Synthesis and Odor of Aliphatic Musks: Discovery of a New Class of Odorants

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Keywords: Conformation analysis / Fragrances / Musks / Olfactory properties / Structure−activity relationships

To find new aliphatic musks, we synthesized the propionates of 2-[1′-(3′′,3′′-dimethylcyclohex-1′′-enyl)ethoxy]-2-methylpropanol (**8**), of 2-[1′-(5′′,5′′-dimethylcyclohex-1′′-enyl)ethoxy]-2-methylpropanol (**11**), of hydroxyacetic acid 1-(3′,3′-dimethylcyclohex-1′-enyl)ethyl ester (**12**), and of hydroxyacetic acid 1-(5′,5′-dimethylcyclohex-1′-enyl)ethyl ester (**13**) starting from 1-(3′,3′-dimethylcyclohex-1′-enyl)ethanone (**5**) and 1-ethynyl-3,3-dimethylcyclohexanol (**9**). We found that the 3,3-dimethylcyclohexenyl derivatives **8** (odor threshold 0.2 ng/air) and **12** (odor threshold 0.6 ng/air) are superior musk odorants, and, thus, we constructed 1,2,4-trimethylpent-2-enyloxy analogues as *seco* versions. The synthesis of the esters **17**–**26** commenced with a Wittig–Horner– Emmons reaction of isobutyric aldehyde (**14**), followed by saponification, alkylation with methyllithium, LAH reduction, etherification with isobutylene oxide, and Steglich esterification. (2′′*E*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl cyclopropanecarboxylate [(2′′*E*)-**19**], which has a powerful and sweet musk odor and slightly fruity nuances, was found to be a typical representative of this new class of musk odorants, was subjected to conformational analysis. In addition, we report the synthesis and olfactory properties of the related ketones **28**–**30**, the 2-methyl-2-(1′,4′,4′-trimethylpent-2′-enyloxy)propyl esters **31**–**33**, and the 2-(1′,4′-dimethylpent-2′-enyloxy)-2-methylpropyl esters **35** and **36**.
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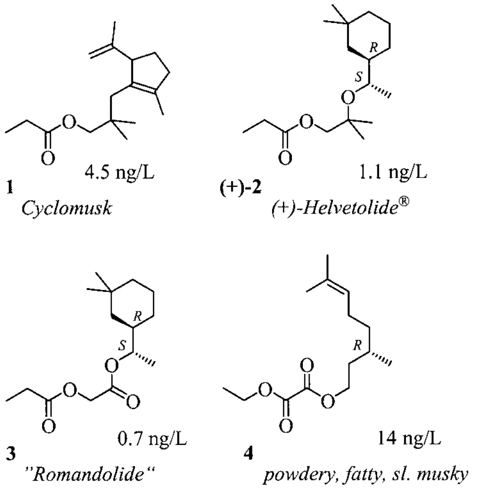
Introduction

Speak of perfumery and at some time you must mention musks. In many classic scents, musk odorants are key foundation stones, and they are indispensable in perfumery for imparting sensuality.[1] Musk odorants refine, exalt, and harmonize compositions, and they convey a smooth, soft, and intimate "skin-on-skin" feeling — a cosy odor impression that is often associated with that of baby skin. In general, three main structural classes of musk odorants are known: nitro arenes, polycyclic musks (PCM), and macrocycles.[2] While the massive production volumes and the non-biodegradability of the former two classes have led to bioaccumulation,[3] the ecologically benign macrocycles are still comparatively expensive and, thus, have not completely replaced benzenoid musks. Therefore, an old fragrance raw material, which had been discovered by Hoffmann and von Fraunberg of BASF in 1975,[4] has gained significance as a lead structure: Cyclomusk® (**1**, Scheme 1), which possesses a fruity, strawberry-type musk odor, but does not belong structurally to one of the three known classes of musk odorants. In 1990, Giersch and Schulte-Elte of Firmenich[5] discovered Helvetolide® (**2**), another representative of this exceptional family of musk odorants. It emanates a musky-floral, fruity, pear-like odor, which was reported to be mainly due to the (1′′*S*,3′′′*R*)-enantiomer (+)-**2**. Eight years later, Williams of Firmenich[6] found that the *gem*-dimethyl ether motive of Helvetolide® (**2**) can be replaced by an ester moiety without losing the musk note. The resulting musk odorant, *rac*-**3**, which was introduced into perfumery as Romandolide, was claimed to be less fruity and more ambrette-like in smell than **2**. Again, the depicted (1′′*S*,3′′′*R*)-enantiomer of **3** was reported to be the more powerful and more characteristic isomer. Both odorants



Scheme 1. Known representatives of the new generation of musk odorants

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DOI: 10.1002/ejoc.200300578

have become fairly popular recently, with usage levels of up to 8.8 (**2**) and 5.0% (*rac*-**3**),[1] respectively. Because of their transparency, both **2** and *rac*-**3**, blended with the isomeric 11/12-pentadecen-15-olides (Habanolide®, Globalide®), are important in so-called "white musk" accords.[1] On the other hand, because of their fruity tonality, they convey in higher dosages a unique signature to perfumes.

Another aliphatic compound that possesses a clearly discernible musk facet is ethyl citronellyl oxalate (*rac*-**4**),[7] even though its main character is floral, powdery, and rosy, with a relatively high odor threshold of 14 ng/L air,[1] and even though it is not used in perfumery as a musk odorant. Beets proposed that this flexible linear molecule may adopt a conformation on the receptor in which it has a cyclic shape,[8] and related the musky aspects of *rac*-**4** to a conformation resembling the musk-smelling macrocycle dodecylene oxalate. Later, Yoshii et al. published a conformational analysis of the (*R*)-enantiomer (**4**).[9] This enantiomer determines the odor of the racemate, *rac*-**4**, because (*S*)-ethyl citronellyl oxalate (*ent*-**4**) is almost odorless. Yoshii et al.[9] rationalized the musky facets of **4** with the two most-stable conformers, determined by PM3 molecular modeling calculations, which indeed possess cyclic shapes.

Conformational Analysis of (+)-2 and 3

Bearing in mind that the odor of macrocyclic musks is strongly diminished by a *gem*-dimethyl group,[10] as well as by an additional carbonyl group, unless in 1,5- or 1,6-arrangements,[10] these structural features of compounds **1**, **2** (2′-Me$_2$), and **3** (2′-C=O) are most surprising. Therefore, we analyzed their conformational importance. In Helvetolide® (**2**), the steric interaction of the 1′′-methyl group with the 2′-*gem*-dimethyl group forces the C-2′−O−C-1′′−C-1′′′ unit into a (−)-*anticlinal* conformation and the C-1′−C-2′−O−C-1′′ unit into an *antiperiplanar* conformation. In turn, steric and electronic effects, i.e., the interaction of σ(O−C-1′) as donor with σ*(C-2′−C-3′) as acceptor, forces the O−C-1′−C-2′−O unit into a (−)-*synclinal* conformation. Thus, the molecule gets bent twice and adopts a horseshoe-shaped conformation, as shown in Figure 1, A. The C−O bond of the propyl ester unit has considerable double-bond character, and steric repulsion in the (*E*)-conformer, as well as electrostatic attraction and n−σ* overlap in the (*Z*)-conformer of the ester group, favors the latter and defines an *all-trans* oxapentyl edge with a (*Z*)-carbonyloxy group. In the diester **3**, the *eclipsed* 1′-carbonyl function performs the role of the bulky *gem*-dimethyl moiety of **2**. Furthermore, the electrostatic attraction of the propyl ester's carbonyl carbon atom and the opposite oxycarbonyl oxygen atom also induces a (−)-*synclinal* conformation of O−C-2′−C-1′−O in Romandolide (**3**, Figure 1, B). Conformational calculations on a PM3 level proved these conformational considerations to be valid, but the energetic differences between the different conformers are very small and, thus, the energetically most favored conformation is not necessarily the one that interacts with the receptor site.

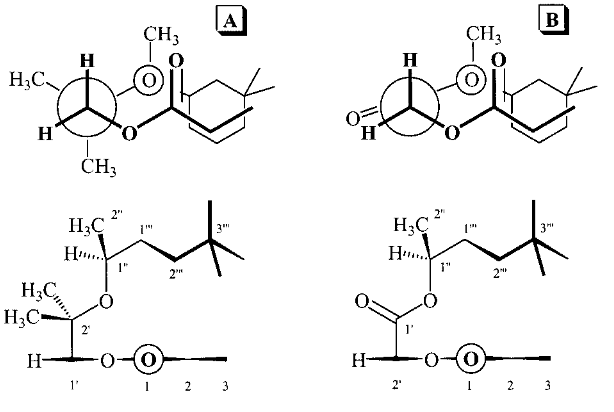
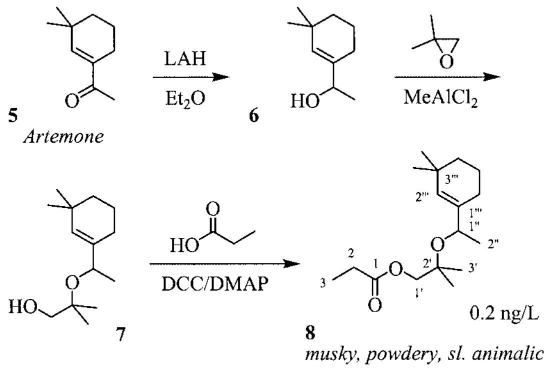


Figure 1. Conformational considerations of Helvetolide® (**2**) and Romandolide (**3**)

Because of their high molecular weight, compounds **1**−**3** are not very diffusive on the smelling strip or in applications, despite their good odor thresholds. Therefore, to increase diffusivity, we planned to synthesize aliphatic musk odorants having higher vacuum pressures. Additionally, to increase their biodegradability, we aimed for "all-aliphatic" target structures: musk odorants without branched alicyclic moieties.

