 75.4; 81.0; 104.8.

MS [e/m (%)]: 267 (M^+, 3); 225 (23); 179 (49); 163 (7); 138 (25); 136 (49); 123 (66); 109 (42); 95 (27); 83 (20); 82 (27); 81 (29); 80 (42); 79 (22); 67 (23); 57 (100); 55 (20); 43 (19); 41 (29).

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.83 (s, 9H); 0.93 (d, 6H, *J* = 6.8 Hz); 3.09 (m, 2H); 4.23 (d, 1H, *J* = 5.6 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 9.5; 17.2; 17.6; 25.1; 25.2; 26.3; 27.6; 31.7; 32.8; 44.9; 47.1; 80.6; 81.9; 105.4.

MS [e/m (%)]: *idem* major *cis* isomers.

2nd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 4.50 (d, 1H, *J* = 4.2 Hz).

MS [e/m (%)]: *idem* major *cis* isomers.

3rd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 4.41 (d, 1H, *J* = 5.6 Hz).

MS [e/m (%)]: *idem* major *cis* isomers.

Example 39: Preparation of 6-*tert*-butyl-2-methyl-4-phenyl-hexahydrobenzo-[1,3]dioxine (I'ca)

[0087] Compound **I'ca** is obtained as white crystals in 21 % yield, according to Example 23, from diol **V'c** (11.55 g, 0.04 mol, obtained in Example 20), acetaldehyde (3.87 g, 0.09 mol) and cyclohexane (20 mL). It consists in a mixture of 3 isomers with 2 major isomers (77%) as *cis* isomers in a 56:44 ratio. The crude product was purified by col-

umn chromatography on SiO_2 (AcOEt/Hexane (5:95)) The *cis* isomers were obtained as white crystals, whereas the minor *trans* isomer was obtained as a colourless oil.
Olfactory profile: green, chemicals.
Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.73 (s, 9H); 0.80-1.80 (m, 7H); 1.46 (d, 3H, *J* = 5.1 Hz); 2.08 (m, 1H); 3.96 (m, 1H); 4.84 (m, 1H); 4.93 (m, 1H); 7.29 (m, 5H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 20.7; 21.2; 21.4; 27.4; 32.1; 32.5; 40.8; 47.1; 74.9; 81.1; 99.1; 125.3; 126.8; 127.9; 140.0.

MS [e/m (%)]:287 (M^+, 1); 229 (2); 151 (27); 138 (20); 107 (100); 80 (24); 77 (7); 57 (30); 51 (1); 39 (2).

Minor *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$. selected data): δ (ppm) 0.71 (s, 9H); 1.45 (d, 3H, *J* = 5.1 Hz); 4.08 (m, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 19.1; 20; 21.2; 27.9; 29.3; 33.4; 35.6; 41.1; 75.4; 80.3; 98.7; 125.1; 126.7; 127.9; 140.3.

MS [e/m (%)]: *idem cis*-isomers.

Minor *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.74 (s, 9H); 0.80-1.75 (m, 6H); 1.42 (d, 3H, *J* = 5.1 Hz); 1.76-1.95 (m, 1H); 2.03 (m, 1H); 3.37 (ddd, 1H, *J* = 4.2 Hz, *J* = 9.7 Hz, *J* = 11.2 Hz); 4.24 (d, 1H, *J* = 9.9 Hz); 4.98 (q, 1H, *J* = 5.1 Hz); 7.31 (m, 5H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 21.3; 25.4; 26.4; 27.5; 31.7; 32.3; 46.3; 46.8; 80.3; 84.4; 99.1; 127.3; 128.0; 128.3; 139.4.

MS [e/m (%)]: *idem* major *cis* isomers.

Example 40: Preparation of 2,4,6,6-tetra-methyl-hexahydro-benzo[1,3]dioxine (I"aa)

[0088] Compound **I"aa** is obtained as a colourless oil in 58% yield, according to Example 23, from diol **V"a** (74.08 g, 0.43 mol, obtained in Example 21), acetaldehyde (61.95 g, 0.86 mol) and cyclohexane (180 mL). It consists in a mixture of 4 isomers with 2 major isomers (75%) as *cis*/*trans* enantiomers in a 55:45 ratio.

