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☑ Description : paged ..1.... to paged 13
☑ Claim(s) : paged .....14.. to paged ..15....
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☐ Abstract : paged ..... to paged .....

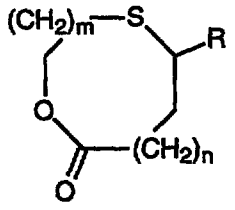
The invention is concerned with novel thiamacrolides, especially musk odorants, having extremely low threshold values, their use in functional perfumery such as fine perfumery, as well as a process for the manufacture of these and analogue compounds.

Because of their *warm, erogenous-animalic and long-lasting* odour, musk odorants number among the compounds which are most used in perfumery. The poor biological degradability, a certain phototoxicity as well as the suspected neurotoxicity of benzoid musk odorants has led in recent times to the increased use of macrocyclic compounds, which are derived from naturally occurring musk substances and which are quite safe from the ecological point of view. However, high production costs prevent their use on a large scale. Macrocycles, which by virtue of their low threshold value could be used in lower concentrations than usual and thereby give rise to lower costs, could provide a solution. Although it is possible to obtain information relating to core structures and in spite of numerous investigations concerning structure-odour relationships of odorants [P. Weyerstahl, *J. prakt. Chem.* **1994**, *336*, 95; K. J. Rossiter, *Chem. Rev.* **1996**, *96*, 3240] a prediction of the intensity or of the threshold value of macrocycles having a musk odour has hitherto been impossible.

We have now found a small class of thiamacrolides **I**, which have extremely low threshold values, namely of 0.1-0.3 ng/l air, i.e. up to 10 times lower than the threshold value of the most frequently used macrolide 15-pentadecanolide (**5**, 1.1 ng/l). This is all the more surprising, since thiamacrolides have already been the object of an invention [Naarden, Netherlands Patent No. 96391]. The compounds synthesized there have, however, been found to have a very much weaker odour than 15-pentadecanolide (**5**) [E. T. Theimer, J. T. Davies, *J. Agr. Food Chem.* **1967**, *15*, 8].

This novel class of thiamacrolides can be represented by the general formula

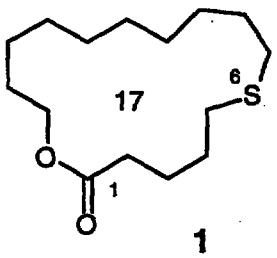
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I

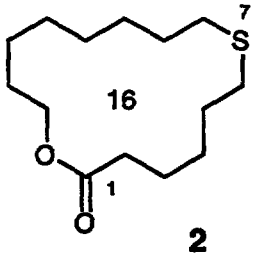
wherein R = H and wherein m = 9 and n = 3, or
m = 7 and n = 4, or
m = 3 and n = 8, or
m = 7 and n = 3.

It accordingly embraces the compounds of formulae **1-4**.



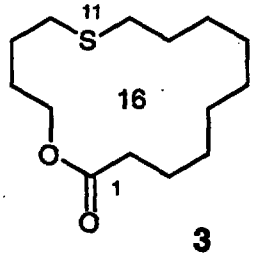
1

0.1 ng/l



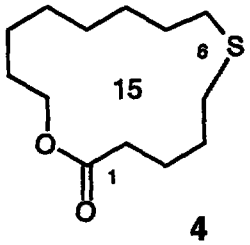
2

0.2 ng/l



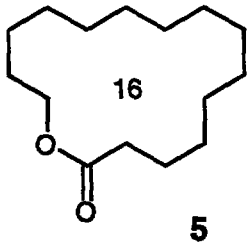
3

0.2 ng/l



4

0.3 ng/l



5

1.1 ng/l

In addition to extremely low threshold values the compounds I have a very good adhesion. All have *intensive musk notes which are often accompanied by powdery-sweet accents.* In contrast to corresponding compounds which do not contain a sulphur atom and analogous unsaturated macrolides, these compounds are also mainly distinguished by *warm, green-mossy nuances.* This interaction of *powdery-sweet and green-mossy elements with a dominant musk note* gives an especially fine perfumistic effect in the case of compound **2**.

