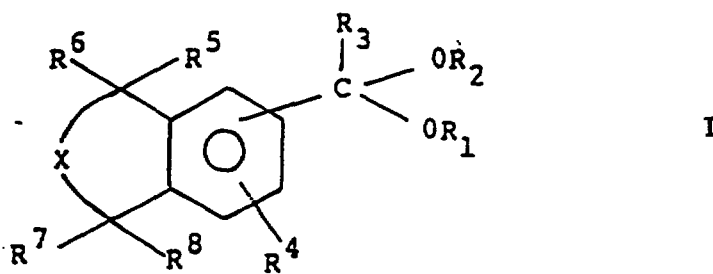


Description

The invention relates to novel odorants, namely acetals, or according to the previous (earlier) nomenclature acetals and ketals, of alkyl-substituted oxo-tetralins and oxo-indanes, for example of oxo-tetralins and oxo-indanes having up to 6 or 7 alkyl substituents.

More particularly, the invention is concerned with the compounds of the formula



wherein

R¹, R² signify

C₁₋₄-alkyl, C₂₋₄-alkenyl

or

R¹ + R² signify

C₂₋₄-alkylene which may be C₁₋₄-alkyl-, C₂₋₄-alkenyl- or hydroxy-C₁₋₄-alkyl- or hydroxy-C₂₋₄-alkenyl-substituted

R³ signifies

H, CH₃

R⁴ signifies

H, C₁₋₄-alkyl

R⁵, R⁶, R⁷, R⁸ signify

H, CH₃, C₂H₅,

CH₂CH₂CH₃,

CH(CH₃)₂

X signifies

methylene, ethylidene, propylidene, ethylene, propylene, 2,3-butyldiene

total number of carbon atoms of R¹, R² < 6

total number of carbon atoms of R¹, R², R³, R⁴ < 11

total number of carbon atoms of R⁵, R⁶, R⁷, R⁸ < 6,

with the exception of those compounds I in which

R³ is

H

R⁴ is

H or CH₃

R⁵, R⁶, R⁷, R⁸ are
X is

CH₃
ethylene

and

R¹, R² are

C₁₋₄-alkyl

Accordingly, the following are sub-groups:

1. The open-chain acetals and ketals of the oxo-tetralins of formula I.

2. The open-chain acetals and ketals of the oxo-indanes of formula I.

3. The cyclic acetals and ketals of the oxo-indanes of formula I.

4. The cyclic acetals and ketals of the oxo-tetralins of formula I.

The compounds of formula I are distinguished by very natural notes in the direction of musk, amber, woody, animalic and even fruity.

In general, fruity notes predominate in the "lighter" molecules. The heavier, e.g. cyclic, molecules possess woody, musky and animalic notes.

The following applies in particular:

Acetals: simple, open-chain	musk, fruity, woody
cyclic	musk
substituted	see below
Ketals: simple, open-chain	musk, woody, stronger
	fruity, less
	camphoraceous than the
	corresponding acetals
cyclic	strongly woody
substituted	complex aspects,
	olfactory strength:
	woody/musk/fruity/amber/
	animalic.

For economic reasons the tetralins are preferred.

Compared with the basic carbonyl compounds, which are also odorants, see e.g. EP-A 301375, 040338 and DE-B-2427465, they are generally stronger, more woody, more animalic and more substantive.

An important technical advantage in the use of I results from the fact that - in contrast to the basic carbonyl compounds - the majority of them are liquid. It

is thus possible by means of the novel compounds I and known musk substances, especially the corresponding "basic" substances, to manufacture by the accurate apportioning of amounts quasi enriched, sophisticated and esthetized musk substances of variable intensity and, respectively, of variable odorous nuance. Such mixtures, i.e. aldehydes or ketones II of the formula given hereinafter and corresponding acetals or ketals I, are, by virtue of their pronounced substantivity and tenacity, also especially suitable for the perfuming of laundry or of fabric conditioners; see in this respect Table III hereinafter.

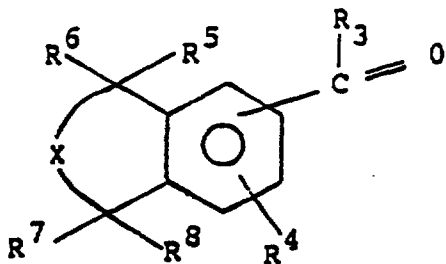
The optimal ratio of compound I/"basic" substance follows in each case from the results of washing tests and, of course, also the solubility of the "basic" substance in the compound I. It lies, for example, between about 1:10 to 1:1, but more extreme values are also possible.

The manufacture of the compositions is carried out in the usual manner, i.e. by mixing, as described below.

