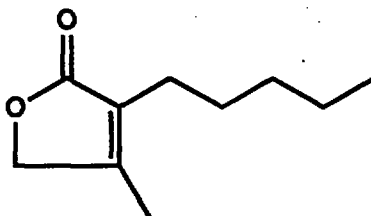


Description

The invention is concerned with a novel odorant and/or flavorant. This is the compound of the formula



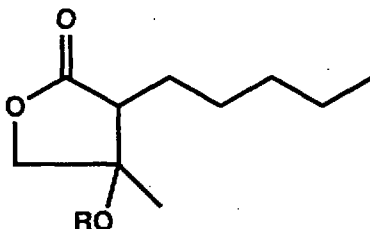
I

namely 4-methyl-3-pentyl-2(5H)-furanone.

Compound I has particular organoleptic properties on the basis of which it is excellently suited as an odorant and/or flavorant.

The invention is accordingly also concerned with the use of the compound I as an odorant and/or flavorant and with odorant and/or flavorant compositions containing I.

The invention is also concerned with a process for its manufacture. This process is characterized by dehydrating a compound of the formula



II

wherein R signifies hydrogen or acyl, e.g. C₁₋₅-alkanoyl, e.g. acetyl.

The dehydration of compound II is conveniently effected using protonic acids, e.g. using mineral acids such as hydrochloric acid, sulphuric acid, phosphoric acid, perchloric acid, etc. or, preferably, using organic sulphonic acids such as p-toluene-sulphonic acid, etc. The dehydration is conveniently carried out in a solvent such as a hydrocarbon or an alcohol or ether and at room temperature or, preferably, at elevated temperature.

The compounds of formula II are novel and form a further object of the present Application.

The preparation of a compound II is effected, for example, from

- a) an alkyl α -haloheptanoate and hydroxyacetone or, even better, an acyl derivative, e.g. a C₁₋₅-alkanoyloxyacetone, according to Reformatzky, or
- b) from the corresponding α -halocarboxylic acid ester, i.e. heptanoic acid ester, of hydroxyacetone by means of an intramolecular Reformatzky reaction.

The compound of formula I, which is used in accordance with the invention as an odorant and/or flavorant, is distinguished by pleasant, pronounced natural flowery and fruity notes: they are powerful and fresh. The side-notes which appear are coconut-like, spicy [and] tobacco-like. Moreover, it is distinguished by a high diffusion capability combined with an extraordinary adhesion. Even when used in low concentrations it intensifies and enriches the olfactory impression of odorant compositions, especially of flowery and fruity compositions or bases. Compound I combines with numerous known odorant ingredients of natural or synthetic origin, whereby the range of the natural raw materials embraces 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 will be evident from the following compilation:

- Natural products: Basil oil, tree moss absolute, mugwort oil, bergamot oil, cassis bud absolute, castoreum, cedarwood oil, ciste labdanum, civet, coriander oil, oak moss, elemi oil, pine needle oil, galbanum, geranium oil, clove oil, jasmin absolute and its synthetic substitute, jonquille absolute, camomile oil, labdanum, lavender oil, mandarin oil, mastix absolute, mentha citrata oil, myrrh oil, palmarosa oil, patchouli oil, petitgrain oil Paraguay, sandalwood oil, thyme oil, vassoura oil, musk infusion, styrax, birch tar, vetiver oil, frankincense, ylang-ylang oil, lemon oil, civet oil, etc.

- Alcohols: Citronellol, Dimetol® (2,6-dimethyl-heptan-2-ol), geraniol, cis-3-hexanol, linalool, Nonadyl® (6,8-dimethyl-nonan-2-ol), phenylethyl alcohol, rhodinol, Sandela® (3-iso-camphyl-5-cyclohexanol), Sandalore® (3-methyl-5-(2',2',3'-trimethyl-cyclopenta-3'-en-1'-yl)-pentan-2-ol), terpeneol, etc.