The thiamacrolides I can in general be used in the same manner as the known musk odorants. Thus, they harmonize with a large number of

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natural and also synthetic products which are customarily used in odorant compositions. In particular, they produce interesting effects in the bottom note in combination with woody and amberous accords, patchouli oil as well as cedarwood and sandalwood odorants. The compounds confer elegance and radiance to flowery essential notes. Some examples of classes of substance which harmonize especially well are:

– Natural products, such as	tree moss absolute, geranium oil, jasmin absolute, patchouli oil, rose oil, sandalwood oil, vetiverol and ylang-ylang oil etc.
– alcohols, such as	citronellol, Ebanol®, geraniol, linalool, phenylethyl alcohol and Sandalore®, etc.
– aldehydes and ketones, such as	Florozone® (3-(4-ethylphenyl)-2,2-dimethypropional), hydroxy citronellal, Iso-E-Super® (1,2,3,4,5,6,7,8-octahydro-2,3,8,8-tetramethyl-2-octanaphthalene), Isoraldein®, maltol, methyl cedryl ketone, methylionone and vanillin, etc.
– ethers and acetals, such as	ambrox, geranyl methyl ether, rose oxide and Spirambrene® (2',2',3,7,7-pentamethyl-spiro[bicyclo[4.1.0]heptane-2,5'-[1,3]dioxan]), etc.
– esters and lactones, such as	Berryflor®, γ-decalactone and γ-undecalactone, etc.

The versatility of the thiamacrolides **I** enables them to be used widely not only in sweet oriental creations, but also in Fougère', 'Chypre' and 'Floral' olfactorily directions. Not only luxury perfumes, but also compositions for cosmetic products, washing agents and similar bulk products are opened up by the low threshold values and the good adhesion.

The compounds of formula **I** can be used in wide limits which can range in compositions, for example, from about 0.1 wt.% (detergents) to about 40 wt.% (alcoholic solutions). It will, however, be appreciated that these values are not limiting values, since the experienced perfumer can

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also produce effects with even lower concentrations or can synthesize novel complexes with even higher dosages. The preferred concentrations range between about 3 wt.% and about 20%. The compositions produced with **I** can be used for all types of perfumed consumer goods (eau de Cologne, toilet water, extracts, lotions, creams, shampoos, soaps, salves, powders, deodorants, detergents, etc.).

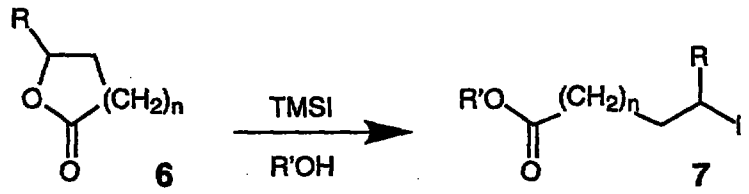
The compounds **I** can accordingly be used in the production of compositions and, as will be evident from the above compilation, a wide range of known odorants or odorant mixtures can be used. In the production of such compositions the odorants or odorant mixtures enumerated above can be used according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

The manufacture of these novel thiamacrolide **I** would be very expensive according to the known process [Chemische Fabriek Naarden, Netherlands Patent No. 96391, 29 June, 1957], since the starting materials (ω-alkenols) required for this are difficultly accessible, not available commercially and very cost-intensive. The same is true for the remaining prior art processes [V. N. Belov, N. P. Solov'eva, T. A. Rudol'fi, I. A. Voronina, *J. Org. Chem. USSR (Engl. Transl.)* **1965**, *1*, 539; H. Matsuyama, T. Nakamura, N. Kamigata, *J. Org. Chem.* **1998**, *54*, 5218].

Accordingly, the manufacture of the thiamacrolides **I** is achieved in accordance with the invention by a novel route which starts from aliphatic diols as well as lactones **6** as readily accessible starting materials.

The route to the thiamacrolides is set for schematically below: it begins with a tandem ring opening-esterification reaction of the lactone **6** in a manner known per se with trimethylsilyl iodide and an alcohol R'OH with 1-6 carbon atoms [M. Kolb, J. Barth, *Synth. Commun.* **1981**, *11*. 763], whereby trimethylsilyl iodide can also be generated *in situ* [e.g. G. A. Olah, S. C. Narrang, G. F. Salem, B. G. B. Gupta, *Synthesis* **1981**, 142].