Especially preferred compounds of formula I are:

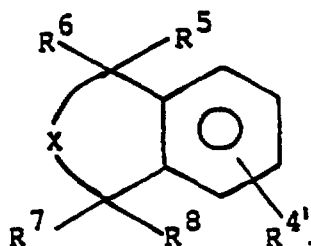
2,4-Dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-
-1,3-dioxolane,
2-methyl-4-ethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-
-1,3-dioxolane,
7-[formyl diethyl acetal]-1,1,2,4,4-pentamethyl-
tetralin,
2,4-dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-
-1,3-dioxane,
6-(acetyl diethyl ketal)-1,1,2,4,4,7-hexamethyl-
-tetralin,
2,4-dimethyl-2-[1,1,2,4,4,7-hexamethyl-tetralin-6-yl]-
-1,3-dioxolane.

The compounds of formula I which stand in the foreground of interest are obtained by acetalizing or ketalizing a compound of the formula



II

in a manner known per se or trans-acetalizing or trans-ketalizing a compound of formula I or electrochemically oxidizing a compound of the formula



III

wherein R^{4'} signifies methyl or ethyl, in the presence of an alcohol R^{2'}OH, namely a C₁₋₃-alkanol, and a conducting salt.

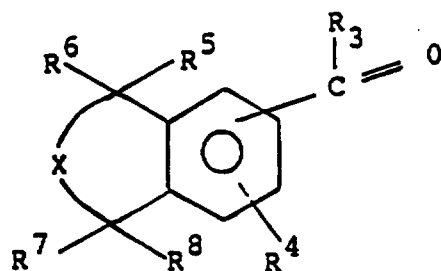
The methodology for the manufacture of acetals and ketals is known, see e.g. A.J. Meskens, Synthesis (1981), 501 et seq. or DT-OS 2848397.

The manufacture is thus effected, for example, according to methods which are known per se:

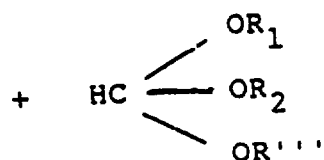
- | | | | |
|---|---|---|------------------------|
| A | Compound II
(the most careful method) | + | orthoformic acid ester |
| B | Compound II
(the most universal method) | + | alcohol |
| C | Compound II
(for cyclene) | + | diol |
| D | Transacetalization or transketalization of a compound I | | |
| E | Electrochemically. | | |

The following are especially applicable to these methods:

A.



II



R¹, R²
R''

C₁₋₄-alkyl
conveniently
corresponding to
R¹, R²

Parameters

Temperature range:

About 10°C to about 110°C,
especially about 20°C - about
40°C

Additional solvent:
(optional)

Alkanols, hexane, cyclohexane,
etc.

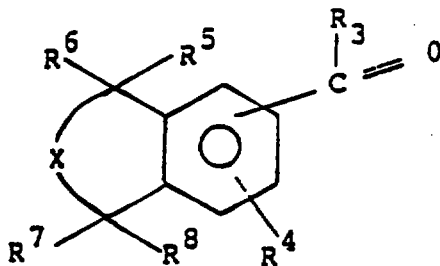
Catalysts:

Acids, e.g. HCl, p-toluene-
sulphonic acid, Al₂O₃·4SiO₂
(n H₂O), acidic salts, e.g.
KHSO₄, acidic ion exchanger

Isolation of the compound:

Distillation under reduced
pressure, column chromato-
graphy

B.



II

+ C₁₋₄-alkanol, C₂₋₄-alkenol

Parameters

Temperature range: About 10°C - about 100°C

Additional solvent: CH₂Cl₂, C₆H₆, toluene, etc.

Catalysts: (Lewis) acids, e.g. HCl, H₂SO₄, HNO₃, toluene-sulphonic acid, BF₃, sulphosalicylic acid, acidic salts, e.g. KHSO₄, ion-exchanger

Isolation of the compound I: Distillation under reduced pressure, column chromatography

C.

Reaction of II with a corresponding, optionally substituted diol, e.g. ethanediol, 1,2-propanediol, 1,3-propanediol, 1,2-butanediol, 2,3-butanediol, 1,3-butanediol, 2-butene-1,4-diol, 2-methyl-1,4-butenediol, etc.

This method can, of course, also be carried out using polyols, e.g. glycerol, 1,2,3-pentanetriol, 1,2,3,4-butanetetraol, 1,2,4-butenetriol and isomers thereof, etc.

Parameters

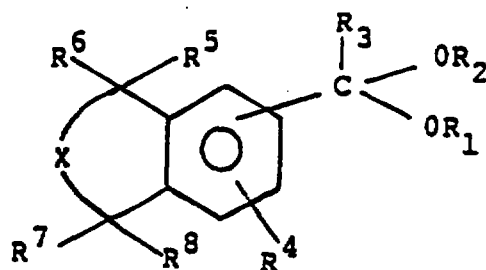
Additional solvent: (optional) Ether, (chlorinated) hydrocarbons

Catalysts: Acids, including Lewis acids, acidic salts, e.g. KHSO₄

Temperature range: About 30°C to about 150°C.

Isolation: Distillation, crystallization

D.