Bp: 52°C / 1.1 torr

Olfactory profile: Aromatic, woody, powerful.

Major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.86 (s, 3H); 0.94 (s, 3H); 0.95-1.65 (m, 6H); 1.11 (d, 3H, *J* = 6.6 Hz); 1.32 (d, 3H, *J* = 5.1 Hz); 1.72 (m, 1H); 3.72 (m, 1H); 3.82 (dq, 1H, *J* = 2.4 Hz, *J* = 6.6 Hz); 4.72 (q, 1 H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.8; 21.2; 24.2; 27.6; 29.9; 32.1; 33.0; 33.2; 35.4; 74.7; 75.3; 98.7.

MS [e/m (%)]: 197 (M^+, 4); 183 (8); 155 (2); 137 (31); 110 (100); 95 (67); 89 (22); 81 (63); 69 (11); 55 (16); 43 (20).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.91 (s, 3H); 0.94 (s, 3H); 1.16 (d, 3H, *J* = 6.3 Hz); 1.33 (d, 3H, *J* = 5.1 Hz); 3.15 (ddd, 1H, *J*= 4.6 Hz, *J*= 9.7 Hz, *J* = 10.9 Hz); 3.35 (dq, 1H, *J* = 6.3 Hz, *J* = 9.3 Hz); 4.78 (q, 1H, *J* = 5.1 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 18.5; 21.2; 25.2; 27.7; 30.7; 32.7; 37.3; 38.9; 42.6; 77.3; 81.1; 98.5.

MS [e/m (%)]: 197 (M^+, 15); 183 (95); 155 (3); 137 (57); 110 (95); 95 (97); 81 (100); 69 (21); 55 (28); 43 (33); 41 (23).

1st minor isomers:

MS [e/m (%)]:197 (M^+-, 11); 183 (100); 155 (8); 137 (68); 110 (42); 95 (68); 81 (77); 69 (19); 55 (24); 43 (28); 41 (19).

Example 41: Preparation of 4,6,6-trimethyl-2-((*E*)-propenyl)-hexahydrobenzo-[1,3]dioxine (I"ac)

[0089] Compound **I"ac** is obtained as a yellow oil in 56% yield, according to Example 23, from diol **V"a** (31.01 g, 0.18 mol, obtained in Example 21), crotonaldehyde (14.72 g, 0.21 mol) and cyclohexane (80 mL). It consists in a mixture of 8 isomers with 2 major isomers (76%) as *cis*/*trans* enantiomers in a 55:45 ratio.

Bp: 80°C / 0.8 torr

Olfactory profile: herbal, minty, fruity

Major *cis*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.96 (s, 6H); 1.00-1.65 (m, 6H); 1.19 (d, 3H, *J* = 9.0 Hz); 1.17-1.85 (m, 1H); 1.71 (d, 3H, *J* = 1.3 Hz); 3.23 (ddd, 1H, *J* = 4.6 Hz, *J* = 10.0 Hz, *J* = 10.7 Hz); 3.44 (dq, 1H, *J* = 6.1 Hz, *J* = 9.0 Hz); 5.04 (d, 1H, *J* = 5.6 Hz); 5.60 (m, 1H); 5.93 (m, 1H).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.7; 25.2; 27.6; 30.7; 32.0; 32.7; 38.9; 42.7; 74.8; 75.4; 100.7; 128.3; 130.7.

MS [e/m (%)]: 223 (M^+, 16); 210 (8); 209 (60); 183 (4); 137(44); 99 (14); 95 (59); 81 (80); 71 (100); 69 (42); 55 (32); 43 (22); 41 (30).