- Aldehydes: α -Amylcinnamaldehyde, cyclamen aldehyde, decanal, dodecanal, heliotropin, α -hexylcinnamaldehyde, hydroxycitronellal, lylal, Adoxal® (2,6,10-trimethyl-9-en-1-al), undecanal, ω -undecylene aldehyde, vanillin, etc.
- Ketones: Isoraldeine® (isomethyl- α -ionone), α -ionone, β -ionone, 3-phenylisocaranone, Vertofix® (= acetylated cedarwood oil), p-methylacetophenone, etc.
- Esters: Ethyl acetoacetate, amyl salicylate, benzyl acetate, cedryl acetate, cinnamyl formate, citronellyl acetate, geranyl acetate, cis-3-hexenyl acetate, cis-3-hexenyl benzoate, linalyl acetate, linalyl anthranilate, methyl dihydrojasmonate, Methambrat® (1-acetoxy-1-methyl-2-sec.-butylcyclohexane), Myraldylacetat® (4-(4-methyl-3-pentenyl)-cyclohex-3-en-1-yl-carbinyl acetate), phenoxyethyl isobutyrate, phenylethyl tiglate, styrallyl acetate, terpenyl acetate, 2,3,6,6-tetramethylcyclohexy-2-ene-carboxylic acid ethyl ester, 3,6,6-trimethyl-2-ethylcyclohex-2-ene-carboxylic acid ethyl ester, vetivenyl acetate, ortho-tert.-butylcyclohexyl acetate, etc.
- Various: Musk ambrette, coumarin, epoxycedrene, eugenol, Fixolide® (1,1,2,4,4,7-hexamethyl-6-acetyl-1,2,3,4-tetrahydronaphthalene), Galaxolid® (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethyl-cyclopenta- γ -2-benzopyran), heliotropin, indole, indolene, isoeugenol, isobutylquinoline, jasmonyl (1,3-diacetoxynonane), musk ketone, limonene, p-menthane-8-thiol-3-one, Madrox® (1-methyl-cyclododecyl methyl ether), methyleugenol, Musk 174® (12-oxahexadecanolide), γ -nonalactone, α -undecalactone, etc.

The compound of formula I can be used in wide limits which can extend in compositions, for example, from 0.1 (detergents)-30 wt.% (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 0.1 and 25%. 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, tobacco, etc.).

Compound I 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 or odorant mixtures enumerated above can be used according to methods known to the perfumer such as e.g. from W.A. Poucher, *Perfumes, Cosmetics, Soaps* 2, 7th Edition, Chapman and Hall, London 1974.

The novel compound of formula I is also excellently suited for use in flavours of the widest variety of kind, but especially for the flavouring of tobacco.

As a flavorant compound I can be used, for example, for the production or improvement, intensification, enhancement or modification of (tropical) fruit flavours, e.g. apricot, peach, passionfruit, pineapple [and] banana flavours. However, nut, coconut, caramel, maple, tea [and] tobacco flavours also come into consideration. As fields of use for these flavours their come into consideration, for example, foodstuffs (yoghurt, confectionery etc.), semi-luxury consumables (tea, tobacco, etc.) and drinks (lemonade etc.).

The pronounced flavour qualities of compound I (sweet, coumarin-like, lactonic, resembling caramel; slightly fruity, fresh) enable it to be used as a flavorant in low concentrations. A suitable dosage, embraces, for example, the range of 0.1 ppm-100 ppm, preferably the range of 0.5 ppm-50 ppm, in the finished product, i.e. the flavoured foodstuff, semi-luxury consumable or drink.

In the flavouring of, for example, tobacco the dosage can, however, also lie higher and can embrace a wider range, for example the range of 1 to 1000 ppm, preferably 30-100 ppm.

The compound can be mixed with the ingredients used for flavouring compositions or added to such flavourings in the usual manner. Under the flavourings used in accordance with the invention there are to be understood flavouring compositions which can be diluted or distributed in edible materials in a manner known per se. They contain, for example, about 0.1-10, especially 0.5-3, wt.%. They can be converted according to methods known per se into the usual forms of use such as solutions, pastes or powders. The products can be spray-dried, vacuum-dried or lyophilized.

The known flavouring substances which are conveniently used in the manufacture of such flavourings are either already referred to in the above compilation or can be taken readily from

the literature such as e.g. J. Merory, Food Flavorings, Composition, Manufacture and Use, Second Edition, The Avi Publishing Company, Inc., Westport, Conn. 1968, or G. Fenaroli, Fenaroli's Handbook of Flavor Ingredients, Second Edition, Volume 2, CRC Press, Inc. Cleveland, Ohio, 1975.

For the manufacture of such usual forms of use there come into consideration, the following carrier materials, thickening agents, flavour improvers, spices and auxillary ingredients, etc.:

Gum arabic, tragacanth salts or brewers' yeast, alginates, carageen or similar absorbents; indoles, maltol, dienals, spice oleoresins, smoke flavours; cloves, diacetyl, sodium citrate; monosodium glutamate, disodium inosine-5'-monophosphate (IMP), disodium guanosine-5-phosphate (GMP); or special flavouring substances, water, ethanol, propylene glycol, glycerine, etc.