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6 (n=1–10, R= H, C_1–C_4 alkyl)

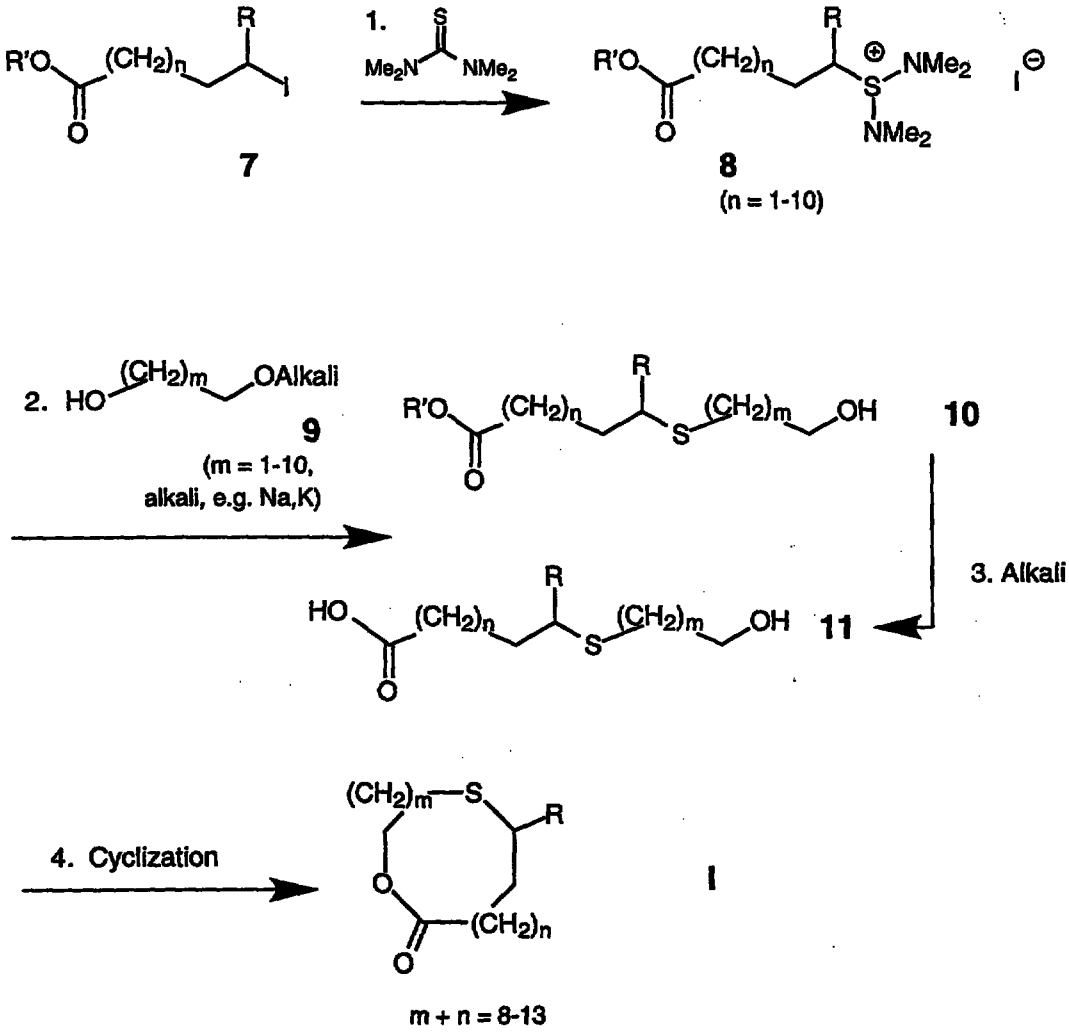
7 (R'= C_1–C_6 alkyl, aryl e.g. phenyl, benzyl)

The iodoesters **7** are then in accordance with the invention converted directly into ω-hydroxy-(n + 3)-thiacarboxylic acids **11**, conveniently in a novel one-pot reaction. In contrast to similar prior art reactions [S. Fujisaki, I. Fujiwara, Y. Norisue, S. Kajigaeshi, *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2429; Y. Takeuchi, K. Sakagawa, M. Kubo, M. Yamato, *Chem. Pharm. Bull.* **1986**, *34*, 1323], which do not lead to the product **10**, in the reaction in accordance with the invention the tetramethylthiouronium salt **8** and the mono-alcoholate **9** are conveniently prepared separately from the corresponding diol and then reacted with each other at elevated temperatures, usually under reflux in an aprotic solvent, especially in acetonitrile.

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The cyclization of the ω-hydroxy-(n + 3)-thiacarboxylic acids **11** (present after the usual basic saponification of the reaction products **10**) to thiamacrolides **I** takes place without intermediate purification of the hydroxy acids. It is preferably carried out by heating **11** with an entraining agent in the presence of as a base as the catalyst, e.g. according to the process of Collaud [Givaudan, U.S. Patent 2234551]. Especially suitable entraining agents are mono- or polyvalent alcohols, for example difficultly volatile alcohols such as glycerol or ethylene glycol, etc. Strong bases such as potassium methylate or sodium methylate especially come into consideration as bases. Suitable temperatures are reflux temperature under reduced pressure, which lie in the range of 100°C to about 200°C.