Results and Discussion

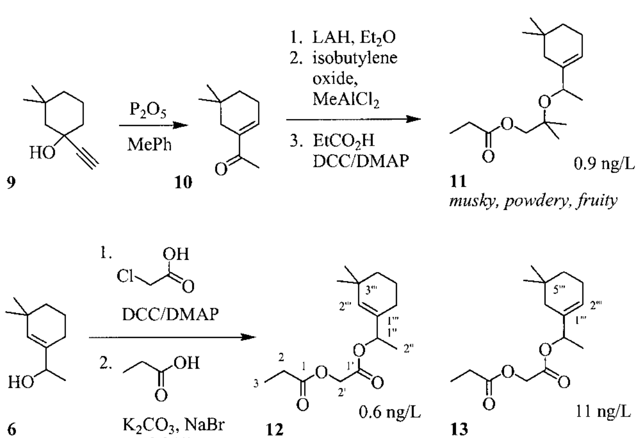
Our first synthetic target was the unsaturated 2′-[1′′-(3′′′,3′′′-dimethylcyclohex-1′′′-enyl)ethoxy]-2′-methylpropyl propionate (**8**), which should provide some insight into the importance of the ring stereocenter. Artemone® [1-(3′,3′-dimethylcyclohex-1′-enyl)ethanone, (**5**)], a commercial herbal-agrestic, thujone-like odorant, constituted an ideal starting material. Standard lithium aluminum hydride (LAH) reduction of **5** provided the corresponding methyl carbinol **6** in 87% yield (Scheme 2). In the presence of half an equivalent of methylaluminum dichloride, isobutylene oxide was opened with **6** to give the hydroxy ether **7**. Although only a moderate yield (19%) of **7** was obtained after 20 h of reaction at ambient temperature, the alcoholysis of isobutylene oxide was completely regioselective, with the nucleophile attacking exclusively at the quaternary carbon



Scheme 2. Synthesis of the unsaturated Helvetolide® derivative **8**

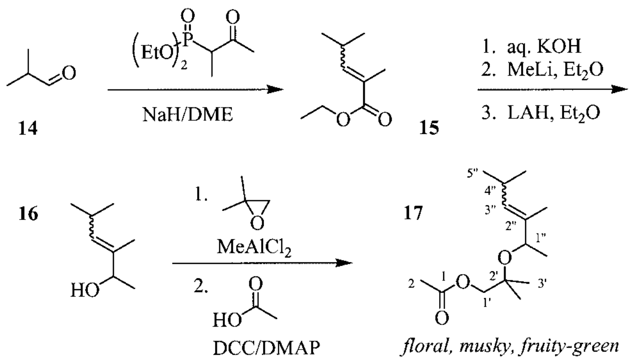
atom, as expected. During the process of epoxide opening, however, the product **7** competes with the methyl carbinol **6**, which is even more sterically crowded. This situation leads to polyethers and may explain the severely diminished yield of this step. Nevertheless, this route seemed to us to be the most straightforward one and, after Steglich esterification[11] of **7** with propionic acid in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) in dichloromethane, the first target structure **8** was isolated by flash chromatography (FC) in 89% yield. Considering the importance of the ring stereocenter of (+)-**2**, it was astonishing and unexpected to us that **8** not only possesses a powerful, powdery musk odor of slightly animalic tonality, but, most of all, that it also has an even lower odor threshold (0.2 ng/L air) than the Helvetolide® enantiomer (+)-**2**.

Thus, we then synthesized the double-bond isomer **11**, starting from the ethynyl cyclohexanol **9** (Scheme 3).[12] Although it proceeded only in quite low yields, Rupe rearrangement[13] of **9** provided a ca. 7:1 mixture of the 1-(5′,5′-dimethylcyclohex-1′-enyl)ethanone (**10**) and Artemone® (**5**),[14] which were separated by flash chromatography. Subjecting **10** to the same sequence of reactions described above — LAH reduction, etherification with isobutylene oxide, and Steglich esterification with propionic acid — furnished the target structure **11**, which also possessed a powdery musk odor. It has, however, a higher odor threshold (only 0.9 ng/L air) and is more fruity in its character than **8**. To complete the series, we also tackled the synthesis of the diesters **12** and **13**, which feature the Romandolide motif. Steglich esterification of the allylic alcohols with chloroacetic acid provided the corresponding chloroacetic esters in 77 and 83% yields, respectively. These compounds were then esterified with propionic acid by employing potassium carbonate in diethyl ketone and dioxane to furnish the odoriferous diesters **12** and **13**. Again the 3′′′,3′′′-dimethylcyclohexenyl derivative **12** possesses a more distinct musk note than the 5′′′,5′′′-dimethylcyclohexenyl diester **13**, and also has a much better odor threshold, i.e., 0.6 vs. 11 ng/L air.



Scheme 3. Syntheses of further 3′′′,3′′′- and 5′′′,5′′′-dimethylcyclohexene analogues **11**−**13**

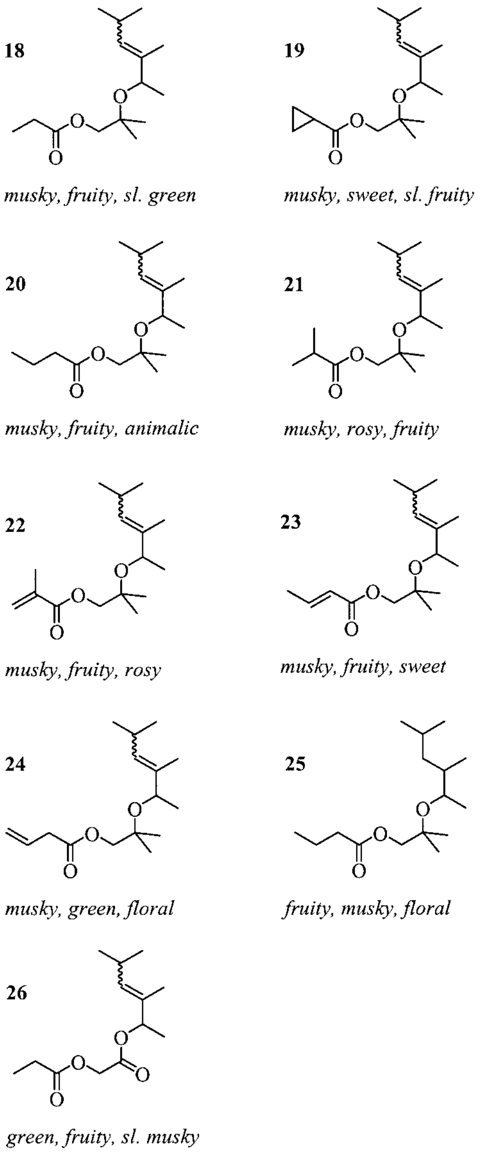
Conceptually, by cutting out the atoms C-4′′′ and C-5′′′, we next replaced the 3′′′,3′′′-dimethylcyclohex-1′′′-enyl group by a 1′′,2′′,4′′-trimethylpent-2′′-enyl moiety. By virtue of the reduced molecular weight, this substitution should increase the vapor pressure and, thereby, the diffusivity of the resulting compounds. To start out with an even lower molecular weight, we selected the acetate **17** as our next target structure.



Scheme 4. Synthesis of the first target structure **17** featuring a 1′′,2′′,4′′-trimethylpent-2′′-enyl moiety

As is shown in Scheme 4, our synthesis of **17** commenced with the Wittig−Horner−Emmons reaction of isobutyric aldehyde (**14**) with triethyl 2-phosphonopropionate, which provided the ethyl 2,4-dimethylpent-2-enoate (**15**) in 75% yield after distillation. This compound was then transformed into the monomethyl carbinol **16** by means of saponification with aqueous potassium hydroxide, reaction of the resulting α,β-unsaturated acid with methyllithium, and subsequent LAH reduction. Carbinol **16** was isolated after flash chromatography in 84% overall yield, and then it was subjected to the standard sequence of etherification with isobutylene oxide and Steglich esterification. Indeed, the resulting acetate **17** emanated a musky note, although accompanied by floral and green-fruity aspects; its odor threshold, however, was quite bad. By GC-olfactometry we measured odor thresholds of 54 ng/L air for the main (2′′-*Z*)-isomer (55%) and 12 ng/L air for the (2′′-*E*)-isomer (45%). The isomeric ratio was determined by NMR spectroscopic analysis. The upfield shift, as a consequence of γ-effects, of the 2′′-Me group at $\delta = 11.1$ ppm in the ^{13}C NMR spectrum is typical for *E*-configured trisubstituted double bonds, while the 2′′-Me group in the *Z*-isomer of **17** resonates at $\delta = 17.6$ ppm.