Example 1

a) 65.37 g (1 mol) of zinc powder and 3.27 g (50 mmol) of iodine are placed in 400 ml of toluene. This violet suspension is heated to 80°C in an oil bath while stirring and treated within 80 minutes with a solution of 118.55 g (500 mmol) of ethyl 2-bromoheptanoate and 87.08 g (750 mmol) of acetoxyacetone in 100 ml of toluene. The exothermic reaction which sets in immediately can be held at 80-90°C by removing the oil bath. After a further 90 minutes at 80°C the reaction mixture, cooled to room temperature, is treated with 400 ml of ice-water and then with 120 ml of 20% HCl and stirred for 30 minutes. Then, it is extracted three times with 500 ml of ether in a separating funnel. The ether phases are washed with 500 ml of sat. NaHCO₃ solution and with 500 ml of sat. NaCl solution, dried over MgSO₄ and concentrated on a rotary evaporator. The crude product distils at 110-112°C/0.06 mbar and gives 49.64 g (43.5%) of 4-acetoxy-4-methyl-3-pentyl-tetrahydrofuran-2-one.

IR (liq. film):	1780s, 1740s, 1460m, 1370s, 1230s, 1025s cm ⁻¹
NMR (CDCl ₃)	200 MHz: 0.9(t,3H), 1.3-1.8(m,8H), 1.54 and 1.70(2s,3H), 2.05 and 2.07(2s/3H), 2.33 and 2.78(2t/1H), 4.40 and 4.46(2q/2H) ppm.
MS (m/e):	169, 158, 89(100%), 43.

b) 125.33 g (549 mmol) of 4-acetoxy-4-methyl-3-pentyl-tetrahydrofuran-2-one are placed with 2.61 g (13.7 mmol) of p-toluenesulphonic acid and held at 150°C for 4 hours while stirring. The acetic acid which is cleaved off is distilled off over a Vigreux column. The reaction solution, cooled to room temperature, is diluted with 500 ml of ether and washed in a separating funnel with 2 x 200 ml of sat. NaCl solution. Drying of the ether phase over MgSO₄ and concentration on a rotary evaporator as well as distillation at 100-103°C/0.12 mbar yields 71.34 g/77.3% of 4-methyl-3-pentyl-2(5H)-furanone.

IR (liq. film): 1750s, 1680s, 1450m, 1090s, 1040s cm⁻¹

NMR (CDCl₃) 200 MHz: 0.9(t,3H), 1.3(m,8H), 1.6(m,2H), 2.03(s/3H), 2.25(t/2H), 4.62(m/2H) ppm.

MS (m/e): 168(M⁺) 153, 139, 126, 112(100%).

Example 2

a) 86.0 g (411.3 mmol) of 2-bromoheptanoic acid are placed in 600 ml of dimethylformamide and 49.95 g (493.6 mmol) of triethylamine are added dropwise thereto within 5 minutes at 20°C and the pale yellow solution is stirred at room temperature for 15 minutes. Now, 57.07 g (617 mmol) of chloroacetone are added dropwise during 30 minutes and the yellow-brown suspension is stirred at room temperature for 90 minutes. The reaction mixture is poured on to 1 l of 1N HCl and ice and extracted in a separating funnel with 3 x 500 ml of ether. The organic phases are washed with 2 x 200 ml of water, dried over MgSO₄ and concentrated on a rotary evaporator. Distillation at 86-88°C/0.05 mbar yields 80.56 g (73.9%) of acetylmethyl 2-bromoheptanoate.

IR (film): 1750s(shoulder), 1735s, 1370m, 1275m, 1145s cm⁻¹

NMR(CDCl₃) 200 MHz: 0.9(t,3H), 1.3-1.6(m,6H), 1.9-2.2(m,2H), 2.2(s,3H), 4.34(t,1H), 4.74(q,2H) ppm.

MS (m/e): 194, 191, 185, 111, 83, 43(100%).

b) 39.61 g (606 mmol) of powdered zinc are suspended in 500 ml of tetrahydrofuran. Then, 1.92 g (15 mmol) of iodine are added and 80.34 g (303 mmol) of acetylmethyl 2-bromoheptanoate in 100 ml of tetrahydrofuran are added dropwise at 67°C within 1 hour. The grey-green suspension is stirred at reflux temperature for a further 1 hour. The cooled reaction mixture is poured on to 500 ml of 1N HCl and ice and stirred for 10 minutes. It is then extracted in a separating funnel with 3 x 500 ml of

ethyl acetate. The organic phases are dried with MgSO_4 , concentrated on a rotary evaporator and dried in high vacuum. There are obtained 77.21 g of 4-hydroxy-4-methyl-3-pentyl-tetrahydrofuran-2-one.