The stereochemistry of the compounds of formulae **I** and **I'** is determined by the residue (R) of the lactone **6** which is used. Thereby, enantiomerically-enriched and enantiomerically-pure alkyl-substituted

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thiamacrolides can consequentially be manufactured. The present formulae **I** and **I'** accordingly embrace all possible stereoisomers.

In the case of the macrocyclic compounds I' with R = C_1-C_4-alkyl suitable as musk odorants the total sum of carbon atoms should conveniently be n + m + R = 14-17 C atoms.

The following Examples illustrate the invention:

Example 1: 7-Thia-15-pentadecanolide (2)

Ethyl 6-iodocaproate (7, n = 3, R = H, R'= Et): 50 ml (0.37 mol) of trimethylsilyl iodide are added dropwise to a solution of 25 ml (0.24 mol) of ε-caprolactone and 35 ml (0.62 mol) of ethanol in 200 ml of dichloromethane under argon at 0°C. After stirring at room temp. for 1 hr. the reaction mixture is poured into 100 ml of water. The organic phase is washed with 100 ml of water and 100 ml of sat. sodium hydrogen carbonate solution, dried over sodium sulphate and concentrated to dryness on a rotary evaporator. After flash chromatography (*n*-pentane/MTBE, 9:1, hR_f = 74) on silica gel there are obtained 30 g (46%) of ethyl 6-iodocaproate as a colourless liquid.

15-Hydroxy-7-thiapentadecanoic acid (9, n = 3, m = 7, R = H): a solution of 14 g (0.11 mol) of tetramethylthiourea and 28 g (0.10 mol) of ethyl 6-iodocaproate in 220 ml of dry acetonitrile is heated under reflux for 2 h. In a further reaction vessel 23 g (0.16 mol) of 1,8-octanediol are dissolved in 650 ml of dry acetonitrile under argon, the solution is treated with 4.5 g (0.11 mol) of a 60 percent sodium hydride suspension in mineral oil and heated under reflux for 45 min. Both batches are left to cool to 50°C and thereupon combined cautiously within 30 min. The combined reaction mixtures are heated to reflux for 14 h., subsequently saponified with 60 ml of 10 percent potassium hydroxide solution for 3 h. at room temp., concentrated on a rotary evaporator and then added to 1 l of water. The mixture is extracted twice with 500 ml of MTBE each time and the organic extracts are washed three times with 50 ml of 2N sodium hydroxide solution each time. The aqueous phase is acidified with conc. phosphoric acid and extracted three times with 500 ml of MTBE each time. After drying the combined organic extracts over magnesium sulphate and removing the solvent on a rotary evaporator there are obtained 22 g of crude 15-hydroxy-7-thiapentadecanoic acid as a yellowish wax-like solid. An analytical sample is

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obtained after flash chromotography (MTBE/ *n*-pentane, 2:1, hR_f = 33) on silica gel.

IR (film): n = 1691 cm^{-1} (n C=O), 1064 cm^{-1} (n C–OH), 1284/1267 cm^{-1} (n CO–O), 3423/3362 cm^{-1} (n O–H), 1198 cm^{-1} (d O–H). – ^{1}H-NMR ($CDCl_3$): d = 1.31–1.49 (m, 10H, 4-,10-H_2–13-H_2), 1.54–1.71 (m, 8H, 2-,5-,9-,14-H_2), 2.36 (t, *J* = 7.6 Hz, 2H, 2-H_2), 2.50 / 2.51 (t, *J* = 7.2 Hz, 4H, 6-,8-H_2), 3.65 (t, *J* = 6.6 Hz, 2H, 15-H_2). – ^{13}C-NMR ($CDCl_3$): d = 24.18 (t, C-3), 25.46 (t, C-13), 28.12 / 28.61 / 28.98 (t, C-4,-10,-11), 29.08 / 29.13 / 29.44 (t, C-5,-9,-12), 31.68 / 31.92 (t, C-6,-8), 32.26 (t, C-14), 33.78 (t, C-2), 62.57 (t, C-15), 178.59 (s, C-1). – MS (EI): m/z (%) = 143 (100) [$C_8H_{15}S^+$], 161 (8) [$C_8H_{17}OS^+$], 175 (4) [$C_9H_{19}OS^+$], 229 (5) [$C_{12}H_{21}O_2S^+$]; 276 (22) [$C_{14}H_{28}O_3S^+$].