I

+ alcohol "high"

In the case of the transacetalization or transketalization of I, especially the residue R^1 or R^2 of a low-boiling alcohol is replaced by the residue of a higher-boiling alcohol "high", whereby H can also be a diol and whereby, as is known, the equilibrium also depends on the amount of the alcohol which is used.

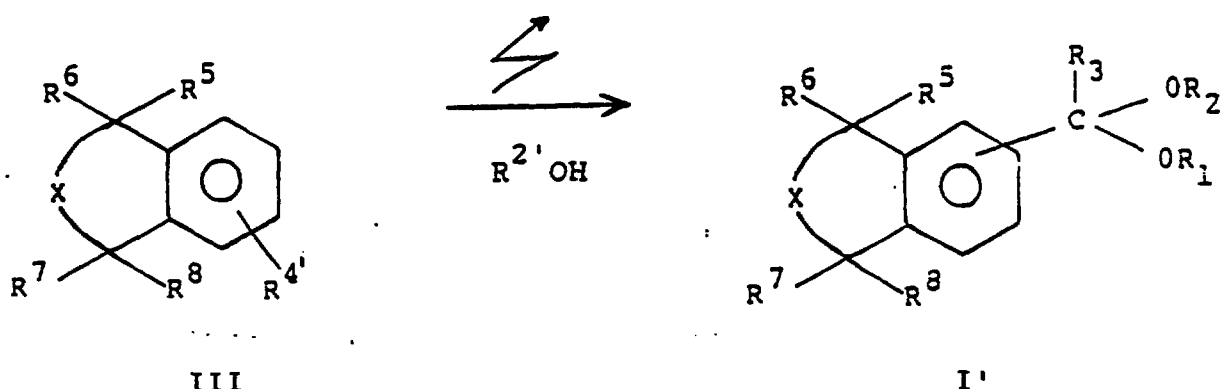
Parameters

Temperature range: About 65°C to 85°C

Additional solvent: Toluene, etc.

Isolation of the compound I: E.g. by distillation

E.



$R^{4'}$ = CH_3 , C_2H_5
 $R^{2'}OH$ = C_{1-3} -alkanol, C_{1-3} -alkanediol

In the compound I the residues R^1 and R^2 correspond to the alcohol $R^{2'}OH$ which is used.

The electrochemical method is conveniently carried out as described in detail e.g. in DT-OS 2848397.

Convenient parameters are accordingly, for example:

Cell	:	Divided or undivided.
Electrolyte	:	Solution of III in the alcohol used, which contains the conducting salt.
Conducting salt	:	Conducting salts which are usual in electrochemistry. Well-suited are e.g. salts which are soluble in the solution to be electrolyzed and which are largely stable under the conditions of the experiment. Examples of especially suitable conducting salts are fluorides such

- as KF, tetrafluoroborates such as Et_4NBF_4 , perchlorates such as Et_4NClO_4 , sulphates such as $\text{Et}_4\text{NSO}_4\text{Et}$, alcoholates such as NaOCH_3 and hydroxides such as KOH.
- Anode material : Examples of suitable anode materials are graphite, graphite-filled plastic materials, noble metals such as platinum and gold as well as noble metal-coated titanium electrodes.
- Cathode material : For example, graphite, iron, steel, lead or noble metal electrodes.
- Current density : For example, 1-5 A/dm².
- Temperature : E.g. temperatures between 0 and about 60°C.
- Working-up : The electrolysis products are generally worked-up by distillation. Excess alcohol and starting material which may still be present are separated from the acetals by distillation and can be recovered by electrolysis.

Examples

General methodology

Method A

0.02 mol of acetyl chloride is added dropwise within approximately 5 minutes to a mixture of the orthoformic ester (ethyl or methyl ester: 0.763 mol), 0.6 mol of ethanol or methanol and 0.28 mol of aldehyde or ketone. The reaction is slightly exothermic, with the temperature rising from about 20°C to about 40°C. The resulting mixture is stirred at room temperature for 2 hrs. and thereupon made alkaline to a pH of 7.5 to 8 by the addition of a 10% solution of potassium hydroxide in ethanol. After filtration, removal of the orthoformate and of the alcohol under reduced pressure, the pure acetal, for example the diethyl acetal or dimethyl acetal, is obtained by distillation.

Method B

1.5 mmol of acetyl chloride are added dropwise within 5 min. to a mixture of 0.075 mol of propanol and 0.022 mol of aldehyde. The reaction mixture is heated to 65°C and stirred at this temperature for 3 hrs. After cooling to room temperature the reaction mixture is neutralized by the addition of a 10% solution of potassium hydroxide in

ethanol. The reaction mixture is filtered and the filtrate is evaporated, whereby the crude acetal separates. This is purified by chromatography on silica gel using isopropyl ether/hexane in the ratio of 1:20 as the eluent.