IR (film): 3400m, 1750s, 1025m cm^{-1}

MS (m/e): 187, 171, 169, 116, 101(100%), 99.

c) 77 g (413.4 mmol) of 4-hydroxy-4-methyl-3-pentyl-tetrahydrofuran-2-one are treated with 1.57 g (8.3 mmol) of p-toluenesulphonic acid and heated at 150°C for 2 hours, whereby the resulting water is distilled off over a column with a weak stream of nitrogen. The cooled reaction solution is diluted with 300 ml of ether and washed in a separating funnel 3 x with 100 ml of water. The aqueous phases are back-washed with 100 ml of ether. Drying of the organic phases over MgSO_4 , concentration on a rotary evaporator and flash distillation over a short Vigreux column at 0.3 mbar yields 44.63 g of a pale yellow liquid. By distillation on a widmer column at $100^\circ\text{C}/0.07$ mbar there are obtained 37.73 g (54.2%) of 4-methyl-3-pentyl-2(5H)-furanone. IR, NMR and MS spectra are identical with Example 1b.

Example 3

In compositions a), b) and c) the compound I converts volume and fullness which reflect especially in the fruity and flowery aspects:

a) Flowery, cosmetic accord:

	<u>Parts by weight</u>	
I		20.00
Benzyl acetate	100.00	100.00
Geranyl acetate	100.00	100.00
p-t-Butylcyclohexyl acetate	100.00	100.00
Verdyl acetate	20.00	20.00
Phenylethyl alcohol	150.00	150.00
Hexyl cinnamaldehyde	100.00	100.00
Bergamot essence	200.00	200.00
Cyclohexylallyl propionate	1.00	1.00
Dimetol	20.00	20.00
Dipropylene glycol	30.00	10.00
Gardenol (methylphenylcarbinyl acetate)	2.00	2.00
Isoeugenol	2.00	2.00
Linalool	50.00	50.00

Geranium oxide 10%/DIP	5.00	5.00
Petitgrain ess. Paraguay	20.00	20.00
Benzyl salicylate	<u>100.00</u>	<u>100.00</u>
Total	1000.00	1000.00

Use: e.g. 2% in bases for soaps, in skin cosmetics.

b) Flowery fresh accord

	<u>Parts by weight</u>	
I		30.00
Benzyl acetate	80.00	80.00
Geranyl acetate	150.00	150.00
Linalyl acetate	200.00	200.00
p-t-Butylcyclohexyl acetate	100.00	100.00
Agrumex (2-tert.butylcyclohexyl acetate)	80.00	80.00
Phenylpropyl alcohol	100.00	100.00
Dipropylene glycol	50.00	20.00
Eugenol	10.00	10.00
Isoraldeine 70 P (isomethyl- α -ionone)	50.00	50.00
Lemarome A (neral-citral mixture)	30.00	30.00
Hexyl salicylate	50.00	50.00
Tetrahydrolinalool	<u>100.00</u>	<u>100.00</u>
Total	1000.00	1000.00

Use: e.g. 2% in a base for shower gels.

c) Flowery elegant accord:

	<u>Parts by weight</u>	
I		10.00
Benzyl acetate	100.00	100.00
Dimethylbenzylcarbinyl acetate	40.00	40.00
Geranyl acetate	30.00	30.00
Phenylethyl alcohol	100.00	100.00
Bergamot RGV 2	200.00	200.00
Ketone alpha (α -methyl-ionone)	50.00	50.00
Cyclohexal	50.00	50.00
Dipropylene glycol	10.00	
Eugenol	10.00	10.00
Galaxolid 50 DEP	100.00	100.00
Gardenol	10.00	10.00
Geraniol extra	60.00	60.00

Hedione	20.00	20.00
Hydroxycitronellal	60.00	60.00
Methylisoeugenol	10.00	10.00
Benzyl salicylate	<u>150.00</u>	<u>150.00</u>
Total	1000.00	1000.00

Use: e.g. 15% in alcohol 90°, for eau de toilette.

d) Hazelnut flavour:

	<u>Parts by weight</u>
3,4-Dimethyl-cyclopenta-1,2-dione	6.00
Vanillin	20.00
2-Acetyl-pyrazine	2.00
Propylene glycol	953.00
Diacetyl	3.00
Dimethyl-resorcinol	3.00
γ-Nonalactone (aldehyde Cl)	1.00
Benzaldehyde	2.00
Furfural	4.00
Trimethyl-pyrazine	1.00
I	<u>5.00</u>
Total	1000.00

Dosage: e.g. 0.1% in milk drinks.