Major t*rans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 0.88 (s, 3H); 0.93 (s, 3H); 1.16 (d, 3H, *J* = 8.9 Hz); 1.74 (d, 3H, *J* = 1.4 Hz); 3.81 (m, 1H); 3.89 (m, 1H); 4.97 (d, 1H, *J* = 6.0 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 17.8; 24.2; 27.7; 29.8; 32.9; 33.1; 35.5; 37.3; 77.4; 81.1; 101.2; 128.6; 130.8.

MS [e/m (%)]: *idem cis*-isomers.

1st minor isomers:

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 96.9; 127.7; 129.8.

MS [e/m (%)]: *idem cis*-isomers.

2nd minor isomers:

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 97.1; 127.9; 129.9.

MS [e/m (%)]: *idem cis*-isomers.

Other minor isomers:

MS [e/m (%)]: 210 (12); 209 (92); 137 (100); 127 (9); 99 (1); 95 (15); 81 (12); 71 (4); 69 (7); 55 (19); 43 (8); 41 (8).

Example 42: Preparation of 4-ethyl-2-isopropyl-6,6-dimethyl-hexahydrobenzo-[1,3]dioxine (I"bg)

[0090] Compound **I"bg** is obtained as a colourless oil in 31% yield, according to Example 23, from diol **V"b** (29.81 g, 0.16 mol, obtained in Example 22), isobutyraldehyde (23.05 g, 0.32 mol) and cyclohexane (70 mL). It consists in a mixture of 4 isomers with 2 major isomers (74%) as *cis*/*trans* enantiomers in a 60:40 ratio.
Bp: 106°C/5.9 torr
Olfactory profile: herbaceous
Major cis-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$): δ (ppm) 0.55-1.00 (m, 15H); 1.01-1.67 (m, 8H); 1.68-1.90 (m, 2H); 3.44 (ddd, 1H, J = 4.0 Hz, J = 7.4 Hz, J = 10.0 Hz); 3.66 (m, 1H); 4.27 (d, 1H, J = 4.6 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 9.8; 17.3; 24.2; 24.6; 27.8; 29.9; 32.4; 32.9; 33.3; 34.1; 37.3; 69.1; 80.9; 105.0.

MS [e/m (%)]: 239 (M^+, 4); 197 (34); 151 (100); 139 (1); 110 (70); 109 (25); 95 (69); 81 (45); 69 (17); 55 (15); 43 (18); 41 (21).

Major *trans*-isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 3.10 (m, 1H); 3.44 (m, 1H); 4.41 (d, 1H, J = 5.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$): δ (ppm) 10.0; 18.5; 24.6; 28.3; 30.9; 33.2; 39.4; 74.5; 77.2; 97.7.

MS [e/m (%)]: 239 (M^+, 5); 197 (69); 151 (68); 139 (26); 110 (14); 109 (27); 95 (100); 81 (44); 69 (27); 55 (24); 43 (23); 41 (24).

1st minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 4.24 (d, 1H, J = 6.0 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 105.6.

MS [e/m (%)]: 239 (M^+, 5); 197 (54); 151 (41); 139 (3); 110 (48); 109 (17); 95 (100); 81 (53); 69 (20); 55 (19); 43 (18); 41 (21).

2nd minor isomers:

^{1}H-NMR (200 MHz, $CDCl_3$, selected data): δ (ppm) 4.48 (d, I H, J = 4.7 Hz).

^{13}C-NMR (50 MHz, $CDCl_3$, selected data): δ (ppm) 97.5.

MS [e/m (%)]: 239 (M^+, 4); 197 (65); 151 (100); 139 (22); 110 (12); 109 (26); 95 (63); 81 (29); 69 (24); 55 (20); 43 (20); 41 (19).