What effect does modifying the ester group have on the musk odor of the 2′-methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl esters? Exchanging acetic acid for different saturated and unsaturated C_3-C_4 acids in the Steglich esterification step provided some answers that are summarized in Figure 2. The propionate **18** is already much more intense, having an odor threshold of 1.2 ng/L for the (*E*)-isomer, which again turned out to be the more-powerful isomer. In addition, its musk odor was much more pronounced and was accompanied only by some fruity and



18 *musky, fruity, sl. green*

19 *musky, sweet, sl. fruity*

20 *musky, fruity, animalic*

21 *musky, rosy, fruity*

22 *musky, fruity, rosy*

23 *musky, fruity, sweet*

24 *musky, green, floral*

25 *fruity, musky, floral*

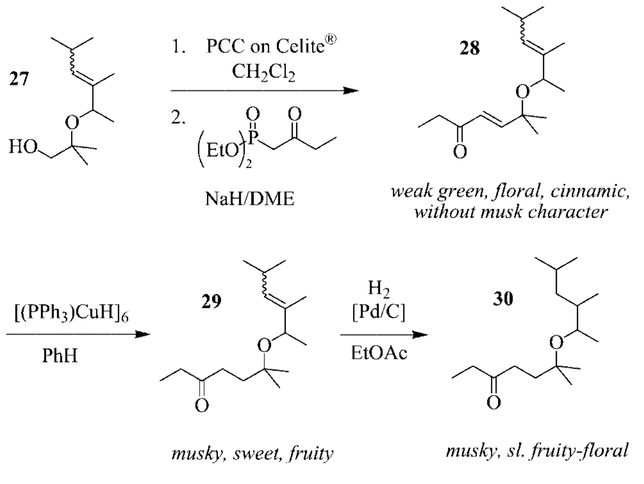
26 *green, fruity, sl. musky*

Figure 2. Overview of further "all-aliphatic" esters **18**−**26** and their odor descriptions

slightly green nuances. The cyclopropanecarboxylate **19** emanated the most distinct musk character of this series (Figure 2); it was sweeter than **18** with only a faint fruity undertone, even though its odor threshold was a bit higher, at 5.7 ng/L air for the stronger *E*-isomer. With an odor threshold of 1.8 ng/L air for the isomeric mixture, the butyrate **20** is more powerful than **18**, but it already has some inflections in the animalic direction. The isobutyrate **21** and the methacrylate **22** are of comparable intensity, at 2.2 and 3.7 ng/L air, respectively, and possess rosy nuances besides their main musk note. The musky, fruity, sweet character of the 2-butenoate **23** is also very pleasant, but at a threshold of 8.5 ng/L air it is already significantly weaker with respect to **18**−**20**. The isomeric 3-butenoate was, at 4.6 ng/L air, again stronger than **23**, and its main musk character was accompanied by green-floral tonalities. This effect demonstrates the influence that the double bond in the ester chain has on the odor.

To study if the double bond in the 1′′,2′′,4′′-trimethylpent-2′′-enyl moiety is really crucial, we hydrogenated **20** in the presence of palladium on activated carbon in ethyl acetate. Astonishingly, the resulting saturated butyrate **25** is still musky, although it has a pronounced fruity character; with an odor threshold of 1.0 ng/L air it has comparable intensity with its synthetic precursor **20**. Next we tackled the synthesis of the diester **26** to investigate if the *gem*-dimethyl group of **18** could be replaced by a carbonyl group. Steglich esterification of **16** with chloroacetic acid and subsequent esterification of the resulting monoester with propionic acid furnished **26** in 33% overall yield. Indeed, **26** has a musky character as well, although it also possesses pronounced green-fruity facets. Compared with **18**, however, **26** is much weaker, possessing an odor threshold of only 16 ng/L air; in addition, its musk character is inferior.

We then explored the structurally related ketones **28**−**30** bearing different degrees of unsaturation. Oxidation of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**) with pyridinium chlorochromate on Celite® furnished in 85% yield the corresponding aldehyde, which was treated with the ylide of diethyl (2-oxobutyl)phosphonate to provide the (4*E*)-configured α,β-unsaturated ketone **28** (Scheme 5). This compound possesses a relatively weak green, floral, cinnamic odor, and is devoid of any musk note. Being part of an *E*-configured double bond, the C-5 unit cannot, of course, adopt a *gauche* conformation and, thus, **28** cannot attain the horseshoe-like shape resembling the conformers depicted in Figure 1. Employing the copper(I) hydride cluster [(Ph$_3$P)CuH]$_6$, as reported by Stryker et al.,[15,16] we selectively reduced the α,β-unsaturated double bond of **28** and obtained, after flash chromatography in 81% yield, the heptan-3-one **29**, which indeed emanates a musky, sweet, and fruity odor with an excellent threshold of 0.55 ng/L air. We then hydrogenated **29** in the presence of palladium on activated carbon to prepare the fully saturated 6-methyl-6-alkyloxy heptan-3-one **30**. This compound also possesses a typical musk odor of a slightly



Scheme 5. Synthesis of an unsaturated (**28**), a partially unsaturated (**29**), and a fully hydrogenated 6-methyl-6-alkyloxyheptan-3-one (**30**)

fruity-floral connotation, and is, with an odor threshold of 0.87 ng/L air, of approximately the same intensity as **29**.

Finally, we wanted to design *all-aliphatic* musks that are even easier and more economical to manufacture on an industrial scale, which, therefore, would make them even more attractive relative to macrocyclic musks in terms of price. If the C-2″-methyl group of the 1″,2″,4″-trimethylpent-2″-enyl moiety was not crucial for the musk odor, simple aldol condensations with acetone would lead to interesting bulky building blocks. Following the procedure of Woodward et al.,[17] we condensed acetone with pivalaldehyde; (3*E*)-5-methylhex-3-en-2-one, the aldol condensation product of acetone with isobutyric aldehyde (**14**), was commercially available. Subsequent standard LAH reductions of these enones provided the corresponding allylic alcohols, which were simply etherified with isobutylene oxide, except for the levulinate **34**, and then esterified with different acids to provide the target molecules summarized in Figure 3. Although their musk characters are less pronounced than those of the corresponding 2′-methyl-2′-(1″,2″,4″-trimethylpent-2″-enyloxy)propyl esters, all compounds **31**−**36** possess an unambiguous musk note. In addition, the propionates **31** and **35** have green notes, while the cyclopropanecarboxylates **32** and **36**, as well as the butyrate **33**, have a fruity character. The pleasant musky, fruity, pear-type odor of the levulinate **34** is noteworthy, and it is accompanied by nuances of ambrette seed oil.

Next, we wanted to investigate the distribution of conformers of a typical representative of the new class of "all-aliphatic" musk odorants. For this purpose we selected (2″*E*)-cyclopropanecarboxylic acid 2′-methyl-2′-(1″,2″,4″-trimethylpent-2″-enyloxy)propyl ester [(2″*E*)-**19**]. As shown in Figure 4, the O−C-1′−C-2′−O unit of the global minimum conformer (PM3) is indeed configured in a (−)-*synclinal* manner, yet it is not the *gem*-dimethyl carbon atom, but the oxymethyne carbon atom, that constitutes the second corner atom of this conformer, with a dihedral angle of −90° for the C-2′−O−C-1″−C-2″ unit. Thus, the resulting overall shape is also horseshoe-like. The following conformer, which is 0.42 kcal/mol higher in energy, quite resembles the global energy minimum, but at 1.54 kcal/mol above the global minimum we find a conformer in which the *gem*-dimethyl carbon atom constitutes a corner atom and the C-1′−C-2′−O−C-1″ unit is in the (−)-*synclinal* conformation. If this conformer were to account for the musky odor characteristics, however, then the dienone **28** should smell musky as well. Two alternative horseshoe-shaped conformers, having energies that are 1.83 and 1.85 kcal/mol above the global minimum, again resemble the two lowest-energy conformers; at 1.88 kcal/mol above the global minimum, however, we find a conformer that resembles conformation **A** in Figure 1. The configuration of the O−C-1′−C-2′−O unit is (−)-*synclinal* and that of the C-2′−O−C-1″−C-2″ unit is (−)-*anticlinal*. Still, we can only

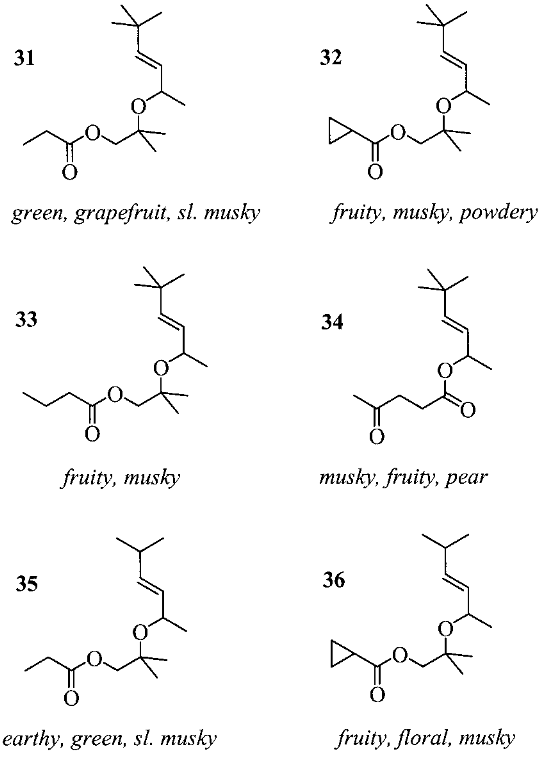


Figure 3. Derivatives **31**−**36** featuring 1″,4″,4″-trimethylpent-2″-enyl and 1″,4″-dimethylpent-2″-enyl moieties

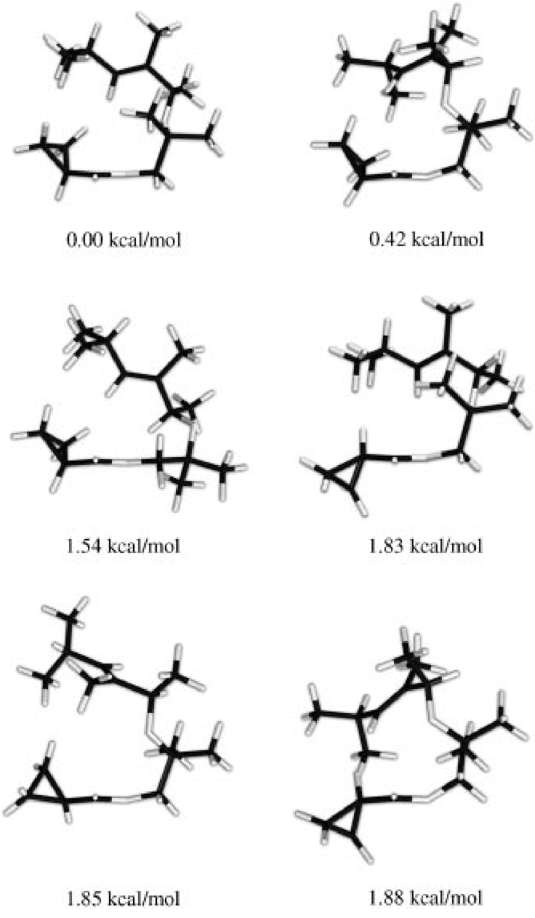


Figure 4. Selected lowest-energy conformers (PM3) of (2″*E*)-cyclopropanecarboxylic acid 2′-methyl-2′-(1″,2″,4″-trimethylpent-2″-enyloxy)propyl ester (**19**)

speculate about the active conformer of these highly flexible musk odorants.