Method C

0.1 mol of aldehyde or ketone, 0.2 mol of diol (for example ethylene glycol or propylene glycol), 200 ml of toluene and 0.15 g of p-toluenesulphonic acid monohydrate are stirred and heated. The water which is formed during the reaction is distilled off azeotropically within 24 hrs. The reaction mixture is brought to a pH value of 7.5 to 8 by the addition of a 10% solution of potassium hydroxide in ethanol. Thereupon, the mixture is filtered. After evaporation of the solvent the crude acetal is purified by distillation or recrystallization.

2,4-Dimethyl-2-[1,1,2,4,4,7-hexamethyl-tetralin-6-yl]-1,3-dioxolane

This method permits this dioxolane to be manufactured starting from 6-acetyl-1,1,2,4,4,7-hexamethyl-tetralin and propylene glycol; b.p. 109°C/0.2 mm Hg, n_D^{20} 1.5182
Odour: musk-like, green, soft, powdery.

Method D

a) 0.1 g of p-toluenesulphonic acid is added to a mixture of 0.066 mol of formyl acetate, e.g. 6-formyl-1,1,3,4,4-pentamethyl-tetralin diethyl acetal, 0.066 mol of allyl alcohol and 50 ml of toluene. The resulting mixture is stirred at 85°C to 90°C for 4 hrs. The ethanol which is formed in the reaction is removed by distillation. Thereupon, the mixture is neutralized by the addition of 10% potassium hydroxide in ethanol, filtered and evaporated, whereby the acetal formed, for example allyl ethyl acetate, is obtained. The isolation is carried out by preparative gas chromatography.

b) 0.1 g of acetyl chloride is added dropwise within 5 min. to a mixture of 0.35 mol of ethyl formate, 0.31 mol of ethanol and 0.13 mol of ketone. The reaction is slightly exothermic, resulting in a temperature increase from 20°C to 28°C. The resulting mixture is stirred at room temperature for 2 hrs. The excess orthoformate is removed by distillation in a vacuum at, for example, 50 mm Hg. The reaction mixture is cooled and 50 ml of toluene and 0.20 mol of propylene glycol are added as well as a further 1.5 mmol of p-toluenesulphonic acid. The resulting mixture is stirred at 85°C to 90°C for 2 1/2 hrs. The ethanol which is formed is removed by

distillation. The mixture is neutralized by the addition of 10% potassium hydroxide in ethanol; it is filtered and the filtrate is evaporated, whereby there separates the crude acetal which can be purified by distillation.

Example 1.A

7-[Formyl diethyl acetal]-1,1,2,4,4-pentamethyl-tetralin

0.02 mol (= 1.65 g) of acetyl chloride are added dropwise at room temperature within 1 min. to a stirred mixture of 113 g (0.76 mol) of ethyl orthoformate, 35 ml of ethanol and 64.3 g (0.28 mol) of 7-formyl-1,1,2,4,4-pentamethyl-tetralin. The reaction is slightly exothermic, which results in a temperature increase from 20°C to 38°C. The resulting mixture is stirred at room temperature for 2 hrs., after which time it is adjusted to a pH of 7.5 to 8 by the addition of a 10% solution of potassium hydroxide in ethanol. After filtration and removal of the excess ethanol and of the ethyl orthoformate by distillation the residual liquid is distilled in a vacuum, whereby there separate mainly 69 g of 7-[formyl diethyl acetal]-1,1,2,4,4-pentamethyl-tetralin as a colourless solution. Boiling point 112°C/0.25 mmHg; n_D^{20} 1.5015. The odour is slightly musk-like.

Example 1.B

7-[Formyl dipropyl acetal]-1,1,2,4,4-pentamethyl-tetralin

0.25 g of acetyl chloride is added dropwise at room temperature to a mixture of 10 g (0.04 mol) of 7-formyl-1,1,2,4,4-pentamethyl-tetralin and 10 g (0.17 mol) of n-propanol. The reaction mixture is heated to 65°C and stirred at this temperature for 2 hrs. After cooling to room temperature the reaction mixture is neutralized by the addition of 10% potassium hydroxide in ethanol. The mixture is filtered and the filtrate is evaporated, whereby there separates crude 7-[formyl dipropyl acetal]-1,1,2,4,4-pentamethyl-tetralin which is purified by chromatography on silica gel. Isopropyl ether/hexane in the ratio of 1:20 is used as the eluent. The acetal is a colourless liquid; n_D^{20} = 1.4980. The odour is distinctly musk-like.

Example 1.C

2,4-Dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane

2 g of p-toluenesulphonic acid monohydrate are added to a suspension of 120 g (0.5 mol) of 6-acetyl-1,1,4,4-tetramethyl-tetralin, 120 g (1.6 mol) of propylene glycol and

600 ml of toluene. The mixture is heated to 110°C. The reaction water is removed azeotropically within 5 hrs. After cooling to room temperature the mixture is adjusted to pH 7.5 to 8 by the addition of 10% potassium hydroxide in ethanol. Thereupon, the mixture is filtered. The solvent is evaporated and the residual liquid is distilled under a vacuum, whereby there separate as the main product 123 g of 2,4-dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane as a mixture of the cis-trans isomers. The boiling point is 112°C at 0.5 mmHg; $n_D^{20} = 1.5130$. The product has a strong woody, animalic odour.