7-Thia-15-pentadecanolide (**2**): 22 g of crude 15-hydroxy-7-thiapentadecanoic acid (**9**, n = 3, m = 7, R = H) are treated with 0.45 ml (4.0 mmol) of 50 percent potassium hydroxide solution and byproducts are distilled off at 180°C/20-23 mbar for 1 h. Thereupon, the reaction vessel is fitted with a condenser and separator and 1.2 g (17 mmol) of potassium methylate in 300 ml of anhydrous glycerol are added to the reaction mixture. The mixture is heated to reflux at 153°C/4-6 mbar over the separator for 2 d., with 1.2 g (17 mmol) of potassium methylate again being added after 14 h. The separated glycerol is poured into 800 ml of water and the crude product is extracted twice with 500 ml of MTBE each time and once with 500 ml of *n*-pentane. The combined organic extracts are dried over magnesium sulphate and concentrated to dryness on a rotary evaporator. After flash chromatography (*n*-pentane/MTBE, 19:1, h*R*f = 46) on silica gel there are obtained 2.9 g (11% overall yield) of 7-thia-pentadecanolide as a colourless wax-like solid with an *intensive, linear musk odour accompanied by green-mossy aspects* with a threshold value of 0.2 ng/l air.

IR (film): n = 1732 cm^{-1} (n C=O), 1247 cm^{-1} (n C-CO-O), 1124 cm^{-1} (n C-O-C). – ^{1}H-NMR ($CDCl_3$): d = 1.26–1.50 (m, 10H, 4-,10-H_2–13-H_2), 1.56–1.77 (m, 8H, 3-,5-,9-,14-H_2), 2.35 (t, *J* = 6.8 Hz, 2H, 2-H_2), 2.52 / 2.53 (t, *J* = 6.8 Hz, 4H, 6-,8-H_2), 4.15 (t, *J* = 5.2 Hz, 2H, 15-H_2). – ^{13}C-NMR ($CDCl_3$): d = 24.68 (t, C-3), 25.16 (t, C-13), 26.11 (t, C-4), 27.12 / 27.25 / 27.58 / 27.73 (t, C-10,-11,-12,-14), 28.32 / 28.36 (t, C-5,-9), 30.66 / 30.92 (t, C-6,-8), 34.36 (t, C-2), 64.01 (t, C-15), 173.65 (s, C-1). – MS (EI): m/z (%) = 143 (100) [$C_8H_{15}S^+$], 157 (7) [$C_9H_{17}S^+$], 229 (7) [$C_{12}H_{21}O_2S^+$], 258 (74) [$C_{14}H_{26}O_2S^+$].

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Example 2: 4-Methyl-5-thia-15-pentadecanolide (I, n = 1, m = 9, R = Me)

Ethyl 4-iodovalerate (7, n = 1, R = Me, R' = Et): Analogously to the synthesis of ethyl 6-iodocaproate (Example 1), 67 ml (0.96 mol) of γ-valerolactone are reacted with 140 ml (2.4 mol) of ethanol and 200 ml (1.4 mol) of trimethylsilyl iodide. After usual working-up and flash chromatography (*n*-pentane/MTBE, 9:1, hR_f = 63) there are obtained 94 g (73%) of ethyl 4-iodovalerate as a colourless liquid.

4-Methyl-5-thia-15-pentadecanolide (I, n = 1, m = 9, R = Me): Analogously to the synthesis of 7-thia-15-pentadecanolide (Example 1) via 15-hydroxy-7 thiapentadecanoic acid, 15 g (0.12 mol) of tetramethylthiourea are reacted with 25 g (0.96 mol) of ethyl 4-iodovalerate in 200 ml of dry acetonitrile and in parallel 20 g (0.12 mol) of decanediol in 640 ml of dry acetonitrile are reacted with 5.1 g (0.12 mol) of 60 percent sodium hydride suspension in mineral oil, the reaction products are combined as described and heated under reflux for 20 h. After the usual working-up there are obtained 19 g of crude 15-hydroxy-4-methyl-5-thiapentadecanoic acid, which is polymerized with 0.07 ml (0.62 mmol) of 50 percent potassium hydroxide solution and depolymerized with two 0.9 g (13 mmol) aliquots of potassium methylate in 300 ml of glycerol as described under Example 1. After usual working-up and flash chromatography there are obtained 3.6 g (14% overall yield) of 4-methyl-5-thia-15-pentadecanolide as a colourless wax-like solid having a *sweet musk-like odour with green and metallic nuances* with a threshold value of 1.8 ng/l air.