Experimental Section

IR: Bruker VECTOR 22/Harrick SplitPea micro ATR (attenuated-total-reflection), Si. NMR: Bruker AVANCE DPX-400; TMS as internal standard. (δ = 0 ppm). MS: Finnigan MAT 95 or HP Chemstation 6890 GC/5973 Mass Sensitive Detector. FC: Merck Kieselgel 60 (particle size 40−63 μm). TLC: Merck Kieselgel 60 F_{254} (particle size 5−20 μm, layer thickness 250 μm on glass, 5 cm × 10 cm); visualization reagent: PMA spray solution for TLC, Merck 1.00480.0100. Melting points: Büchi Melting Point B545 (uncorrected). Elemental analyses: Eidgenössische Materialprüfungs- und Forschungsanstalt (EMPA), Überlandstrasse 129, Dübendorf. All reactions were performed under N_2 using reagents and solvents (purity "*puriss.*" or "*purum*") from Fluka without further purification, except Artemone® [1-(3′,3′-dimethylcyclohex-1′-enyl)ethanone, **5**], which is a commercial product of Givaudan, and isobutylene oxide, which was supplied by BASF. The odor thresholds were determined by GC-olfactometry.[18,19] Different dilutions of the sample substance were injected into a gas chromatograph in descending order of concentration until the panelist fails to detect the respective substance at the sniffing port. The panelist smells in blind and presses a button on perceiving an odor. If the recorded time matches the retention time, the sample is further diluted. The last concentration detected at the correct retention time is the individual odor threshold. The reported threshold values are the geometrical means of the individual odor thresholds of the different panelists.

2′-[1′′-(3′′′,3′′′-Dimethylcyclohex-1′′′-enyl)ethoxy]-2′-methylpropyl Propionate (8): At room temp. under N_2, a solution of Artemone® [1-(3′,3′-dimethylcyclohex-1′-enyl)ethanone, **5**, 152 g, 1.00 mol] in Et_2O (500 mL) was added dropwise whilst stirring within 3 h to a suspension of LAH (10.4 g, 275 mmol) in Et_2O (1 L). The reaction mixture was heated under reflux for 150 min, and then quenched at 0 °C by the dropwise addition of water (50 mL). Aqueous HCl (2 N, 200 mL) was then added and the mixture was poured into water (200 mL). The product was extracted with Et_2O (2 × 500 mL), and the combined extracts were washed with water (200 mL) and brine (100 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator. The resulting residue (154 g) was purified by FC (silica gel; pentane/Et_2O, 4:1; R_f = 0.28) to afford 1-(3′,3′-dimethylcyclohex-1′-enyl)ethanol (**6**; 133 g 87%). During a period of 1 h, a solution of $MeAlCl_2$ (1 M, 150 mL, 150 mmol) in hexane was added dropwise with stirring at 0 °C to a solution of **6** (46.3 g, 300 mmol) and isobutylene oxide (26.0 g, 360 mmol) in cyclohexane (300 mL). The cooling bath was removed, and stirring was continued at room temp. for 20 h and then the reaction mixture was poured into ice/water (1:1, 200 mL). Concd. aq. H_3PO_4 was added until the slurry dissolved, and the product was extracted with Et_2O (2 × 200 mL). The combined organic extracts were washed with water (200 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated on a rotary evaporator. The resulting residue (60.5 g) was purified by FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.14) followed by distillation at 55 °C/1.5 mbar to furnish 2-[1′-(3′′,3′′-dimethylcyclohex-1′′-enyl)ethoxy]-2-methylpropan-1-ol (**7**; 12.7 g, 19%). At 0 °C under N_2, DCC (2.27 g, 11.0 mmol) was added to a stirred solution of **7** (2.26 g, 10.0 mmol), propionic acid (740 mg, 10.0 mmol), and DMAP (120 mg, 1.00 mmol) in CH_2Cl_2 (15 mL). The cooling bath was removed, and the reaction mixture was stirred for 2 h at room temp. prior to vacuum filtration. The precipitate was washed with CH_2Cl_2 (2 ×), and the combined filtrates were concentrated under reduced pressure. The crude material (3.25 g) was purified by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.46) to afford the odoriferous title compound (2.52 g, 89%). IR (ATR): ṽ = 1741 (s, νO=CO), 1168/1068 (s, νC−O), 1366 (m, δCH_3) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.93/0.94 (2 s, 6 H, 3′′′-Me_2), 1.14 (d, *J* = 6.5 Hz, 3 H, 2′′-H_3), 1.16 (t, *J* = 7.5 Hz, 3 H, 3-H_3), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.37 (m_c, 2 H, 4′′′-H_2), 1.60 (m_c, 2 H, 5′′′-H_2), 1.81−2.06 (m, 2 H, 6′′′-H_2), 2.37 (q, *J* = 7.5 Hz, 2 H, 2-H_2), 3.90 (d, *J* = 11.0 Hz, 1 H, 1′-H_b), 3.99 (q, *J* = 7.5 Hz, 1 H, 1′′-H), 4.01 (d, *J* = 11.0 Hz, 1 H, 1′-H_a), 5.30 (s, 1 H, 2′′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.99 (q, C-3), 19.6 (t, C-5′′′), 22.4 (q, C-2′′), 23.4 (t, C-6′′′), 23.5/23.6 (2 q, 2′-Me_2), 27.5 (t, C-2), 29.3/29.9 (2 q, 3′′′-Me_2), 31.2 (s, C-3′′′), 37.3 (t, C-4′′′), 69.7 (t, C-1′), 72.2 (d, C-1′′), 74.3 (s, C-2′), 131.3 (d, C-2′′′), 139.0 (s, C-1′′′), 174.1 (s, C-1) ppm. MS (70 eV): *m*/*z* = 153 (15) [$C_{10}H_{17}O^+$], 147 (3) [$C_7H_{15}O_3{}^+$], 137 (67) [$C_{10}H_{17}{}^+$], 129 (36) [$C_7H_{13}O_2{}^+$], 121 (29) [$C_9H_{13}{}^+$], 107 (17) [$C_8H_{11}{}^+$], 95 (28) [$C_7H_{11}{}^+$], 93 (27) [$C_7H_9{}^+$], 79 (19) [$C_6H_7{}^+$], 57 (100) [$C_3H_5{}^+$]. Odor: Musky, powerful, powdery, slightly animalic. Odor threshold: 0.2 ng/L air.

2′-[1′′-(5′′′,5′′′-Dimethylcyclohex-1′′′-enyl)ethoxy]-2′-methylpropyl Propionate (11): Phosphorus pentoxide (33.1 g, 233 mmol) was added to a solution of 1-ethynyl-3,3-dimethylcyclohexanol (**9**, 152 g, 1.00 mol) in MePh (800 mL). The slurry was heated to reflux, and then stirred at that temp. for 90 min. The reaction mixture was cooled to room temp. and then poured into ice/water (1:1, 500 mL). The product was extracted with Et_2O (2 × 500 mL), and then the combined organic extracts were washed with water (500 mL) and brine (100 mL), dried (Na_2SO_4), and concentrated under reduced pressure. FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.70) provided 1-(5′,5′-dimethylcyclohex-1′-enyl)ethanone (**10**; 13.8 g, 9%). A solution of **10** (13.1 g, 85.8 mmol) in Et_2O (50 mL) was added dropwise with stirring over 50 min to a suspension of LAH (895 mg, 23.6 mmol) in Et_2O (150 mL). The reaction mixture was heated under reflux for 1 h prior to quenching at 0 °C by the careful addition of water (50 mL), followed by 5 N aq. HCl (50 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined ethereal solutions were washed with water and brine, dried (Na_2SO_4), and then concentrated in a rotary evaporator. FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.14) of the resulting residue (14.7 g) gave 1-(5′,5′-dimethylcyclohex-1′-enyl)ethanol (11.2 g, 85%). At 0 °C under N_2, a 1 M solution of $MeAlCl_2$ (33.6 mL, 33.6 mmol) in hexane was added dropwise during 1 h to a stirred solution of 1-(5′,5′-dimethylcyclohex-1′-enyl)ethanol (10.4 g, 67.2 mmol) and isobutylene oxide (5.82 g, 80.7 mmol) in cyclohexane (67 mL). The cooling bath was removed and the reaction mixture was stirred at room temp. for 23 h before being poured into ice/water (1:1, 200 mL). The slurry was brought into solution by addition of conc. aq. H_3PO_4, and the product was extracted with Et_2O (2 × 100 mL). The combined organic extracts were washed with water (100 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated in a rotary evaporator. The crude material (12.4 g) was purified by FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.17) to provide 2-[1′-(5′′,5′′-dimethylcyclohex-1′′-enyl)ethoxy]-2-methylpropan-1-ol (3.31 g, 22%). Following the same procedure as described for the preparation of **8**, Steglich esterification of 2-[1′-(5′′,5′′-dimethylcyclohex-1′′-enyl)ethoxy]-2-methylpropan-1-ol (1.29 g, 5.70 mmol) with propionic acid (420 mg, 5.70 mmol), and purification by FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.56) furnished the odoriferous title compound **11** (420 mg, 26%). IR (ATR): ṽ = 1169/1068 (s, νC−O), 1741 (s, νO=CO), 1365 (m, δCH_3) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.89/0.91 (2 s, 6 H, 5′′′-Me_2), 1.14 (d, *J* = 6.5 Hz, 3 H, 2′′-H_3), 1.16 (t, *J* = 7.5 Hz, 3 H, 3-H_3), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.29 (t, *J* = 6.5 Hz, 2 H, 4′′′-H_2), 1.69

