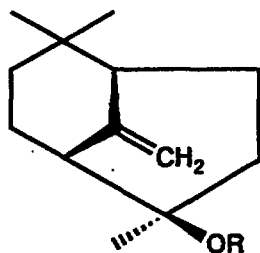


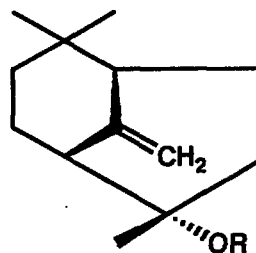
Description

The invention is concerned with novel odorant mixtures, namely mixtures of compounds of the formulae



Ia

and



Ib

wherein R signifies C₁₋₄-alkyl, e.g. methyl, ethyl, propyl, isopropyl, butyl, in a ratio of at least 1.1:1, especially of 2.2-3.0:1.

Hereinafter, Ia is also denoted as the exo form, Ib is denoted as the endo form. The mixtures in accordance with the invention are also denoted hereinafter as "I".

The invention is also concerned with a process for the manufacture of the mixtures I in accordance with the invention.

This process is characterized by cyclizing a dihydro- α -ionone, di-C₁₋₄-alkyl ketal or a C₁₋₄-alkyl enol ether of dihydro- α -ionone by means of a strong acid.

Protonic acids or Lewis acids come into consideration as strong acids. Examples are: hydrogen chloride gas, sulphuric acid, phosphoric acid, trifluoroacetic acid, methanesulphonic acid, p-toluenesulphonic acid, camphorsulphonic acid, BF₃, BF₃·Et₂O, BF₃·H₃PO₄, acidic ion exchangers, e.g. Dowex 50, Nafion, inter alia, etc.

The aforementioned starting materials are preferably prepared in situ; conveniently by reacting dihydro- α -ionone with a corresponding ketalizing agent. Especially suitable ketalizing agents are the ortho-esters HC(OR)₃. These esters are conveniently reacted with dihydro- α -ionone in the presence of one of the aforementioned acids at about 40°C to about 50°C.

Suitable amounts of acid are not only catalytic amounts, but also larger amounts, e.g. up to about 10 mol%.

The cyclization is optionally carried out in a solvent, e.g. an optionally halogenated hydrocarbon. Convenient solvents are accordingly hexane, cyclohexane, methylene chloride, ethylene chloride, chloroform, ethanol etc.

The ketal and enol ether stages are passed through in this procedure. Since especially the enol ether cyclizes spontaneously under the influence of catalytic amounts of acid, when it is used as the starting material the cyclization can be carried out at low temperatures, i.e. about -10°C to $+10^{\circ}\text{C}$, especially 0°C to 10°C . Although catalytic amounts of acid suffice, higher amounts, e.g. up to about 0.15 mol/mol of educt, also come into consideration.

For the working-up, the reaction product is conveniently neutralized with a base and thereupon, for isolation, it can be distilled.

The mixtures I are distinguished especially by powerful and very natural-warm notes in the direction of tobacco, ambergris and wood. In compositions this latter woody note comes into play especially and at the same time there are observed pronounced harmonizing effects which usually can be produced only with additions of ethereal oils of a complex composition. Moreover, the compositions are distinguished by an increased diffusion and a greatly improved substantivity.

It has now surprisingly been found that it is just the higher content of exo isomers Ia which is responsible for the interesting organoleptic effects of the mixtures in accordance with the invention, and which higher content of exo isomers is made available by the process in accordance with the invention. A possibly higher content of Ia is obtained e.g. by isolating, conveniently as described above, at the enol ether stage.

The ethyl ether stands in the foreground of interest, it has a woody, amber-like, flowery odour (in the direction of iris roots) with aspects of patchouli, muscatel sage and tobacco.

The methyl ester has similar olfactory properties.

The invention is accordingly also concerned with the use of the mixtures I as odorants.

On the basis of their natural olfactory notes the mixtures I are especially suitable for modifying known compositions.

The manner in which the mixtures I round-off and harmonize the olfactory notes of known compositions without, however, dominating in an unpleasant manner is remarkable.