Example 1.D

2,4-Dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane

0.15 g of acetyl chloride is added dropwise at room temperature to a mixture of 52.5 g (0.35 mol) of ethyl orthoformate, 30 g (0.13 mol) of 6-acetyl-1,1,4,4-tetramethyl-tetralin and 18 ml of ethanol. The reaction is slightly exothermic, which results in a temperature increase from 20°C to 28°C. The mixture is stirred at this temperature for 2 hrs. The excess ethyl orthoformate and ethanol are removed by vacuum distillation (120°C/100 mm Hg). After this time the reaction mixture is cooled and 50 ml of toluene, 22.5 g (0.29 mol) of propylene glycol and 0.3 g of p-toluenesulphonic acid are added rapidly. The mixture is stirred at 85°C to 90°C for 2 1/2 hrs. The ethanol which is formed is removed by distillation. Thereupon, the residual mixture is neutralized by the addition of a 10% solution of potassium hydroxide in ethanol, filtered and the filtrate is evaporated. Crude 2-dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane is obtained. The product is purified by vacuum distillation and there are obtained 23.7 g of pure product. The boiling point of the pure product is 112°C at 0.45 mmHg.

Example 1.E

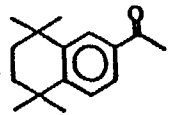
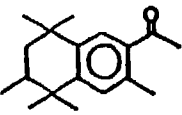
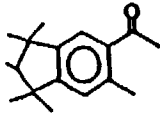
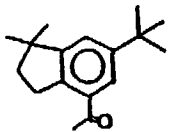
200 g of 1,1,2,4,4,7-hexamethyl-tetralin dissolved in 500 g of cyclohexane (anhydrous) are placed in a 3 l four-necked vessel having heating, a tap in the bottom and a reflux condenser and 1 kg of ethanol (anhydrous) containing 14 g of sulphuric acid (98%) is added while stirring. This mixture is circulated by means of a pump (10 l/min.) through the electrolysis cell (filter press type having graphite anodes and Inox cathodes 6 mm apart, effective surface: 220 cm²) (potential difference 35-42 volt at 3.5-4 ampere, duration 38 hours, reservoir temperature 25-30°C). A GC analysis indicates a content of

the desired compound, namely 7-[formyl-diethyl acetal]-1,1,2,4,4-pentamethyl-tetralin, of 77%. After the addition of 18.5 g of sodium carbonate the mixture is evaporated (40°C, 20 mmHg). The 285 g remaining behind are washed with 300 g of sodium chloride solution (10%) and distilled over a Vigreux column (130°C, 3 mmHg). Yield: 224 g, 87%, purity 83% (GC), main impurity: 1,1,2,4,4-pentamethyl-7-formyl-tetralin (GC 11%).

Further compounds in accordance with Table I are manufactured:

Table I

a) Ketals (open-chain $R^3 = CH_3$)

Starting material	R^1	R^2	Method	B.p. °C (mmHg)	M.p. °C	n_D^{20}	Odour
	CH_3	CH_3	A		44.5-46		Woody, amber
	C_2H_5	C_2H_5	A	$^{93}_{(0.1)}$		1.4985	Slightly woody
	CH_3	CH_3	A		80-81.5		Musk, amber animalic
	C_2H_5	C_2H_5	A		85-87		Musk
	C_2H_5	C_2H_5	A		62-63		Musk, woody
	C_2H_5	C_2H_5	A	$^{94}_{(0.2)}$		1.4945	Musk, animalic
	C_2H_5	C_2H_5	A				

b) Acetals (open-chain $R^3 = CH_3$)

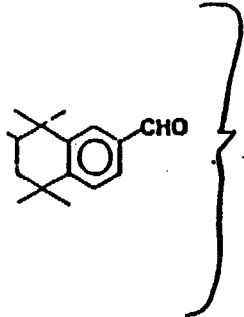
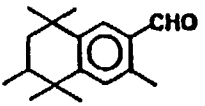
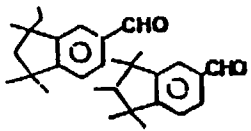
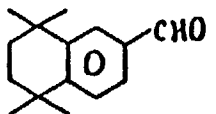
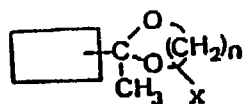
	CH_3	CH_3	A	103(0.1)	1.5120	Slightly after musk, flowery
	C_2H_5	C_2H_5	A	112(0.25)	1.5015	Slightly after musk, flowery
	$n-C_3H_7$	$n-C_3H_7$	B			After musk
	Allyl	Allyl	D(a)			After musk
	CH_3	CH_3	A		50-51	After musk
	C_2H_5	C_2H_5	A	108(0.1)	1.5030	After musk, powdery
	CH_3	CH_3	A	146(9.5)	1.5045	After musk, delicate, flowery
	C_2H_5	C_2H_5	A	98(0.1)	1.4950	Slightly after musk
	C_2H_5	C_2H_5	A	145(0.05)		After honey, green, flowery