Example 43: Fragrance composition comprising the compound obtained in Example 28

[0091] A green woody fougere composition was prepared from the following ingredients:

Ingredients	**Composition A**	**Composition B**
Adoxal® 10% in DPG.	3	3
Allyl amyl glycolate	15	15
Basilic Indes ess.	3	3
Bergamote	100	100
Bouleau feuilles	5	5

Ingredients	Composition A	Composition B
Calone 1951® 10% in DPG	10	10
Cedramber®	60	60
Cedre feuilles ess.	5	5
Cinnamique 10% in DPG	5	5
Citron	50	50
Citronellol pur	10	10
Corps lrg 0201 10% in DPG	40	40
Coumarine 10% in DPG	150	150
Dihydromyrcenol	90	90
Eugenol rect. VMF	10	10
Floralozone® 10% in DPG	15	15
Folione® 10% in DPG	1	1
Geranium chine ess.	5	5
Helional®	15	15
cis-3-Hexenol 10% in DPG	10	10
Ionone beta	15	15
Lavandin grosso ess.	10	10
Linalol	25	25
Linalyle acetate	50	50
Mazarine®	5	5
Melonal® 10% in DPG	5	5
Methyl dihydrojasmonate	50	50
cis-6-Nonenol 1% in DPG	5	5
Octahydro tetramethyl acetonaphtone	133	133
Orcanox®	1	1

Ingredients	**Composition A**	**Composition B**
Patchouly ess.	15	15
Quinoleine isobutyl 10% in DPG	5	5
Sandalore®	20	20
Styrallyle acetate	5	5
Verdox® 50% in DPG	54	54
2-Ethyl-4-methylhexahydro-*4H*-benzo[*d*][1,3]dioxine (Example 28)	-	**10**
DPG	100	90
TOTAL	1000	1000

[0092] Evaluated at usual dilution in alcohol, composition A was described as very aromatic, with a tarragon note and a cyste-moss dry-down note whereas composition B (containing 2-ethyl-4-methylhexahydro-4*H*-benzo[*d*][1,3]dioxine) has a fresher note (hesperidic, grapefruit, with a slight sulphur undertone) and marine facets giving a more modern impact to the fragrance.

[0093] Evaluated at usual dilution in a shower gel base, compositions A and B show no real difference in the fragrance perception, however adding 2-ethyl-4-methylhexahydro-*4H*-benzo[*d*][1,3]dioxine to the composition brings more power to the note.

Example 44: Fragrance composition comprising the compound obtained in Example 28

[0094] A floral hesperidic watery composition was prepared from the following ingredients:

Ingredients	Composition A	Composition B
Allyl Cyclohexylpropionate	1	1
Ambrettolide VMF	10	10
Benzyl Salicylate 50% in DPG	30	30
Bourgeonal®	3	3
Calone 1951® 10% in DPG	12	12
Citron	104	104
Citronellyl acetate	2	2
Corps LRG 0201 10% in DPG	10	10
Methylpamplemousse	10	10
Cyclamen Aldehyde Extra®	1	1
Cyclemone A® 10% in DPG	50	50
Dihydromyrcenol	10	10
Ethyl Linalol	25	25
Floralozone®	1	1
Florol®	35	35
Gamma Decalactone 10% in DPG	8	8
Geraniol	10	10
Hexalon®	3	3
cis-3-Hexenol 10% in DPG	50	50
cis-3-Hexenyl Acetate 10% in DPG	3	3
Hexylcinnamic aldehyde	20	20
Indol 10% in DPG	1	1
Ionone Beta	10	10
Lemarome®	2	2

Ingredients	Composition A	Composition B
Liffarome® 10% in DPG	6	6
Linalol	35	35
Linalyl Acetate	60	60
Melonal® 10% in DPG	4	4
Methyl dihydrojasmonate	142	142
Octahydro tetramethyl acetonaphtone	35	35
Orange Bresil val. Ess.	80	80
Patchouly Ess.	4	4
Styrallyl acetate	2	2
Triplal® 10% in DPG	15	15
Vanilline 10% in DPG	4	4
Verdox® 50% in DPG	2	2
DPG	200	195
2-Ethyl-4-methylhexahydro-*4H*-benzo[*d*][1,3]dioxine (Example 28)	-	**5**
TOTAL	800	800

[0095] These two compositions were used in a shower gel base and in alcohol at usual dilutions, known from the person of the art, and the samples containing the compound 2-ethyl-4-methylhexahydro-*4H*-benzo[*d*][1,3]dioxine showed a fresher lemon zest note.