The mixtures I combine with numerous known odorant ingredients of natural or synthetic origin, whereby the range of the natural raw materials can embrace not only readily-volatile but also moderately-volatile and difficultly-volatile components and that of the synthetics can embrace representatives from practically all classes of substances, as is evident from the following compilation:

- Natural products such as tree moss absolute, basil oil, citrus oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil, Paraguay, wormwood oil,
- alcohols such as farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol,
- aldehydes such as citral, Helional®, α -hexyl cinnamaldehyde, hydroxycitronellal, Lilial® (p-tert.butyl- α -methyl-dihydrocinnamaldehyde), methylnonylacetaldehyde,
- ketones such as allylionone, α -ionone, β -ionone, isoraldein (isomethyl- α -ionone), methy lionone,
- esters such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate (citronellyl . O - CO -CO . OC₂H₅), decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, ethyl acetylacetate, hexenyl isobutyrate, linalyl acetate, methyl dihydrojasmonate, styrallyl acetate, vetiveryl acetate, etc.
- lactones such as γ -undecalactone,
- various components often used in perfumery such as musk ketone, indole, p-menthane-8-thiol-3-one, methyleugenol.

The mixtures I can be used in wide limits which can extend in compositions, for example, from about 0.1 (detergents) - about 20% (alcoholic solutions), but without these values being limiting values, since the experienced perfumer can also achieve effects with even lower concentrations or can synthesize novel complexes with even higher amounts. The preferred concentrations range between about 1 and about 10%. The compositions manufactured with I can be used for all kinds of perfumed consumer goods (eau de cologne, eau de toilette, extracts, lotions, creams, shampoos, soaps, salves, powders, toothpastes, mouth washes, deodorants, detergents, fabric conditioners, tobacco, etc.).

The mixtures I can accordingly be used in the manufacture of compositions and, as the above compilation shows, a wide range of known odorants or odorant mixtures can be used. In the manufacture of such compositions the known odorants enumerated above can be used according to methods known to the perfumer, such as e.g. from W.A. Poucher, *Perfumes, Cosmetics and Soaps* 2, 7th Edition, Chapman and Hall, London, 1974.

Example 1

2-Methoxy-9-methylene-2.6.6-trimethyl-bicyclo[3.3.1]nonane

120 g (0.563 mol) of dihydro- α -ionone, 65 g (0.612 mol) of trimethyl orthoformate and 200 ml of methylene chloride are treated dropwise while stirring during 15 minutes with a solution of 8 g of boron trifluoride etherate in 60 ml of methylene chloride and the mixture is subsequently held under reflux for 105 minutes. The reaction mixture is cooled and poured into 500 ml of a 5% aqueous potassium hydroxide solution. After the addition of 500 ml of methylene chloride and vigorous intermixing the phases are separated, the organic phase is washed with water and the solvent is distilled off. The residue (197.1 g) is fractionated in a vacuum over a 15 cm Widmer column. There are obtained 100.2 g of product of b.p. 44-47°/0.06-0.07 mbar (yield 87% of theory based on pure dihydro- α -ionone) as a colourless liquid which contains 72.3% of exo isomer and 20.1% of endo isomer of the desired bicyclo-nonane.

Example 2

2-Ethoxy-9-methylene-2.6.6-trimethyl-bicyclo[3.3.1]nonane

480 g (2.21 mol) of dihydro- α -ionone, 368 g (2.48 mol) of triethyl orthoformate and 480 ml of abs. ethanol are treated drop-

wise while stirring during 15 minutes with a solution of 34.5 g (0.31 mol) of boron trifluoride etherate in 500 ml of ethanol and the mixture is subsequently heated to an internal temperature of 46-48° for 60 minutes. After cooling the reaction mixture to room temperature it is stirred with 600 ml of a 10% aqueous sodium hydroxide solution. After extraction with ether and evaporation of the organic phase there are obtained 668.7 g of a slightly yellow liquid which, after flash distillation in a vacuum, gives 480.5 g of crude product (b.p. 45-73°, 0.07 mbar). After fractionation in a vacuum over a 20 cm Widmer column there are obtained 406.2 g (82.7% of theory) of a slightly yellowish coloured liquid (b.p. 48-67°, 0.06 mbar) which contains the desired bicyclo-nonane in an isomer ratio of exo:endo = 2:1.