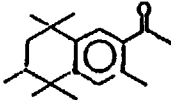
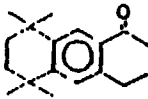
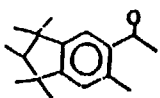
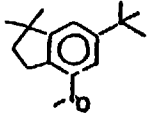
Table II

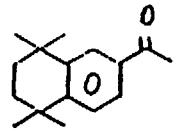
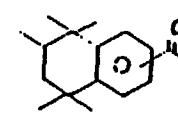
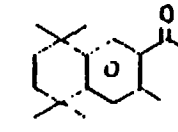
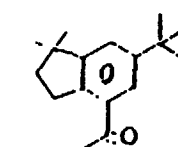
a) Ketals



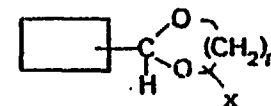
$$C_{x+n} \leq 6$$

Starting material	n	x	Method	B.p. °C (mmHg)	M.p. °C	n_D^{20}	Odour
	CH ₂ OHCH ₂ OH	2	H	C	77		woody, after musk
	CH ₂ OHCHOHCH ₂ OH	2	CH ₂ OH	C	180 (0.04)	1.5265	woody, animalic
	CH ₂ OHCHOHCH ₃	2	CH ₃	C, E	112 (0.45)	1.5130	woody, animalic
	CH ₂ OHCH ₂ OH	2	H	C	111-112		After musk, animalic
	CH ₂ OHCH ₂ OH	2	H	C	112		Slightly after musk

	<chem>CH2OHCH2OH</chem>	2	H	C		119-120	After musk, tonka
	<chem>CH3CHOHCH2OH</chem>	2	CH ₃	C	109 _(0.2)	1.5182	After musk, green, powdery, sweet
	<chem>CH2OHCH2OH</chem>	2	H	C		110-111	Slightly after musk
	<chem>CH2OHCH2OH</chem>	2	H	C		108-110	After musk, animalic
	<chem>CH2OHCH2OH</chem>	2	H	C		71-72	Woody, after musk
	<chem>CH3CHOHCH2OH</chem>	2	CH ₃	C	109 _(0.5)	1.5065	Woody, animalic
	<chem>CH2OHCHOHCH2CH3</chem>	2	C ₂ H ₅	C	109 _(0.5)		Woody, amber, animalic, tobacco

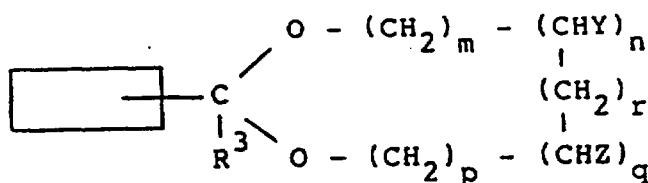
	CH ₃ CHOHCHOHCH ₃	2	CH ₃ .CH ₃	C	111(0.3)	woody, amber, after musk
	CH ₂ OH	3	H	C	94(0.15)	
	CH ₂					Slightly woody, slightly fatty
	CH ₂ OH					
	CH ₂ OH	3	CH ₃	C	90-92	After musk, amber, woody, animalic
	CH ₂					
	CHOH					
	CH ₃					
	CH ₂ OHCHOHCH ₃	2	CH ₃	C	100(0.08)	Woody, animalic
	CH ₂ OHCHOHCH ₃	2	CH ₃	C	122(0.9)	Slightly after musk
	CH ₂ OH	2	CH ₂ OH	C	140(0.65)	Slightly after musk, woody
	CHOH	3	OH			
	CH ₂ OH					

b) Acetals



	$\text{CH}_2\text{OHCH}_2\text{OH}$	2	H	C	73-74	After musk, fruity
	$\text{CH}_2\text{OHCHOHCH}_3$	2	CH_3	C	70-73	After musk, camphor
	$\text{CH}_2\text{OHCH}=\text{CH}-\text{CH}_2\text{OH} \quad -\text{CH}_2\text{CH}_2=\text{CHCH}_2$		H	C	75-76	Slightly after musk, green
	$\text{CH}_2\text{OHCH}_2\text{OH}$	2	H	C	66-67	Slightly after musk, fatty
	$\text{CH}_2\text{OHCH}_2\text{OH}$	2	H	C	72-73	Slightly after musk
	$\text{CH}_2\text{OHCH}_2\text{OH}$	2	H	C	110(0.18) 50-58	After musk, green, musty

The formulae for the cyclic acetals and ketals (5-7 membered rings) can, in principle, be explained in more detail as follows:



R^3	= H, CH_3	m, n, p, q, r	= 0, 1
X, Z	= $\text{CH}_3 \dots \text{C}_4$	$m + n + p + q + r$	= ≤ 4
	$-\text{CR}_2\text{OH} \dots \text{C}_4-\text{OH}$		

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

- Natural products, such as tree moss absolute, basil oil, citrus fruit 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), methylionone,
- esters, such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate (citronellyl) . O -CO -CO . OC_2H_5), 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, methyl-eugenol.