[0096] In alcohol, composition B was also described as having green acidulous facets with a more floral indolic middle note, imparting a nicer and less "technique" impact to the fragrance.

Example 45: Fragrance composition comprising the compound obtained in Example 27

[0097] A wisteria accord was prepared from the following ingredients:

Ingredients	**Composition A**	**Composition B**
Ambrettolide	20	20
Anisic aldehyde	20	20
Benzyl acetate	40	40
Benzylsalicylate	125	125
Cinnamyl acetate	50	50
DPG	10	-
Geraniol	200	200
Heliotropine	50	50
Hydroxycitronellal	120	120
Isobutyl phenylacetate	50	50
Jasmine Absopop™	10	10
Methyl phenylacetate	5	5
Mimosa Inde abs.	20	20
Oranger Absopop™	10	10
Phenylethyl alcohol	60	60
Terpineol	100	100
Ylang-Ylang ess. extra	60	60
2-Benzyl-4-methyl-hexahydro-benzo[1,3]dioxine (Example 27)	**-**	**10**
TOTAL	950	950

[0098] Adding 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxine to Composition A (Composition B) brings a more floral, honey-like and natural aspect to the wisteria accord, giving a rounder, sugary facet, with some lily-of-the-valley undertone.

Example 46: Fragrance composition containing the derivative obtained in Example 27

[0099] A rose accord was prepared from the following ingredients:

Ingredients	**Composition A**	**Composition B**
Aldehyde C11 lenique, 10% DPG	7	7
Bacdanol®	4	4
Citronellol	240	240
Citronellyl acetate	3	3
DPG	10	-
Eugenol	3	3
Geraniol	30	30
Lilial®	15	15
Methyl phenylacetate	6	6
Methylionantheme	15	15
Phenyl oxide	6	6
Phenylacetic aldehyde dimethyl acetal	5	5
Phenylethyl acetate	6	6
Phenylethyl alcohol	420	420
Rosafix®	15	15
Triplal®	5	5
2-Benzyl-4-methyl-hexahydro-benzo[1,3]dioxine (Example 27)	**-**	**10**
TOTAL	790	790

[0100] Adding 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxine to Composition A (Composition B) gives a more natural and green aspect to the rose accord and adds sweet, powdery facets.

Example 47: Fragrance composition comprising the compound obtained in Example 27

[0101] A mimosa accord was prepared from the following ingredients:

Ingredients	**Composition A**	**Composition B**
Anisic aldehyde	130	130
DPG	485	475
Heliotropine	15	15
Hexyl cinnamic aldehyde	370	370
2-Benzyl-4-methyl-hexahydro-benzo[1,3]dioxine (Example 27)	**-**	**10**
TOTAL	1000	1000

[0102] Adding 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxine to Composition A (Composition B) really impacts the fragrance to a nice mimosa note, with powdery and green aspects.

Example 48: Fragrance composition comprising the compound obtained in Example 27

[0103] A nenuphar accord was prepared from the following ingredients:

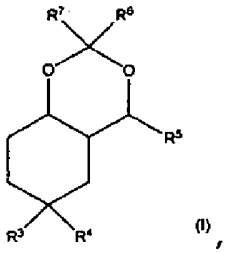
Ingredients	**Composition A**	**Composition B**
Benzyl acetate	360	360
Beta-Ionone	28	28

Ingredients	**Composition A**	**Composition B**
Canthoxal	4	4
Dihydromyrcenol	90	90
DPG	10	-
Ethyl phtalate	52	52
EThyl vanillin	2	2
Eugenol	8	8
Gamma-decalactone	4	4
Geraniol	15	15
Helional	8	8
Hexyl acetate	10	10
Hexyl cinnamic aldehyde	20	20
Indol	2	2
Lauric aldehyde	2	2
Linalol	160	160
Melonal	2	2
Methyl dihydro jasmonate	120	120
Musc T	30	30
Phenyl ethyl alcohol	50	50
Propyl gaiacol	8	8
Triplal	1	1
2-Benzyl-4-methyl-hexahydro-benzo[1,3]dioxine (Example 27)	**-**	**10**
TOTAL	790	790

[0104] Adding 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxine to Composition A (Composition B) gives a more natural and sweet water-lily note, with a slight jasminic facet.