(dd, *J* = 17.0, 2.0 Hz, 1 H, 6′′′-H_b), 1.83 (dd, *J* = 17.0, 2.0 Hz, 1 H, 6′′′-H_a), 2.01 (m_c, 2 H, 3′′′-H_2), 2.36 (q, *J* = 7.5 Hz, 2 H, 2-H_2), 3.92 (d, *J* = 11.0 Hz, 1 H, 1′-H_b), 4.00 (d, *J* = 11.0 Hz, 1 H, 1′-H_a), 4.02 (q, *J* = 6.5 Hz, 1′′-H), 5.54 (s, 1 H, 2′′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.98 (q, C-3), 22.4 (q, C-2′′), 22.7 (t, C-3′′′), 23.4 (t, C-6′′′), 23.4/23.6 (2 q, 2′-Me_2), 27.5 (t, C-2), 27.9/28.0 (2 q, 5′′′-Me_2), 28.6 (s, C-5′′′), 35.2 (t, C-4′′′), 37.5 (t, C-6′′′), 69.8 (t, C-1′), 71.9 (d, C-1′′), 74.2 (s, C-2′), 119.1 (d, C-2′′′), 140.4 (s, C-1′′′), 174.1 (s, C-1) ppm. MS (70 eV): *m*/*z* = 153 (16) [$C_{10}H_{17}O^+$], 147 (2) [$C_7H_{15}O_3^+$], 137 (59) [$C_{10}H_{17}^+$], 129 (30) [$C_7H_{13}O_2^+$], 121 (37) [$C_9H_{13}^+$], 107 (29) [$C_8H_{11}^+$], 95 (29) [$C_7H_{11}^+$], 93 (39) [$C_7H_9^+$], 79 (48) [$C_6H_7^+$], 57 (100) [$C_4H_9^+$]. Odor: Musky, powdery, fruity. Odor threshold: 0.9 ng/L air.

1′′-(3′′′,3′′′-Dimethylcyclohex-1′′′-enyl)ethoxycarbonylmethyl Propionate (12): DCC (50.9 g, 247 mmol) was added at 0 °C under N_2 to a solution of 1-(3′,3′-dimethylcyclohex-1-enyl)ethanol (34.6 g, 224 mmol), chloroacetic acid (21.2 g, 224 mmol), and DMAP (2.74 g, 22.4 mmol) in CH_2Cl_2 (320 mL). The cooling bath was removed and the reaction mixture was stirred for 2.5 h at room temp. before separating the precipitates by vacuum filtration. The filtrate was concentrated under reduced pressure and the resulting residue was purified by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.80) to furnish 1′-(3′′,3′′-dimethylcyclohex-1′′-enyl)ethyl chloroacetate (39.6 g, 77%). A mixture of 1′-(3′′,3′′-dimethylcyclohex-1′′-enyl)ethyl chloroacetate (2.00 g, 8.67 mmol), propionic acid (640 mg, 8.67 mmol), K_2CO_3 (2.39 g, 17.3 mmol), and NaBr (500 mg, 4.86 mmol) in Et_2CO/dioxane (3:1, 20 mL) was heated under reflux for 1.5 days before it was poured into water (50 mL). The product was extracted with Et_2O (2 × 50 mL) and the combined extracts were washed with water (50 mL) and brine (25 mL). After drying with Na_2SO_4 and evaporating the solvent under reduced pressure, FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.24) afforded the odoriferous title compound (1.45 g, 62%). IR (ATR): ṽ = 1162 (s, νC−O), 1747 (s, νO=CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.95/0.96 (2 s, 6 H, 3′′′-Me_2), 1.19 (t, *J* = 7.5 Hz, 3 H, 3-H, 3-H_3), 1.30 (d, *J* = 6.5 Hz, 3 H, 2′′-H_3), 1.36−1.91 (m, 6 H, 4′′′-H_2−6′′′-H_2), 2.45 (q, *J* = 7.5 Hz, 2 H, 2-H_2), 4.57 (d, *J* = 16 Hz, 1 H, 2′-H_b), 4.61 (d, *J* = 16.0 Hz, 1 H, 2′-H_a), 5.29 (q, *J* = 6.5 Hz, 1 H, 1′′-H), 5.41 (s, 1 H, 2′′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.82 (q, C-3), 18.6 (q, C-2′′), 19.4 (t, C-5′′′), 23.0 (t, C-6′′′), 27.0 (t, C-2), 29.4/29.7 (2 q, 3′′′-Me_2), 31.3 (s, C-3′′′), 36.8 (t, C-4′′′), 60.6 (t, C-2′), 75.4 (d, C-1′′), 133.9 (s, C-1′′′), 134.4 (d, C-2′′′), 167.1 (s, C-1′), 173.6 (s, C-1) ppm. MS (70 eV): *m*/*z* = 268 (1) [M^+], 253 (1) [$M^+ - CH_3$], 154 (2) [$C_{10}H_{18}O^+$], 136 (44) [$C_{10}H_{16}^+$], 121 (100) [$C_9H_{13}^+$], 107 (32) [$C_8H_{11}^+$], 93 (75) [$C_7H_9^+$], 79 (47) [$C_6H_7^+$], 41 (25) [$C_3H_5^+$]. Odor: Musky, floral-fruity, ionone-like. Odor threshold: 0.6 ng/L air.

1′′-(5′′′,5′′′-Dimethylcyclohex-1′′′-enyl)ethoxycarbonylmethyl Propionate (13): DCC (2.58 g, 12.5 mmol) was added at 0 °C under N_2 to a solution of 1-(5′,5′-dimethylcyclohex-1-enyl)ethanol (1.75 g, 11.3 mmol), chloroacetic acid (1.07 g, 11.3 mmol), and DMAP (140 mg, 1.13 mmol) in CH_2Cl_2 (15 mL). The cooling bath was removed and the reaction mixture was stirred for 1 h at room temp. before the precipitates were separated by vacuum filtration. The filtrate was concentrated under reduced pressure and the resulting residue was purified by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.65) to furnish 1′-(5′′,5′′-dimethylcyclohex-1′′-enyl)ethyl chloroacetate (2.17 g, 83%). A mixture of 1′-(5′′,5′′-dimethylcyclohex-1′′-enyl)ethyl chloroacetate (1.00 g, 4.33 mmol), propionic acid (320 mg, 4.33 mmol), K_2CO_3 (1.20 g, 8.67 mmol), and NaBr (450 mg, 4.33 mmol) in Et_2CO/dioxane (4:1, 10 mL) was heated under reflux for 1 day before it was poured into water (50 mL). The product was extracted with Et_2O (2 × 50 mL) and the combined extracts were washed with water (50 mL) and brine (25 mL). After drying with Na_2SO_4 and evaporation of the solvent under reduced pressure, FC (silica gel; pentane/Et_2O, 9:1; R_f = 0.41) afforded the odoriferous title compound (370 mg, 32%). IR (ATR): ṽ = 1161 (s, νC−O), 1747 (s, νO=CO) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.89/0.91 (2 s, 6 H, 5′′′-Me_2), 1.19 (t, *J* = 7.5 Hz, 3 H, 3-H, 3-H_3), 1.31 (d, *J* = 6.5 Hz, 3 H, 2′′-H_3), 1.34 (m_c, 2 H, 4′′′-H_2), 1.69 (d, *J* = 16.5 Hz, 1 H, 6′′′-H_b), 1.78 (d, *J* = 16.5 Hz, 1 H, 6′′′-H_a), 2.05 (m_c, 2 H, 3′′′-H_2), 2.45 (q, *J* = 7.5 Hz, 2 H, 2-H_2), 4.56 (d, *J* = 16.0 Hz, 1 H, 2′-H_b), 4.61 (d, *J* = 16.0 Hz, 1 H, 2′-H_a), 5.32 (q, *J* = 6.5 Hz, 1 H, 1′′-H), 5.67 (br. s, 1 H, 2′′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.81 (q, C-3), 18.5 (q, C-2′′), 22.7 (t, C-3′′′), 27.0 (t, C-2), 27.5/28.3 (2 q, 5′′′-Me_2), 28.6 (s, C-5′′′), 34.7 (t, C-4′′′), 37.5 (t, C-6′′′), 60.6 (t, C-2′), 75.5 (d, C-1′′), 123.1 (d, C-2′′′), 135.2 (s, C-1′′′), 167.1 (s, C-1′), 173.5 (s, C-1) ppm. MS (70 eV): *m*/*z* = 154 (3) [$C_{10}H_{18}O^+$], 136 (58) [$C_{10}H_{16}^+$], 121 (86) [$C_9H_{13}^+$], 107 (75) [$C_8H_{11}^+$], 93 (100) [$C_7H_9^+$], 79 (100) [$C_6H_7^+$], 41 (36) [$C_3H_5^+$]. Odor: Musky, green. Odor threshold: 11 ng/L air.