The acetals can be used in wide limits which can range in compositions, for example, from about 0.1 (detergents) - about 20% (alcoholic solutions), without these values being, however, limiting values, as 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 acetals can accordingly be used in the manufacture of compositions and - as the above compilation shows - using a wide range of known odorants or odorant mixtures. In the manufacture of such compositions the known odorants referred to 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.

Odorant composition

	<u>Parts by weight</u>	<u>Parts by weight</u>
Bergamot essence	250.00	250.00
Lemon essence	150.00	150.00
Lavandin essence	100.00	100.00
Cetone alpha (α -isomethylionone)	50.00	50.00
Hedione (methyl dihydrojasmonate)	50.00	50.00
Sandalore	20.00	20.00
Fixolide	40.00	40.00
Coumarin cryst.	20.00	20.00
Nutmeg essence	20.00	20.00
Clove essence	20.00	20.00
Estragon essence	5.00	5.00
Allylamyl glycolate	2.00	2.00
LRG 1201 Evernyl (methyl 2,4-dihydroxy- -3,6-dimethylbenzoate)	5.00	5.00
Geranyl acetate pure	50.00	50.00
Benzyl acetate extra	40.00	40.00
I		70.00

Pêche pur (gamma-undecalactone)	2.00	2.00
Isoeugenol	5.00	5.00
Methyl anthranilate extra	1.00	1.00
Basil essence	10.00	10.00
Carbitol	<u>160.00</u>	<u>90.00</u>
	1000.00	1000.00

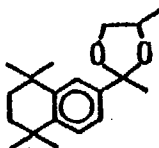
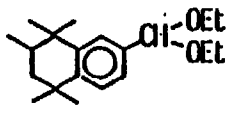
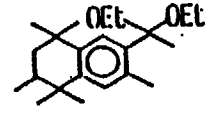
The addition of 70‰ (i.e. per 1000) of I (2,4-dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane) confers to the composition an elegant woody note accompanied by a warm amber-like undertone. At the same time the citrus notes are underlined in an agreeable manner. The composition receives much more freshness and volume.

The perfuming of laundry, which stands in the foreground of interest, can be documented as follows:

For this purpose, a conventional laundry conditioner, e.g. based on the usual cation active or pseudo-cation active substances, e.g. of the quaternary ammonium type, was perfumed with 0.3% (w/w) of odorant mixture in the usual manner and, after the washing operation (60°C), was added for the last rinsing in an amount of a few g/l, e.g. about 3-6, of water, in the special case of 4.5 g/l.

It was compared with an odorant mixture of 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta- γ -2-benzopyran ("Galaxolide")/1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-tetrahydronaphthalene ("Fixolide") as the standard.

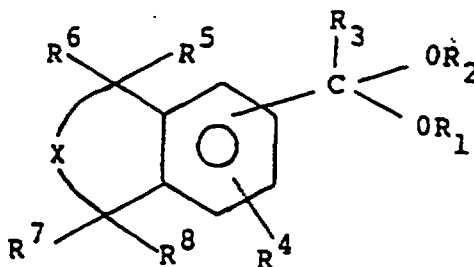
Comparative laundry test (conventional fabric conditioner perfumed
with 0.3% of odorant mixture)

Ref	acetal Musk/or % w/w ketal (all liquid)	Evaluation		
		Wet laundry		Dry laundry
A	GALAXOLIDE/FIXOLIDE [standard] 50:50	- relatively little intensity - musk note hardly appears		- rather unpleasant - scarcely musk, fatty
B	GALAXOLIDE/ 50:50	 stronger than all others, accentuated animalic woody note and costus aspect		stronger than all others, harmonic accord with animalic and patchouli notes
C	FIXOLIDE/ 50:50	musk note of average strength	 + earthy aspects	- agreeable musk note with non-woody aspect
D	FIXOLIDE/ 55:45			
E	FIXOLIDE/ 45:55		 + vanilla and nitromusk aspects	- "clean" musk note with good persistence



Claims

1. Compounds of the formula



I

wherein

R¹, R² signify

C₁₋₄-alkyl, C₂₋₄-alkenyl

or

R¹ + R² signify

C₂₋₄-alkylene which may be C₁₋₄-alkyl-, C₂₋₄-alkenyl- or hydroxy-C₁₋₄-alkyl- or hydroxy-C₂₋₄-alkenyl-substituted

R³ signifies

H, CH₃

R⁴ signifies

H, C₁₋₄-alkyl

R⁵, R⁶, R⁷, R⁸ signify

H, CH₃, C₂H₅,

CH₂CH₂CH₃,

CH(CH₃)₂

X signifies

methylene, ethylidene, propylidene, ethylene, propylene, 2,3-butyldiene

total number of carbon atoms of R¹, R² ≤ 6

total number of carbon atoms of R¹, R², R³, R⁴ ≤ 11

total number of carbon atoms of R⁵, R⁶, R⁷, R⁸ ≤ 6.