PATENTKRAV

1. Forbindelse med formlen:



(I),

hvor:

- R^3 og R^4 uafhængigt er et hydrogenatom, en C1-C6-alkylgruppe eller en C2-C6-alkenylgruppe,

- R^5 er en methyl-, ethyl-, *i*-butyl-, *t*-butyl-, n-pentyl-, en C2-C6-alkenylgruppe eller en $(CH_2)_{0-2}$-arylgruppe,

- R^6 er en C1-C6-alkylgruppe, en C2-C6-alkenylgruppe, en $(CH_2)_{0-2}$-arylgruppe eller en C5-C6-cycloalkyl- eller cycloalkenylgruppe, og

- R^7 er et hydrogenatom, en C1-C6-alkylgruppe eller en C2-C6-alkenylgruppe;

eller

- R^3, R^4 og R^5 er som defineret ovenfor, og

- R^6 og R^7 sammen med det carbonatom, til hvilket de er bundet, danner en C5-C6-cycloalkyl- eller cycloalkenylgruppe;

med det forbehold, at forbindelsen ikke er:

- 2,2-dimethyl-4-ethylhexahydrobenzo[1,3]dioxin

- 2,2-dimethyl-4-*n*-penthylhexahydrobenzo[1,3]dioxin

- 2,2-dimethyl-4-phenylhexahydrobenzo[1,3]dioxin

- 2,4-dimethylhexahydrobenzo[1,3]dioxin

- 2,4-diphenylhexahydrobenzo[1,3]dioxin

- 4-ethyl-2-methylhexahydrobenzo[1,3]dioxin

- 4-methyl-2-phenylhexahydrobenzo[1,3]dioxin

- 2,2,4-trimethylhexahydrobenzo[1,3]dioxin.

2. Forbindelse ifølge krav 1, hvor:

- R^3 og R^4 uafhængigt er valgt fra gruppen bestående af et hydrogenatom, methyl, ethyl, *i*-propyl, *i*-butyl og *t*-butyl,

- R^5 er valgt fra gruppen bestående af methyl, ethyl, *i*-butyl, *t*-butyl, *n*-pentyl, 1-propen-1-yl, allyl, vinyl og phenyl,

- R^6 er valgt fra gruppen bestående af methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, *n*-pentyl, 1-propen-1-yl, phenyl, benzyl og 2,4-dimethylcyclohexen-3-yl, og

- R^7 er valgt fra gruppen bestående af et hydrogenatom, methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, *i*-butyl, *t*-butyl, *n*-pentyl og 1-propen-1-yl.

3. Forbindelse ifølge krav 1 eller 2, hvor:

- R^3 og R^4 er hydrogenatomer,

- R^5 er valgt fra gruppen bestående af methyl, ethyl, *i*-butyl og phenyl,

- R^6 er valgt fra gruppen bestående af methyl, ethyl, *i*-propyl, phenyl, benzyl og 2,4-dimethylcyclohexen-3-yl, og

- R^7 er valgt fra gruppen bestående af et hydrogenatom, methyl og *n*-butyl.

4. Forbindelse ifølge krav 3, hvor:

- R^3, R^4 og R^7 er hydrogenatomer, og
- R^5 er methyl, og
- R^6 er ethyl eller benzyl.

5. Forbindelse ifølge krav 1 eller 2, hvor:

- R^3 og R^7 er hydrogenatomer,
- R^4 er *t*-butyl,
- R^5 er methyl, ethyl eller phenyl, og
- R^6 er methyl eller *i*-propyl.