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl Acetate (17): Within a period of 90 min, a solution of triethyl 2-phosphonopropionate (238 g, 1.00 mol) in dimethoxyethane (DME, 150 mL) was added dropwise with stirring under an atmosphere of N_2 to a solution of NaH (43.6 g, 1.00 mol) in DME (600 mL). The mixture was then heated under reflux for 15 min before isobutyric aldehyde (14, 72.1 g, 1.00 mol) was added dropwise. After a further 30 min of stirring under reflux, the mixture was poured into ice/water (1:1, 1 L). AcOH (60 mL) was added, and the product was extracted with Et_2O (2 × 200 mL). The combined organic extracts were washed with water (400 mL) and brine (100 mL), dried (Na_2SO_4), and concentrated in a rotary evaporator. The resulting residue was distilled (86−75 °C/27 mbar) to provide ethyl 2,4-dimethylpent-2-enoate (**15**; 117 g, 75%). A mixture of **15** (116 g, 742 mmol) and 85% KOH (147 g, 2.23 mol) in water/EtOH (1:1, 2.0 L) was heated under reflux for 1 d. The EtOH was stripped off on a rotary evaporator, and the remaining mixture was washed with Et_2O. The combined ethereal washings were extracted with 2 N aq. NaOH (100 mL) and all aqueous solutions were combined. After cooling in an ice/water bath, conc. aq. H_3PO_4 (200 mL) was added to adjust the combined aqueous solutions to pH 3, and then the product was extracted with Et_2O (200 mL). The ethereal solution was washed with water (200 mL) and brine (25 mL). After drying (Na_2SO_4), the solvent was evaporated in a rotary evaporator to furnish 2,4-dimethylpent-2-enoic acid (94.2 g, 99%). IR (ATR): ṽ = 1685 (s, νC=O), 1272 (s, νO−C=O), 1642 (m, νC=C), 2963 (br. m, νO−H) cm^{-1}. (2′′-*E*)-Isomer: ^1H NMR ($CDCl_3$): δ = 1.03 (d, *J* = 7.0 Hz, 6 H, 4-Me_2), 1.85 (d, *J* = 1.5 Hz, 3 H, 2-Me), 2.66 (dsept, *J* = 10.0, 7.0 Hz, 1 H, 4-H), 6.74 (dq, *J* = 10.0, 1.5 Hz, 1 H, 3-H), 12.2 (br. s, 1 H, CO_2H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.8 (q, 2-Me), 21.7 (q, 4-Me_2), 28.1 (d, C-4), 124.5 (s, C-2), 151.7 (d, C-3), 174.4 (s, C-1). (2′′-*Z*)-Isomer: ^1H NMR ($CDCl_3$): δ = 0.99 (d, *J* = 7.0 Hz, 6 H, 4-Me_2), 1.89 (d, *J* = 1.5 Hz, 3 H, 2-Me), 3.36 (dsept, *J* = 10.0, 7.0 Hz, 1 H, 4-H), 5.87 (dq, *J* = 10.0, 1.5 Hz, 1 H, 3-H), 12.2 (br. s, 1 H, CO_2H) ppm. ^{13}C NMR ($CDCl_3$): δ = 20.4 (q, 2-Me), 22.5 (q, 4-Me_2), 28.3 (d, C-4), 124.0 (s, C-2), 153.1 (d, C-3), 174.1 (s, C-1) ppm. MS (70 eV): *m*/*z* = 128 (54) [M^+], 113 (36) [$M^+ - CH_3$], 95 (20) [$M^+ - CH_3 - H_2O$], 85 (10) [$M^+ - C_3H_7$], 83 (96) [$C_6H_{11}^+$], 70 (34) [$C_5H_{10}^+$], 67 (85) [$M^+ - C_3H_7 - H_2O$], 59 (99) [$C_3H_7O^+$], 55 (100) [$C_6H_{11}^+ - C_2H_4$], 41 (87) [$C_3H_5^+$].

Under an atmosphere of N_2, a solution of MeLi in Et_2O (1.6 M, 500 mL, 800 mmol) was added dropwise over 105 min to a stirring solution of 2,4-dimethyl-pent-2-enoic acid (41.0 g, 320 mmol) in Et_2O (1.6 L) at 0−10 °C. The reaction mixture was heated under reflux for 1 h, and then 5 N HCl (200 mL) was added dropwise at 5−15 °C. The organic layer was separated and the aqueous phase was extracted with Et_2O (200 mL). The combined organic solutions were washed with water (200 mL) and brine (100 mL), dried (Na_2SO_4), and concentrated in a rotary evaporator to afford crude 3,5-dimethylhex-3-en-2-one, which was taken up in Et_2O (160 mL). Under N_2 at room temp., this solution was added dropwise with stirring to a suspension of LAH (3.34 g, 880 mmol) in Et_2O (320 mL) over 1 h. The reaction mixture was heated under reflux for 2 h, and then quenched between 0−5 °C by the addition of water (10 mL) and brine (20 mL). The organic layer was separated and the aqueous phase extracted with Et_2O (100 mL). The combined ethereal extracts were washed with water (100 mL) and brine (50 mL), dried (Na_2SO_4), and concentrated under reduced pressure. FC (silica gel; pentane/Et_2O, 4:1; $R_f = 0.40$) of the resulting residue provided 3,5-dimethylhex-3-en-2-ol (**16**; 34.7 g, 85% over 2 steps). At 0 °C under N_2, a 1 M solution of $MeAlCl_2$ (50 mL, 50 mmol) in hexane was added dropwise with stirring during a period of 1 h to a solution of **16** (12.8 g, 100 mmol) and isobutylene oxide (8.65 g, 120 mmol) in cyclohexane (100 mL). The cooling bath was removed and stirring was continued for 16 h before the mixture was poured into ice/water (1:1, 100 mL). The resulting slurry was dissolved by addition of conc. aq. H_3PO_4, and the product was extracted with Et_2O (2 × 100 mL). The combined organic extracts were washed with water (100 mL) and brine (25 mL), dried (Na_2SO_4), and concentrated in a rotary evaporator. The resulting residue was purified by FC (silica gel; pentane/Et_2O, 19:1; $R_f = 0.12$) to afford 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**; 3.10 g, 15%). At 0 °C under N_2, DCC (1.03 g, 5.00 mmol) was added to a stirred solution of **27** (830 mg, 4.14 mmol), acetic acid (250 mg, 4.14 mmol), and DMAP (50 mg, 410 mmol) in CH_2Cl_2 (10 mL). After stirring for 1 h at room temp., the precipitate was separated by vacuum filtration and washed with CH_2Cl_2. The combined filtrates were concentrated under reduced pressure, and the resulting residue was purified by FC (silica gel; pentane/Et_2O, 19:1; $R_f = 0.36$) to furnish the odoriferous title compound (710 mg, 71%). IR (ATR): $\tilde{\nu}$ = 1232/1044 (s, νC−O), 1744 (s, νO−C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.91/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.07/2.08 (2 s, 3 H, 2-H_3), 2.48/2.60 (2 m_c, 1 H, 4′′-H), 3.89/3.90/3.99 /4.00 (4 d, J = 11.0, 2 H, 1′-H_2), 4.01/4.57 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.1/17.6 (2 q, 2′′-Me), 20.7/20.8 (2 q, C-2), 22.3/22.4/22.6/22.8/23.1/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.4/23.5/23.5/23.6 (4 q, 2′-Me_2), 26.4/26.5 (d, C-4′′), 66.0/73.3 (2 d, C-1′′), 69.7/69.8 (2 t, C-1′), 74.1/74.2 (2 s, C-2′), 131.6/131.9 (2 d, C-3′′), 136.3/136.7 (2 s, C-2′′), 170.7/170.7 (2 s, C-1) ppm. MS (70 eV): m/z = 242 (1) [M^+], 227 (1) [$M^+ - CH_3$], 199 (1) [$M^+ - C_3H_7$], 115 (42) [$C_6H_{11}O_2^+$], 111 (46) [$C_8H_{15}^+$], 110 (30) [$C_8H_{14}^+$], 95 (26) [$C_8H_{14}^+ - CH_3$], 81 (7) [$C_8H_{14}^+ - C_2H_5$], 69 (45) [$C_8H_{14}^+ - C_3H_5$], 55 (30) [$C_4H_7^+$], 43 (100) [$C_3H_7^+$]. $C_{14}H_{26}O_3$ (242.4): calcd. C 69.38, H 10.81; found C 69.51, H 11.02. Odor: Floral, musky, fruity-green. GC-Olfactometry: (E/Z) = 45:55, both isomers smell musky, the (E)-isomer is more intense. Odor thresholds: 12 ng/L (E), 54 ng/L (Z).

2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl Propionate (18): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 830 mg, 4.14 mmol) with propionic acid (310 mg, 4.14 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; $R_f = 0.50$) furnished the odoriferous title compound (690 mg, 65%). IR (ATR): $\tilde{\nu}$ = 1072/1169 (s, νC−O), 1741 (s, νO−C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.91/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.16/1.16 (2 t, J = 8.0 Hz, 3 H, 3-H_3), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.36/2.36 (2 q, J = 8.0 Hz, 2 H, 2-H_2), 2.48/2.59 (2 m_c, 1 H, 4′′-H), 3.90/3.91/3.99/4.00 (4 d, J = 11.0, 2 H, 1′-H_2), 4.02/4.57 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.96/8.96 (2 q, C-3), 11.1/17.6 (2 q, 2′′-Me), 22.3/22.4/22.6/22.8/23.1/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.4/23.5/23.6/23.6 (4 q, 2′-Me_2), 26.4/26.5 (d, C-4′′), 27.4/27.5 (2 t, C-2), 66.0/73.3 (2 d, C-1′′), 69.6/69.7 (2 t, C-1′), 74.2/74.3 (2 s, C-2′), 131.5/131.8 (2 d, C-3′′), 136.3/136.7 (2 s, C-2′′), 174.1/174.1 (2 s, C-1) ppm. MS (70 eV): m/z = 256 (1) [M^+], 241 (1) [$M^+ - CH_3$], 147 (1) [$C_7H_{15}O_3^+$], 129 (27) [$C_7H_{13}O_2^+$], 111 (52) [$C_8H_{15}^+$], 110 (28) [$C_8H_{14}^+$], 95 (26) [$C_8H_{14}^+ - CH_3$], 81 (9) [$C_8H_{14}^+ - C_2H_5$], 69 (40) [$C_8H_{14}^+ - C_3H_5$], 57 (100) [$C_4H_9^+$]. $C_{15}H_{28}O_3$ (256.4): calcd. C 70.27, H 11.01; found C 70.50, H 11.18. Odor: Powerful, musky, fruity, slightly green. GC-Olfactometry: (E/Z) = 45:55, both isomers smell musky, the (E)-isomer is more intense. Odor thresholds: 1.2 ng/L (E), 5.4 ng/L (Z).