IR (film): n = 1734 cm^{-1} (n C=O), 1163 / 1194 cm^{-1} (n C-O), 1268 cm^{-1} (n C-CO-O). – ^{1}H-NMR ($CDCl_3$): d = 1.28 (d, *J* = 6.8 Hz, 3H, 4-Me), 1.31–1.65 (m, 16H, 7-H_2–13-H_2), 1.79 (dddd, *J* = 7.2, 6.8, 6.4 and 1.0 Hz, 1H, 3-H_b), 1.79 (dddd, *J* = 7.2, 6.8, 6.4 and 1.0 Hz, 1H, 3-H_b), 1.89 (dddd, *J* = 7.2, 6.8, 6.8 and 6.4 Hz, 1H, 3-H_a), 2.41 (ddd, *J* = 15.6, 6.4 and 6.4 Hz, 1H, 2-H_b), 2.49 (ddd, *J* = 12.8, 6.8 and 6.8 Hz, 1H, 6-H_b), 2.55 (ddd, *J* = 12.8, 6.8 and 6.8 Hz, 1H, 6-H_a), 2.65 (ddd, *J* = 15.6, 7.2 and 7.2 Hz, 1H, 2-H_a), 2.80 (qdd, *J* = 6.8, 6.8 and 1.0 Hz, 1H, 4-H), 4.06 (ddd, *J* = 10.8, 6.4 and 3.6 Hz, 1H, 15-H_b), 4.23 (ddd, *J* = 10.8, 8.0 and 3.6 Hz, 1H, 15-H_a). – ^{13}C-NMR ($CDCl_3$): d = 21.43 (q, 4-Me), 24.25 (t, C-3), 26.10 / 26.11 / 26.20 (t, C-8,-13,-14), 26.69 / 27.01 / 27.89 / 28.11 (t, C-9,-10,-11,-12), 29.17 (t, C-7), 31.43 / 31.56 (t, C-2,-6), 38.87 (d, C-4), 63.79 (t, C-15), 173.53 (s, C-1). – MS (EI) m/z (%) = 87 (100) [$C_4H_7S^+$], 101 (97) [$C_5H_9S^+$], 114 (77) [$C_6H_{10}S^+$], 132 (35) [$C_7H_{16}S^+$], 171 (23) [$C_{10}H_{19}S^+$], 257 (1) [$C_{14}H_{25}O_2S^+$], 272 (16) [$C_{15}H_{28}O_2S^+$].

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The following compounds are accessible in a corresponding manner. Therefore, only the spectroscopic data are set forth for them:

Example 3: 6-Thia-16-hexadecanolide (1)

Intensive musk odour with powdery-dry effect with a threshold value of 0.1 ng/l air. – IR (film): n = 1734 cm^{-1} (n C=O), 1256 cm^{-1} (n C-CO-O), 1181 / 1128 cm^{-1} (n C-O). – ^{1}H-NMR ($CDCl_3$): d = 1.32–1.46 (m, 12H, 9-H_2–14-H_2), 1.56–1.67 (m, 6H, 3-,4-,8-H_2), 1.72–1.79 (m, 2H, 15-H_2), 2.35 (t, *J* = 7.2 Hz, 2H, 2-H_2), 2.51 / 2.52 (2t, *J* = 7.2 Hz, 4H, 5-,7-H_2), 4.15 (dd, *J* = 5.6 and 5.6 Hz, 2H, 16-H_2). – ^{13}C-NMR ($CDCl_3$): d = 24.32 (t, C-3), 25.06 (t, C-14), 26.75 / 26.92 / 26.92 (t, C-10,-11,-12), 27.34 / 27.64 (t, C-9,-13), 28.32 / 28.46 (t, C-4,-8), 29.79 (t, C-15), 31.61 / 31.93 (t, C-5,-7), 34.28 (t, C-2), 64.05 (t, C-16), 173.43 (s, C-1). – MS (EI) m/z (%) = 87 (100) [$C_4H_7S^+$], 101 (61) [$C_5H_9S^+$], 117 (27) [$C_6H_{13}S^+$], 171 (31) [$C_{10}H_{19}S^+$], 272 (18) [$C_{15}H_{28}O_2S^+$].