Example 3

2-Methoxy-9-methylene-2,6,6-trimethyl-bicyclo[3.3.1]nonane

100 g of montmorillonite K-10 (Fluka AG, Buchs, Switzerland) are stirred with 450 ml of trimethyl orthoformate. The suspension is filtered over a suction filter and sucked off. The filter residue (216.3 g) is suspended in 300 ml of hexane. 53.5 g (0.258 mol) of dihydro- α -ionone are added dropwise to the suspension, which is cooled to 0°, during 5-10 minutes while stirring. The suspension is subsequently stirred at 0° for 15 minutes. After filtration over a suction filter and concentration of the filtrate there remain 63.7 g of a colourless liquid which consists to about 95% of 6-(3,3-dimethoxybutyl)-1,5,5-trimethyl-cyclohexene (dihydro- α -ionone dimethyl ketal).

The crude dimethyl ketal can be purified by vacuum distillation over sodium carbonate; b.p. 61-65°/0.04-0.05 mbar.

14.1 g of crude dimethyl ketal are treated with 0.1 g of montmorillonite K-10 and heated to 110° in a distillation apparatus. Methanol begins to distil off at this temperature. After about 2 hours (110-120°) methanol no longer passes over. After cooling to 45° the mixture is fractionated in a vacuum (0.05-0.06 mbar). The product contains 80% of the desired bicyclo-nonane with an amount of 55.2% of exo isomer and 24.8% of endo isomer.

Example 42-Methoxy-9-methylene-2,6,6-trimethyl-bicyclo[3.3.1]nonane

50.8 g of crude dimethyl ketal (purity 95%, 0.2 mol) are heated to 320° in a distillation apparatus in the presence of glass Raschig rings. Methanol begins to distil off at a temperature of 230°. The dimethyl ketal is converted after about 7 hours. The reaction mixture is cooled to about 50° and distilled over a 10-cm Widmer column in a vacuum. At 52-56°/0.05 mbar there pass over 34.4 g (81.7% of theory) of a colourless liquid which consists to about 93% of an isomer mixture of 6-(3-methoxy-butenyl)-1,5,5-trimethyl-cyclohexene [namely E- and Z-6-(3-methoxy-2-butenyl)- as well as 6-(3-methoxy-3-butenyl)-1,5,5-trimethyl-cyclohexene].

2.0 g of this enol ether mixture (9.6 mmol) are dissolved in 3.5 ml of methylene chloride and treated at 0° with 2.4 ml of a 10% solution of boron trifluoride etherate in methylene chloride. After 5 minutes the mixture is filtered over a layer of Alox B, act. 1 (JCN Biomedicals, Eschwege, Germany). After evaporation of the solvent there are obtained 1.9 g (95% of theory) of a colourless liquid which contains 68.7% of exo isomer and 4.6% of endo isomer of the desired bicyclo-nonane.

Example 52-Ethoxy-9-methylene-2,6,6-trimethyl-bicyclo[3.3.1]nonane

19.4 g of dihydro- α -ionone (purity 93.6%, 0.094 mol), 25.5 g of triethyl orthoformate, 10 ml of ethanol and 5.0 g of montmorillonite KSF (Fluka AG, Buchs, Switzerland) are stirred at room temperature for about 32 hours. After filtration and evaporation of the filtrate there are obtained 26.7 g of a yellowish liquid which contains 88% of 6-(3,3-diethoxy-butyl)-1,5,5-trimethyl-cyclohexene (dihydro- α -ionone diethyl ketal) in addition to about 4.5% of educt.

The crude diethyl ketal can be purified by flash distillation in a vacuum over sodium carbonate; b.p. 67-74°/0.06-0.07 mbar.

Upon distilling the crude diethyl ketone over a 15 cm Widmer column ethanol is cleaved off when a bath temperature of about 140° is attained and the ethanol distills off up to a bath temperature of about 160°. The distillation residue is cooled to 80-82° and the resulting product is fractionated in a vacuum. At

82-86°/0.09-0.1 mbar there passes over a colourless liquid which consists to 88.5% of an isomer mixture of 6-(3-ethoxy-butenyl)-1,5,5-trimethyl-cyclohexene [namely E- and Z-6-(3-ethoxy-2-butenyl)- as well as 6-(3-ethoxy-3-butenyl)-1,5,5-trimethylcyclohexene] (yield: 73.0% of theory based on dihydro- α -ionone used).