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl Cyclopropanecarboxylate (19): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (27, 830 mg, 4.14 mmol) with cyclopropane carboxylic acid (360 mg, 4.14 mmol) and purification by FC (silica gel; pentane/Et_2O, 99:1; $R_f = 0.07$) furnished the odoriferous title compound (680 mg, 61%). IR (ATR): $\tilde{\nu}$ = 1163/1072 (s, νC−O), 1731 (s, νO−C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.85/0.85 (2 m_c, 2 H, 3-,4-H_b), 0.91/0.92/0.95/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.00/1.01 (2 m_c, 2 H, 3-,4-H_a), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.17/1.18/1.18/1.19 (4 s, 6 H, 2′-Me_2), 1.63/1.64 (2 m_c, 2 H, 2-H), 1.60/1.69 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.49/2.61 (2 m_c, 1 H, 4′′-H), 3.89/3.90/3.99/4.01 (4 d, J = 11.0, 2 H, 1′-H_2), 4.01/4.58 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 8.13/8.13/8.15/8.15 (4 q, C-3,-4), 11.1/17.6 (2 q, 2′′-Me), 12.7/12.8 (2 d, C-2), 22.3/22.4/22.7/22.8/23.1/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.5/23.6/23.6/23.6 (4 q, 2′-Me_2), 26.4/26.5 (d, C-4′′), 66.0/73.3 (2 d, C-1′′), 69.6/69.7 (2 t, C-1′), 74.2/74.3 (2 s, C-2′), 131.6/131.9 (2 d, C-3′′), 136.3/136.7 (2 s, C-2′′), 174.4/174.5 (2 s, C-1) ppm. MS (70 eV): m/z = 268 (1) [M^+], 253 (1) [$M^+ - CH_3$], 225 (1) [$M^+ - C_3H_7$], 159 (2) [$C_8H_{15}O_3^+$], 141 (17) [$C_8H_{13}O_2^+$], 111 (38) [$C_8H_{15}^+$], 110 (20) [$C_8H_{14}^+$], 95 (16) [$C_8H_{14}^+ - CH_3$], 81 (6) [$C_8H_{14}^+ - C_2H_5$], 69 (100) [$C_8H_{14}^+ - C_3H_5$], 55 (21) [$C_4H_7^+$], 41 (27) [$C_3H_5^+$]. $C_{16}H_{28}O_3$ (268.4): calcd. C 71.60, H 10.52; found C 71.66, H 10.70. Odor: Powerful, musky, sweet, slightly fruity. GC-Olfactometry: (E/Z) = 45:55, both isomers smell musky, the E-isomer is more intense. Odor thresholds: 8.1 ng/L (Z), 5.7 ng/L (E).

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl Butyrate (20): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 1.72 g, 8.59 mmol) with butyric acid (2.43 mL, 26.4 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; $R_f = 0.42$) furnished the odoriferous title compound (2.30 g, 99%). IR (ATR): $\tilde{\nu}$ = 1168/1073 (s, νC−O), 1739 (s, νO−C=O) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90/0.92/0.93/0.94 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 0.95/0.96 (2 t, J = 7.5 Hz, 3 H, 4-H_3), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 1.62−1.70 (m, 2 H, 3-H_2), 2.32 (br. t, J = 7.5 Hz, 2 H, 2-H_2), 2.49/2.60 (2 m_c, 1 H, 4′′-H), 3.90/3.91/3.99/4.00 (4 d, J = 11.0, 2 H, 1′-H_2), 4.02/4.58 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2/17.8 (2 q, 2′′-Me), 13.7/13.7 (2 q, C-4), 18.3/18.4 (2 t, C-3), 22.4/22.5/22.7/22.8/22.9/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.4/23.5/23.7/23.7 (4 q, 2′-Me_2), 26.5/26.6 (2 d, C-4′′), 36.1/36.2 (2 t, C-2), 66.1/73.5 (2 d, C-1′′), 69.6/69.8 (2 t, C-1′), 74.3/74.4 (2 s, C-2′), 131.7/132.0 (2 d, C-3′′), 136.5/136.8 (2 s, C-2′′), 173.4/173.5 (2 s, C-1) ppm. MS (70 eV): m/z = 270 (1) [M^+], 255 (1) [$M^+ - CH_3$], 143 (30) [$C_8H_{15}O_2^+$], 127 (8) [$C_8H_{15}O^+$], 111 (79) [$C_8H_{15}^+$], 95 (25) [$C_8H_{14}^+ - CH_3$], 81 (10) [$C_8H_{14}^+ - C_2H_5$], 71 (100) [$C_4H_7O^+$], 69 (48) [$C_8H_{14}^+ - C_3H_5$], 43 (48) [$C_3H_7^+$]. Odor: Musky, fruity, animalic. Odor threshold (*2′′E*/*Z* mixture): 1.8 ng/L air.

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl Isobutyrate (21): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 1.72 g, 8.59 mmol) with isobutyric acid (2.45 mL, 26.4 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.50) furnished the odoriferous title compound (1.94 g, 84%). IR (ATR): $\tilde{\nu}$ = 1072/1153 (s, νC−O), 1737 (s, νO−C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.91/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.19/1.20 (2 d, J = 6.5 Hz, 6 H, 2-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.45−2.67 (m, 1 H, 2-H), 2.48/2.58 (2 m$_c$, 1 H, 4′′-H), 3.89/3.90/3.99/4.00 (4 d, J = 11.0, 2 H, 1′-H_2), 4.00/4.59 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2/17.8 (2 q, 2′′-Me), 18.90/18.91/18.94/18.95 (4 q, 2-Me_2), 22.4/22.5/22.7/22.8/22.9/23.2 (6 q, 1′′-Me, 4′′-Me_2), 23.4/23.5/23.7/23.8 (4 q, 2′-Me_2), 26.5/26.6 (2 d, C-4′′), 34.0/34.0 (2 d, C-2), 66.1/73.5 (2 d, C-1′′), 69.6/69.7 (2 t, C-1′), 74.4/74.5 (2 s, C-2′), 131.7/132.0 (2 d, C-3′′), 136.5/136.8 (2 s, C-2′′), 176.7/176.8 (2 s, C-1) ppm. MS (70 eV): m/z = 270 (1) [M^+], 255 (1) [$M^+ - CH_3$], 227 (1) [$M^+ - C_3H_7$], 143 (33) [$C_8H_{15}O_2^+$], 127 (10) [$C_8H_{15}O^+$], 111 (93) [$C_8H_{15}^+$], 95 (29) [$C_8H_{14}^+ - CH_3$], 81 (13) [$C_8H_{14}^+ - C_2H_5$], 71 (100) [$C_4H_7O^+$], 69 (57) [$C_8H_{14}^+ - C_3H_5$], 43 (80) [$C_3H_7^+$]. Odor: Musky, rosy, fruity. Odor threshold (*2′′E*/*Z* mixture): 2.2 ng/L air.

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl 2-Methylacrylate (22): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 1.72 g, 8.59 mmol) with 2-methylacrylic acid (2.45 mL, 26.4 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.37) furnished the odoriferous title compound (1.93 g, 84%). IR (ATR): $\tilde{\nu}$ = 1156/1073 (s, νC−O), 1721 (s, νO−C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.91/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.20/1.21 (2 s, 6 H, 2′-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 1.97 (m$_c$, 3 H, 2-Me), 2.45/2.61 (2 m$_c$, 1 H, 4′′-H), 3.97/3.98/3.99/4.03 (4 d, J = 11.0, 2 H, 1′-H_2), 4.07/4.60 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H), 5.57/6.14 (m$_c$, 2 H, 3-H_2) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2/17.7 (2 q, 2′′-Me), 18.3/22.4/22.5/22.5/22.7/22.8/22.9/23.3 (8q, 2-Me, 1′′-Me, 4′′-Me_2), 23.5/23.7/23.8/23.8 (4 q, 2′-Me_2), 26.5/26.6 (2 d, C-4′′), 66.1/73.5 (2 d, C-1′′), 70.0/70.1 (2 t, C-1′), 74.4/74.5 (2 s, C-2′), 125.3/125.4 (2 t, C-3), 131.7/132.0 (2 d, C-3′′), 136.3/136.4/136.5/136.8 (4 s, C-2,-2′′), 167.1/167.2 (2 s, C-1) ppm. MS (70 eV): m/z = 159 (1) [$C_8H_{15}O_3^+$], 141 (22) [$C_8H_{13}O_2^+$], 127 (6) [$C_8H_{15}O^+$], 111 (44) [$C_8H_{15}^+$], 95 (18) [$C_8H_{14}^+ - CH_3$], 85 (5) [$C_4H_5O_2^+$], 81 (7) [$C_8H_{14}^+ - C_2H_5$], 69 (100) [$C_4H_5O^+$], 55 (22) [$C_4H_7^+$], 41 (35) [$C_3H_5^+$]. Odor: Musky, fruity, rosy. Odor threshold (*2′′E*/*Z* mixture): 3.7 ng/L air.

(2*E*,2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl But-2-enoate (23): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 1.72 g, 8.59 mmol) with *trans*-crotonic acid (2.27 g, 26.4 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.38) furnished the odoriferous title compound (2.05 g, 89%). IR (ATR): $\tilde{\nu}$ = 1169/1074 (s, νC−O), 1722 (s, νO−C=O), 1660 (s, νC=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.90/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.14/1.15 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.19/1.20 (2 s, 6 H, 2′-Me_2), 1.59/1.67 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 1.89/1.88 (2 d, J = 7.0 Hz, 3 H, 4-H_3), 2.46/2.60 (2 m$_c$, 1 H, 4′′-H), 3.95/3.96/4.02/4.04 (4 d, J = 11.0 Hz, 2 H, 1′-H_2), 4.05/4.59 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.84/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H), 5.88 (br. dq, J = 15.5, 1.5 Hz, 1 H, 2-H), 6.97/7.01 (2 dq, J = 15.5, 7.0 Hz, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2/17.8 (2 q, 2′′-Me), 17.9/17.9 (2 q, C-4), 22.4/22.5/22.5/22.7/22.9/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.5/23.6/23.7/23.8 (4 q, 2′-Me_2), 26.5/26.6 (2 d, C-4′′), 66.1/73.5 (2 d, C-1′′), 69.5/69.6 (2 t, C-1′), 74.5/74.5 (2 s, C-2′), 122.5/122.7 (2 d, C-2), 131.7/132.0 (2 d, C-3′′), 136.5/136.8 (2 s, C-2′′), 144.5/144.6 (2 d, C-3), 166.3/166.3 (2 s, C-1) ppm. MS (70 eV): m/z = 253 (1) [$M^+ - CH_3$], 159 (1) [$C_8H_{15}O_3^+$], 141 (16) [$C_8H_{13}O_2^+$], 127 (6) [$C_8H_{15}O^+$], 111 (35) [$C_8H_{15}^+$], 95 (14) [$C_8H_{14}^+ - CH_3$], 81 (7) [$C_8H_{14}^+ - C_2H_5$], 69 (100) [$C_4H_5O^+$], 55 (18) [$C_4H_7^+$], 41 (21) [$C_3H_5^+$]. Odor: Musky, fruity, sweet. Odor threshold (*2′′E*/*Z* mixture): 8.5 ng/L air.