Example 4: 11-Thia-15-pentadecanolide (3)

Intensive musk odour with a note of freshly pressed wax and a characteristic soapy-wax like accent essentially for nitromusk substances with a threshold value of 0.2 ng/l air. – IR (film): n = 1734 cm^{-1} (n C=O), 1245 cm^{-1} (n C-CO-O), 1164 cm^{-1} (n C-O). – ^{1}H-NMR ($CDCl_3$): d = 1.34–1.47 (m, 10H, 4-H_2–8-H_2), 1.58–1.75 (m, 8H, 3-,9-,13-,14-H_2), 2.34 (t, *J* = 7.2 Hz, 2H, 2-H_2), 2.51 / 2.52 (2t, *J* = 3.6 Hz, 4H, 10-,12-H_2), 4.14 (t, *J* = 4.8 Hz, 2H, 15-H_2). – ^{13}C-NMR ($CDCl_3$): d = 24.65 (t, C-3), 26.14 / 26.16 (t, C-13,-14), 26.65 / 26.87 (t, C-4,-8), 27.18 / 27.59 / 27.78 / 28.02 (t, C-5,-6,-7,-9), 30.48 / 30.86 (t, C-10,-12), 34.17 (t, C-2), 63.64 (t, C-15), 173.79 (t, C-1). – MS (EI) m/z (%) = 88 (100) [$C_4H_8S^+$], 101 (14) [$C_5H_9S^+$], 115 (6) [$C_6H_{11}S^+$], 133 (6) [$C_7H_{17}S^+$], 151 (7) [$C_9H_{11}O_2^+$], 199 (7) [$C_{11}H_{19}OS^+$], 217 (6) [$C_{11}H_{21}O_2S^+$], 258 (10) [$C_{14}H_{26}O_2S^+$].

Example 5: 6-Thia-14-tetradecanolide (4)

Sweet musk note green-earthy impact with a threshold value of 0.3 ng/l air. – IR (film): n = 1730 cm^{-1} (n C=O), 1261 / 1221 cm^{-1} (n C-CO-O), 1131 / 1156 cm^{-1} (n C-O). – ^{1}H-NMR ($CDCl_3$): d = 1.38–1.56 (m, 10H, 3-H_2,9-H_2–12-H_2), 1.63–1.70 (m, 4H, 4-,8-H_2), 1.73–1.78 (m, 2H, 13-H_2), 2.38 (t, *J* = 6.4 Hz, 2H, 2-H_2), 2.50 / 2.52 (2t, *J* = 7.6 / 6.4 Hz, 4H, 5-,7-H_2), 4.16 (dd, *J* = 5.2 and 4.0 Hz, 2H, 14-H_2). – ^{13}C-NMR ($CDCl_3$): d = 24.53 / 24.61 (t, C-3,-12), 25.78 (t, C-

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13), 26.35 / 26.83 (t, C-10,-11), 28.13 / 28.16 (t, C-4,-9), 30.51 (t, C-8), 31.85 / 32.86 (t, C-5,-7), 34.20 (t, C-2), 63.87 (t, C-14), 173.53 (s, C-1). – MS (EI) m/z (%) = 87 (100) [$C_4H_7S^+$], 101 (55) [$C_5H_9S^+$], 117 (32) [$C_6H_{13}S^+$], 143 (51) [$C_8H_{15}S^+$], 159 (4) [$C_8H_{15}OS^+$], 215 (2) [$C_{12}H_{24}OS^+$], 244 (21) [$C_{13}H_{24}O_2S^+$].

Example 6: Fresh-spicy wood accord, for use in masculine perfume and body care products

	Parts by weight
7-THIA-15-PENTADECANOLIDE (2)	50
BENZYL ACETATE EXTRA	30
GERANYL ACETATE PURE	50
2-PENTYLOXYGLYCOLIC ACID ALLYL ESTER	3
METHYL ANTHRANILATE	1
BASIL OIL	10
BERGAMOT OIL	200
CARBITOL	20
METHYL-ALPHA-IONONE	50
CITRUS OIL	100
COUMARIN CRYST.	20
DIHYDROMYRCENOL	100
TARRAGON OIL	5
EVERNYL	3
CLOVE FLOWER OIL	15
METHYL DIHYDROJASMONATE	50
ISO E SUPER	50
ISOEUGENOL	3
LAVANDIN OIL	100
METHYL CEDRYL KETONE	60
NUTMEG OIL	20
PATCHOULI OIL	30
γ-UNDECALACTONE	1
PETITGRAIN OIL PARAGUAY	7
SANDALORE	20
VANILLIN	2
	1000

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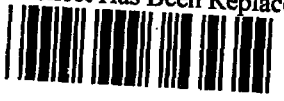
7-Thia-15-pentadecanolide (2) confers to the composition a sweet musk note, additional volume and softness, and underlines the body care aspect of cosmetic articles.