2.0 g of this enol ether mixture (7.9 mmol) are dissolved in 3 ml of methylene chloride and treated at 0° with 2.2 ml of a 10% solution of boron trifluoride etherate in methylene chloride. After 5 minutes the mixture is filtered over a layer of Alox B, act. 1 (see Example 4). After evaporation of the solvent there are obtained 1.9 g (95% of theory) of a colourless liquid which contains the exo and endo isomers of the desired bicyclo-nonane in a ratio of exo:endo = 5:1.

Example 6

Odorant compositions

In the following Examples there is to be understood under product I a mixture Ia:Ib = 2:1, with R = ethyl, in accordance with the invention and under product X there is to be understood a known product - see US-PS 2803662 (Examples 3, 5). In the case of the known product the corresponding isomer ratio Ia:Ib is about 1:2.

The reason why different reaction products occur will be evident from the fact that the starting material is dihydro- α -ionone in the state of the art and a dihydro- α -ionone di-C₁₋₄-alkyl ketal or a C₁₋₄-alkyl enol ether of dihydro- α -ionone in the present case. Moreover, in the known case low temperatures are used, e.g. -13°C in Example 2, [while] higher temperatures are used in the present case, by which the reactions leading to different mixtures can be explained, see also *Helv. Chim. Acta* 38, [6], 1955, 1573 seq.

a) Lily of the valley base

	<u>Parts by weight</u>	
Linalyl acetate synth.	30	30
Benzyl acetate	30	30
Linalool synth.	40	40
Geranyl acetate	50	50
Lyrat® (IFF)	100	100
Citronellol extra	100	100
Benzyl salicylate	100	100
Sandela (Givaudan)	100	100
α -Hexylcinnamaldehyde	200	200
Product I	250	---
Product X	---	250

By virtue of its amber-like note the addition of the mixture I in accordance with the invention confers to this composition a substantially more elegant, flowery character which manifests itself primarily in the 24 hours values of the evaluation and which can be clearly recognized even after 3 days. In contrast, the composition with "X" becomes "harsh". The diffusion is quite generally increased by the addition of I in comparison to "X". This unexpected, intensified effect can last over several days.

b) Fougère base

	<u>Parts by weight</u>	
Coumarin crystallized	20	20
Basil oil	20	20
Geranium oil China	20	20
Tree moss absolute	40	40
Amyl salicylate	50	50
Benzyl salicylate	100	100
Lavender oil 40/42%	350	350
Product I	400	---
Product X	---	400

The fougere composition with "X" has, freshly dipped, a rather unpleasant, obtrusive smell which is reminiscent of the typical odour of lavender oil distillation installations. In contrast, the addition of the mixture I in accordance with the invention brings the so-called rustic ("agrestic") olfactory notes into harmony with the woody and mossy notes in an excellent manner

and confers softness and fullness to the composition, which can be clearly recognized even over several days as the odour fades away.

c) Tobacco base

	<u>Parts by weight</u>	
Eugenol, pure	20	20
Coumarin cryst.	30	30
Benzoin resinoid Siam	50	50
2,3,6,6-Tetramethyl-cyclohex(2)- ene-carboxylic acid ethyl ester mixture + 2-ethyl-6,6-dimethyl-cyclohex(2)- ene-carboxylic acid ethyl ester	50	50
Phenoxyethyl isobutyrate	100	100
Methyl cedryl ketone	150	150
Sandela® (Givaudan)	200	200
Product I	400	---
Product X	---	400

In this composition the addition of the mixture I in accordance with the invention, in contrast to product X, exhibits an unexpected sweetness in the freshly dipped state, which after 24 hours makes way for an underlining of the woody-amber like and spicy note. In contrast, the composition with "X" becomes more fatty and exhibits less character. Fullness and diffusion of the tobacco composition are only clearly underlined and intensified by the addition of I.

From the above Examples 6 a) to c) it is clearly evident that with a mixture I, in which in accordance with the invention the exo isomer predominates, there can be achieved effects which can not be produced with the known mixture in which the endo isomer predominates: the novel mixtures I are particularly "more powerful" odorants.