In the above hazelnut flavour the 0.5 ppm of compound I produces a creamy body [and] mouth-feel. It thereby intensifies especially the nut character of the flavour.

e) Chocolate flavour:

	<u>Parts by weight</u>
Vanillin	80.00
Phenylacetic acid	3.00
Ethyl-vanillin	50.00
Cocoa shell extract PG	850.80
Benzaldehyde	0.20
iso-Butyric acid	0.50
Phenylethyl alcohol	2.00
Ethylphenyl acetate	1.50
iso-Valeraldehyde	2.00

Ethyl 2-dimethyl-3,5(or 6)-pyrazine	2.00
iso-Butyraldehyde	1.00
Trimethylpyrazine	2.00
I	<u>5.00</u>
Total	1000.00

Dosage: 0.1% in milk drinks, etc.

In the above chocolate flavour the 0.5 ppm of compound I produces body and mouth-feel; it intensifies the character of the composition.

f) Pineapple flavour:

	<u>Parts by weight</u>	
Ethyl valerate	1	1
γ -Decalactone	1	1
Ethyl caproate	4	4
Ethyl 2-methylbutyrate	4	4
2-Methylbutyric acid	5	5
iso-Amyl acetate	9	9
Ethyl acetate	10	10
Methyl 2-methylbutyrate	10	10
Homofuronol 20% in PG	15	15
Ethyl butyrate	16	16
Allyl caproate	25	25
I	--	5
Propyleneglycol	<u>900</u>	<u>895</u>
Total	1000	1000

The addition of compound I produces body, a natural juicy and fresh note [and] more fullness.

g) Passionfruit flavour

	<u>Parts by weight</u>	
Mandarin oil	0.500	0.500
Phenethyl alcohol	0.500	0.500
Geraniol	0.500	0.500
cis-3-Hexenol	0.500	0.500
Citral	0.500	0.500
α -Ionone	0.500	0.500
γ -Undecalactone	1	1

Linalool	1	1
α -Terpineol	1	1
Linalyl acetate	1	1
Styralyl acetate	2	2
Ethyl butyrate	4	4
Ethyl isovalerate	5	5
Hexyl caproate	14	14
Homofuronol 20% in PG (2-ethyl-4-hydroxy-5-methyl-dihydrofuran-3(2H)-one)	20	20
Ethyl caproate	38	38
Hexyl butyrate	30	30
I	--	5
Triethyl citrate	80	75
Propylene glycol	<u>800</u>	<u>800</u>
Total	1000	1000

The addition of I accentuates the fresh and juicy note, [and] produces fullness and body.

h) Apricot flavour:

	<u>Parts by weight</u>	
Hexyl acetate	1	1
β -Damascone 10% in PG	1	1
γ -Undecalactone	2	2
cis-3-Hexenol	2	2
Benzaldehyde	3	3
trans-2-Hexenol	3	3
Linalool	5	5
γ -Dodecalactone	5	5
Butyric acid	10	10
Ethyl acetate	10	10
γ -Dodecalactone	8	8
Ethyl propionate	10	10
iso-Amyl acetate	10	10
2-Methylbutyric acid	10	10
Acetic acid	20	20
Homofuronol 20% in PG	20	20
I	--	5
Propylene glycol	<u>880</u>	<u>875</u>
Total	1000	1000

The addition of I produces body, fullness, rounding-off, [and] a more juicy, more fruity and ripe and fresh note.



Claims

1. 4-Methyl-3-pentyl-2(5H)-furanone.
2. 4-Hydroxy (or acyloxy)-4-methyl-3-pentyl-tetrahydro-furan-2-one.
3. An odorant and/or flavorant composition, characterized by a content of 4-methyl-3-pentyl-2(5H)-furanone.
4. A process for the manufacture of 4-methyl-3-pentyl-2(5H)-furanone, characterized by dehydrating 4-hydroxy (or acyloxy)-4-methyl-3-pentyl-tetrahydrofuran-2-one.
5. The use of 4-methyl-3-pentyl-2(5H)-furanone as an odorant and/or flavorant.