with the exception of those compounds I in which

R³ is

H

R⁴ is

H or CH₃

R⁵, R⁶, R⁷, R⁸ are

CH₃

X is

ethylene

and

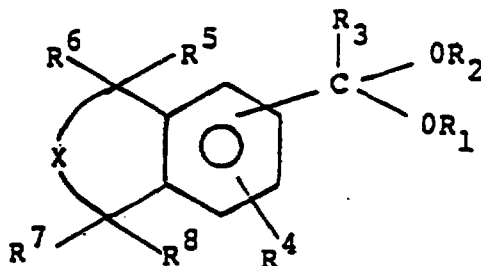
R¹, R² are

C₁₋₄-alkyl

2. The open-chain acetals and ketals of the oxo-tetralins of formula I in accordance with claim 1.



3. The open-chain acetals and ketals of the oxo-indanes of formula I in accordance with claim 1.
4. The cyclic acetals and ketals of the oxo-indanes of formula I in accordance with claim 1.
5. The cyclic acetals and ketals of the oxo-tetralins of formula I in accordance with claim 1.
6. 2,4-Dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane.
7. 2-Methyl-4 ethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane.
8. 7-[Formyl diethyl acetal]-1,1,2,4,4-pentamethyl-tetralin.
9. 2,4-Dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxane.
10. 6-(Acetyl diethyl ketal)-1,1,2,4,4,7-hexamethyl-tetralin.
11. 2,4-Dimethyl-2-[1,1,2,4,4,7-hexamethyl-tetralin-6-yl]-1,3-dioxolane.
12. 2,4-Dimethyl-2-[1,1,2,4,4,7-hexamethyl-tetralin-6-yl]-1,3-dioxolane.
13. An odorant composition, characterized in that it contains a compound of formula I in accordance with claim 1.
14. An odorant composition, characterized in that it contains 2,4-dimethyl-2-[1,1,4,4-tetramethyl-tetralin-6-yl]-1,3-dioxolane.
15. An odorant composition, characterized in that it contains 7-[formyl diethyl acetal]-1,1,2,4,4-pentamethyl-tetralin.
16. A process for the manufacture of the compounds



I



wherein
R¹, R² signify

C₁₋₄-alkyl, C₂₋₄-alkenyl

or
R¹ + R² signify

C₂₋₄-alkylene which may be C₁₋₄-alkyl-, C₂₋₄-alkenyl- or hydroxy-C₁₋₄-alkyl- or hydroxy-C₂₋₄-alkenyl-substituted

R³ signifies
R⁴ signifies
R⁵, R⁶, R⁷, R⁸ signify

H, CH₃
H, C₁₋₄-alkyl
H, CH₃, C₂H₅, CH₂CH₂CH₃, CH(CH₃)₂
methylene, ethylidene, propylidene, ethylene, propylene, 2,3-butyldiene

X signifies

total number of carbon atoms of R ¹ , R ²	< 6
total number of carbon atoms of R ¹ , R ² , R ³ , R ⁴	< 11
total number of carbon atoms of R ⁵ , R ⁶ , R ⁷ , R ⁸	< 6,

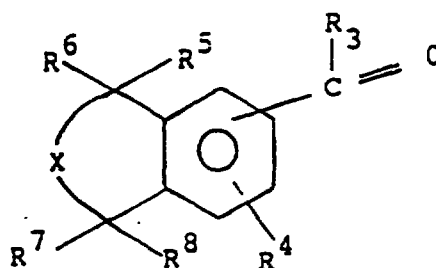
with the exception of those compounds I in which

R ³ is	H
R ⁴ is	H or CH ₃
R ⁵ , R ⁶ , R ⁷ , R ⁸ are	CH ₃
X is	ethylene

and

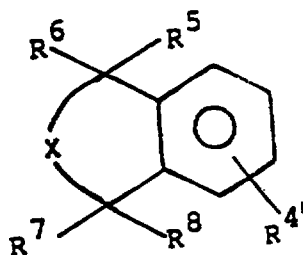
R ¹ , R ² are	C ₁₋₄ -alkyl
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characterized by acetalizing or ketalizing a compound of the formula



II

in a manner known per se, or transacetalizing or transketalizing a compound I, or electrochemically oxidizing a compound of the formula



III

wherein $R^{4'}$ signifies
 R^5, R^6, R^7, R^8
have

CH_3, C_2H_5 and
the above
significance.

in the presence of a C_{1-3} alkanol $R^{2'}OH$ and a
conducting salt.

17. The use of a compound of formula I in accordance
with claim 1 as an odorant.

18. The use of 2,4-dimethyl-2-[1,1,4,4-tetramethyl-
-tetralin-6-yl]-1,3-dioxolane as an odorant.

19. The use of 7-[formyl diethyl acetal]-1,1,2,4,4-
-pentamethyl-tetralin as an odorant.