Claims

1. Mixtures of compounds of the formulae



and confers softness and fullness to the composition, which can be clearly recognized even over several days as the odour fades away.

c) Tobacco base

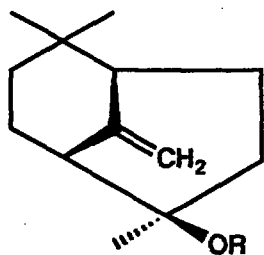
	<u>Parts by weight</u>	
Eugenol, pure	20	20
Coumarin cryst.	30	30
Benzoin resinoid Siam	50	50
2,3,6,6-Tetramethyl-cyclohex(2)-ene-carboxylic acid ethyl ester mixture + 2-ethyl-6,6-dimethyl-cyclohex(2)-ene-carboxylic acid ethyl ester	50	50
Phenoxyethyl isobutyrate	100	100
Methyl cedryl ketone	150	150
Sandela® (Givaudan)	200	200
Product I	400	---
Product X	---	400

In this composition the addition of the mixture I in accordance with the invention, in contrast to product X, exhibits an unexpected sweetness in the freshly dipped state, which after 24 hours makes way for an underlining of the woody-amber like and spicy note. In contrast, the composition with "X" becomes more fatty and exhibits less character. Fullness and diffusion of the tobacco composition are only clearly underlined and intensified by the addition of I.

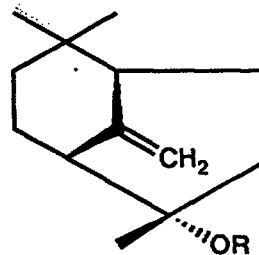
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Claims

1. Mixtures of compounds of the formulae



Ia



Ib

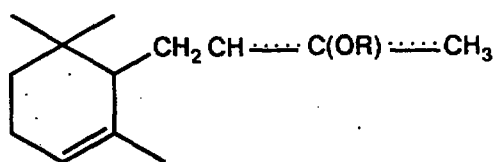
and

wherein R signifies C₁₋₄-alkyl,
in a ratio of at least 1.1:1, especially of 2.2-3.0:1.

2. Mixtures in accordance with claim 1, wherein R signifies methyl.

3. Mixtures in accordance with claim 1, wherein R signifies ethyl.

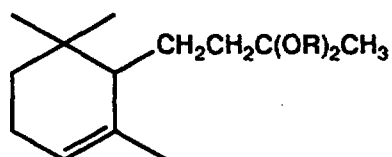
4. Enol ethers of the formula



II

wherein R signifies C₁₋₄-alkyl and one of the dotted lines represents an additional bond.

5. Ketals of the formula



III

wherein R signifies C₁₋₄-alkyl.

6. An odorant composition, characterized by a content of a mixture in accordance with any one of claims 1 to 3.

7. A process for the manufacture of the mixtures in accordance with any one of claims 1 to 3, characterized by



cyclizing a dihydro- α -ionone di-C₁₋₄-alkyl ketal or a C₁₋₄-alkyl enol ether of dihydro- α -ionone by means of a strong acid.

8. A process according to claim 7, characterized in that the strong acid is used in catalytic amounts.

9. A process according to claim 8, characterized in that a protonic acid or a Lewis acid is used as the strong acid.

10. A process according to any one of claims 7-9, characterized in that hydrogen chloride gas, sulphuric acid, phosphoric acid, trifluoroacetic acid, methanesulphonic acid, p-toluenesulphonic acid, camphorsulphonic acid, BF₃, BF₃·Et₂O, BF₃·H₃PO₄ or an acidic ion exchanger is used.

11. A process according to any one of claims 7 to 10, characterized in that the starting material is prepared in situ by reacting dihydro- α -ionone with the corresponding ketalizing agent at temperatures of about 40-50°C.

12. A process according to claim 11, characterized in that a compound of the formula HC(OR)₃ is used as the ketalizing agent.

13. A process according to claim 11 or 12, characterized in that the starting material is cyclized under the reaction conditions of its preparation to the mixture Ia/Ib.

14. The use of the mixtures in accordance with any one of claims 1 to 3 as odorants.