Example 7: *Fresh flowery bouquet, suitable for use in soaps and body care products*

	Parts by weight
11-THIA-15-PENTADECANOLIDE (3)	50
BENZYL ACETATE EXTRA	30
L-BORNYL ACETATE EXTRA	6
LINALYL ACETATE SYNTH.	80
PARA-TERT.-BUTYLCYCLOHEXYL ACETATE	100
VERDYL ACETATE	15
ALPHA-HEXYLCINNAMALDEHYDE	130
2-PENTYLOXYGLYCOLIC ACID	3
CEDARWOOD OIL	10
DAMASCENONE, 10% DIETHYL PHTHALATE	5
DIHYDROMYRCENOL	80
2,5-DIMETHYL-2-OCTEN-6-ONE	7
FLORHYDRAL (3-(3-ISOPROPYLPHENYL)-BUTANAL)	4
GIVESCONE	10
METHYL DIHYDROJASMONATE	40
INDOLINE	4
ISORALDEINE 95	100
CITRAL	5
LINALOOL SYNTH.	200
NECTARYL	10
OKOUMAL (2,4-DIMETHYL-2-(1,1,4,4-TETRAMETHYL-TETRALIN-6-YL)-1,3-DIOXOLANE)	10
TANGERINOL (6,10-DIMETHYL-5,9-UNDECADIEN-ACETIC ACID-2-YL ESTER)	1
ACETYLCEDRENE	100
	1000

The 11-thia-15-pentadecanolide(3) confers to the composition a fine musk note, gives it sweetness and volume and emphasises the skin care character of cosmetic articles.

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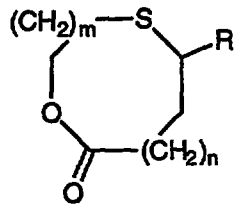
The above technical expressions can be identified e.g. on the basis of the monograph Allured Flavor and Fragrance Materials, 1996, Allured Publishing Company, Carol Stream, IL (USA).

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Claims

1. Compounds of the formula



I

wherein R = H and wherein m = 9 and n = 3, or
m = 7 and n = 4, or
m = 3 and n = 8, or
m = 7 and n = 3.

2. 6-Thia-16-hexadecanolide.

3. 7-Thia-15-pentadecanolide.

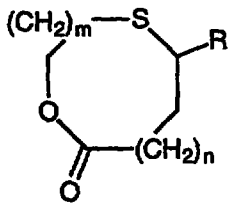
4. 11-Thia-15-pentadecanolide.

5. 6-Thia-14-tetradecanolide.

6. Odorant compositions, which contain a compound of formula I in accordance with claim 1.

7. The use of a compound in accordance with claim 1 to 5 as an odorant.

8. A process for the manufacture of the compounds of the formula



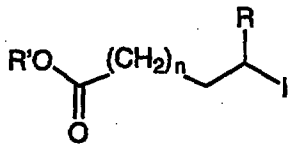
I'

wherein R = H or C_1-C_4 alkyl
and m = 1-10, n = 1-10,
as well as n + m = 8-13,

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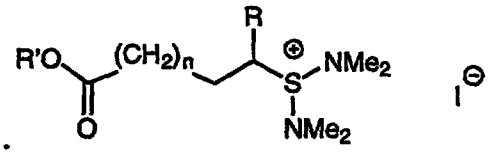
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which process comprises reacting an iodo ester of the formula



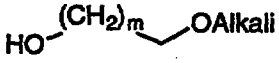
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wherein R' signifies C_{1-6}-alkyl or aryl,
with tetramethylurea to give a tetramethylthiouronium salt of the formula



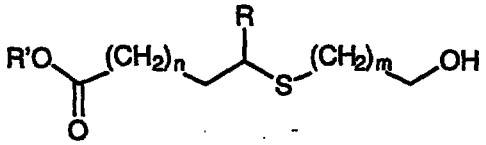
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and reacting this salt **8** at an elevated temperature with a monoalcoholate of the formula



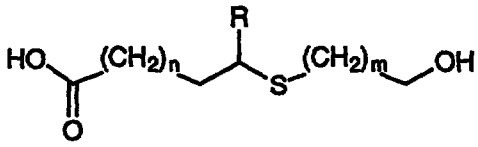
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to give a compound



10

saponifying this compound **10** basically to give a compound of the formula



11

and cyclizing the compound **11** in a manner known per se to give a lactone of formula **I'**.

9. A process according to claim 8, wherein the compound **11** is cyclized by heating with an entraining agent in the presence of a base.

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