6. Forbindelse ifølge krav 1 eller 2, hvor:

- R^3 og R^4 er methyl,
- R^5 er methyl eller ethyl,
- R^6 er valgt fra gruppen bestående af methyl, *i*-propyl og 1-propen-1-yl, og
- R^7 er et hydrogenatom.

7. Forbindelse ifølge krav 1, som er valgt fra gruppen bestående af:

- 2,4-dimethyl-hexahydro-benzo[1,3]dioxin
- 4-methyl-2-pentyl-hexahydro-benzo[1,3]dioxin
- 4-methyl-2-propenyl-hexahydro-benzo[1,3]dioxin
- 4-methyl-2-phenyl-hexahydro-benzo[1,3]dioxin

- 2-benzyl-4-methyl-hexahydro-benzo[1,3]dioxin

- 2-ethyl-4-methylhexahydro-4*H*-benzo[*d*][1,3]dioxin

- 2,2,4-trimethylhexahydro-4*H*-benzo[*d*][1,3]dioxin

- 2-butyl-2,4-dimethylhexahydro-4*H*-benzo[*d*][1,3]dioxin

- 4-methylhexahydro-4*H*-spiro[benzo[*d*][1,3]dioxin-2,1'-cyclopentan]

- 2-(2,4-dimethylcyclohex-3-enyl)-4-methylhexahydro-4*H*-benzo[d][1,3]dioxin

- 2-(2,4-dimethylcyclohex-3-enyl)-4-methylhexahydro-4*H*-benzo[d][1,3]dioxin

- 4-ethyl-2-isopropyl-hexahydro-benzo[1,3]dioxin

- 2-methyl-4-phenyl-hexahydro-benzo[1,3]dioxin

- 4-isobutyl-2-methylhexahydro-4H-benzo[d][1,3]dioxin

- 6-*tert*-butyl-2,4-dimethyl-hexahydro-benzo[1,3]dioxin

- 6-*tert*-butyl-4-ethyl-2-isopropyl-hexahydro-benzo[1,3]dioxin

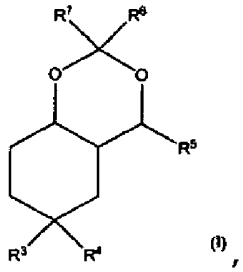
- 6-*tert*-butyl-2-methyl-4-phenyl-hexahydro-benzo[1,3]dioxin

- 2,4,6,6-tetra-methyl-hexahydro-benzo[1,3]dioxin

- 4,6,6-trimethyl-2-((*E*)-propenyl)-hexahydro-benzo[1,3]dioxin

- 4-ethyl-2-isopropyl-6,6-dimethyl-hexahydro-benzo[1,3]dioxin.

8. Duftpræparat, der som duftmiddel omfatter mindst én forbindelse med formlen:



(I)

hvor:

- R^3 og R^4 uafhængigt er et hydrogenatom, en C1-C6-alkylgruppe eller en C2-C6-alkenylgruppe,

- R^5 er en C1-C6-alkylgruppe, en C2-C6-alkenylgruppe eller en $(CH_2)_{0-2}$-arylgruppe,

- R^6 er en C1-C6-alkylgruppe, en C2-C6-alkenylgruppe, en $(CH_2)_{0-2}$-arylgruppe eller en C5-C6-cycloalkyl- eller cycloalkenylgruppe, og

- R^7 er et hydrogenatom, en C1-C6-alkylgruppe eller en C2-C6-alkenylgruppe;

eller

- R^3, R^4 og R^5 er som defineret ovenfor, og

- R^6 og R^7 sammen med det carbonatom, til hvilket de er bundet, danner en C5-C6-cycloalkyl- eller cycloalkenylgruppe.

9. Præparat ifølge krav 8, der som duftmiddel omfatter mindst én forbindelse ifølge et hvilket som helst af kravene 1 til 7.

10. Præparat ifølge krav 8 eller 9, som er valgt fra gruppen bestående af parfumerede baser, koncentrater, duftstoffer, parfumer og lignende produkter.

11. Præparat ifølge krav 8 eller 9 som maskeringsmiddel for lugte.