(2′′*E*/*Z*)-2′-Methyl-2′-(1′′,2′′,4′′-trimethylpent-2′′-enyloxy)propyl But-3-enoate (24): Following the procedure for the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 1.72 g, 8.59 mmol) with but-3-enoic acid (2.27 g, 26.4 mmol) and purification by FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.33) furnished the odoriferous title compound (2.21 g, 96%). IR (ATR): $\tilde{\nu}$ = 1164/1073 (s, νC−O), 1741 (s, νO−C=O), 1644 (s, νC=C) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.91/0.92/0.93/0.95 (4 d, J = 6.5 Hz, 6 H, 4′′-Me_2), 1.13/1.14 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.17/1.18 (2 s, 6 H, 2′-Me_2), 1.60/1.68 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.47/2.59 (2 m$_c$, 1 H, 4′′-H), 3.12 (br. dt, J = 7.0, 1.5 Hz, 2 H, 2-H_2), 3.92/3.93/4.01 /4.02 (4 d, J = 11.0 Hz, 2 H, 1′-H_2), 3.97/4.57 (2 q, J = 6.5 Hz, 1 H, 1′′-H), 4.85/5.14 (2 d, J = 9.5 Hz, 1 H, 3′′-H), 5.15−5.20 (m, 2 H, 4-H_2), 5.96 (m$_c$, 1 H, 3-H) ppm. ^{13}C NMR ($CDCl_3$): δ = 11.2/17.8 (2 q, 2′′-Me), 22.4/22.5/22.5/22.7/22.8/23.3 (6 q, 1′′-Me, 4′′-Me_2), 23.5/23.6/23.7/23.7 (4 q, 2′-Me_2), 26.5/26.6 (2 d, C-4′′), 39.1/39.2 (2 t, C-2), 66.2/73.5 (2 d, C-1′′), 70.1/70.2 (2 t, C-1′), 74.3/74.4 (2 s, C-2′), 118.5/118.6 (2 t, C-4), 125.3/125.4 (2 t, C-4), 130.2/132.0 (2 d, C-3′′), 131.7/131.7 (2 d, C-3), 136.5/136.8 (2 s, C-2′′), 171.3/171.3 (2 s, C-1) ppm. MS (70 eV): m/z = 268 (1) [$M^{+]}$, 253 (1) [$M^+ - CH_3$], 141 (28) [$C_8H_{13}O_2^+$], 127 (5) [$C_8H_{15}O^+$], 111 (56) [$C_8H_{15}^+$], 95 (26) [$C_8H_{14}^+ - CH_3$], 85 (8) [$C_4H_5O_2^+$], 81 (9) [$C_8H_{14}^+ - C_2H_5$], 69 (100) [$C_4H_5O^+$], 55 (29) [$C_4H_7^+$], 41 (51) [$C_3H_5^+$]. Odor: Musky, green, floral. Odor threshold (*2′′E*/*Z* mixture): 4.6 ng/L air.

2′-Methyl-2′-(1′′,2′′,4′′-trimethylpentyloxy)propyl Butyrate (25): A suspension of **20** (1.00 g, 3.70 mmol) and 10% Pd/C (100 mg, 0.09 mmol) in EtOAc (12 mL) was evacuated three times, and flushed with N_2. Following two cycles of flushing and evacuating with H_2, the reaction mixture was stirred at room temp. for 3 h under a positive pressure of H_2. The catalyst was removed by vacuum filtration through a pad of Celite, and the filtrate was concentrated under reduced pressure. FC (silica gel; pentane/Et_2O, 19:1; R_f = 0.40) of the resulting residue furnished the odoriferous title compound (980 mg, 98%). IR (ATR): $\tilde{\nu}$ = 1168/1105/1072 (s, νC−O), 1739 (s, νO−C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 0.82/0.84 (2 d, J = 7.0 Hz, 3 H, 2′′-Me), 0.85/0.90 (2 d, J = 7.0 Hz, 6 H, 4′′-Me_2), 0.93−1.16 (m, 2 H, 3′′-H_2), 0.95/0.96 (2 t, J = 7.5 Hz, 3 H, 4-H_3), 0.99/1.03 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.18 (br. s, 6

H, 2′-Me$_2$), 1.62 (m$_c$, 2 H, 2′′-,4′′-H), 1.68 (m$_c$, 2 H, 3-H$_2$), 2.32/2.33 (2 t, J = 7.5 Hz, 2 H, 2-H$_2$), 3.54 (m$_c$, 1 H, 1′′-H), 3.94 (br. s, 2 H, 1′-H$_2$) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.7/13.9 (2 q, C-4), 15.9/17.4 (2 q, 2′′-Me), 17.4/18.7 (2 q, 1′′-Me), 18.4/18.4 (2 t, C-3), 21.6/22.0/23.7/23.7 (4 q, 4′′-Me$_2$), 23.8/23.8/23.9/24.0 (4 q, 2′-Me$_2$), 25.2/25.3 (2 d, C-4′′), 36.2/36.3 (2 t, C-2), 36.8/37.1 (2 d, C-2′′), 40.9/43.0 (2 t, C-3′′), 70.1/70.3 (2 t, C-1′), 70.8/71.4 (2 d, C-1′′), 73.6/73.7 (2 s, C-2′), 173.4/173.5 (2 s, C-1) ppm. MS (70 eV): m/z = 187 (1) [M$^+$ − C$_6$H$_{13}$], 171 (2) [M$^+$ − C$_5$H$_9$O], 143 (75) [C$_8$H$_{15}$O$_2$$^+$], 113 (27) [C$_8H_{17}$$^+$], 71 (100) [C$_4H_7O^+$], 57 (30) [C$_4H_9$$^+$], 43 (44) [C$_3H_7$$^+$]. C$_{16}H_{32}O_3$ (272.43): calcd. C 70.54, H 11.84; found C 70.41, H 11.73. Odor: Fruity, musky, floral. Odor threshold: 1.0 ng/L air.

(2′′*E*/*Z*)-Propionic Acid (1′′,2′′,4′′-Trimethylpent-2-enyloxy)carbonylmethyl Ester (26): A solution of DCC (5.99 g, 29.0 mmol) in CH$_2$Cl$_2$ (13 mL) was added dropwise to a stirred solution of **16** (4.00 g, 9.36 mmol), chloroacetic acid (2.49 g, 26.4 mmol) and DMAP (320 mg, 2.64 mmol) in CH$_2$Cl$_2$ (26 mL). The reaction mixture was stirred for 5 min at room temp. before the yellow precipitate was separated by vacuum filtration. The precipitate was washed with CH$_2$Cl$_2$ (2 ×) and the combined filtrates were concentrated under reduced pressure. The crude material (7.70 g) was purified by FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.54) to provide 1′,2′,4′-trimethylpent-2-enyl chloroacetate (1.15 g, 60%). A mixture of this ester (1.09 g, 5.33 mmol), propionic acid (0.39 g, 5.33 mmol), and K$_2$CO$_3$ (1.47 g, 10.6 mmol) in Et$_2$CO/dioxane (4:1, 12.5 mL) was heated under reflux for 2 days, with another portion of K$_2$CO$_3$ (1.47 g, 10.6 mmol) being added after 1 day. The reaction mixture was then poured into ice/water (1:1, 50 mL) and the product was extracted with Et$_2$O (2 × 50 mL). The combined ethereal extracts were washed with water (50 mL) and brine (25 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.23) of the resulting residue afforded the odoriferous title compound (0.71 g, 55%). IR (ATR): ṽ = 1162/1059 (s, νC−O), 1748 (s, νO−C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.91/0.93/0.94/0.96 (4 d, J = 6.5 Hz, 6 H, 4′′-Me$_2$), 1.19 (t, J = 7.5 Hz, 3 H, 3-H, 3-H$_3$), 1.31/1.32 (2 d, J = 6.5 Hz, 3 H, 1′′-Me), 1.62/1.66 (2 d, J = 1.5 Hz, 3 H, 2′′-Me), 2.45/2.46 (2 q, J = 8.0 Hz, 2 H, 2-H$_2$), 2.65/2.68 (2 m$_c$, 1 H, 4′′-H), 4.53/4.57 (2 d, J = 17.0 Hz, 1 H, 2′-H$_b$), 4.59/4.61 (2 d, J = 17.0 Hz, 1 H, 2′-H$_a$), 5.07/5.27 (2 br. d, J = 10.0 Hz, 1 H, 3′′-H), 5.31/5.84 (2 q, J = 6.5 Hz, 1 H, 1′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 8.89/8.89 (2 q, C-3), 17.5/18.0 (2 q, 2′′-Me), 23.0/23.3/26.6/26.7/27.0/27.1 (6 q, 1′′-,4′′-Me$_2$), 26.6/26.7 (2 d, C-4′′), 27.0/27.2 (2 t, C-2), 60.6/60.7 (t, C-2′), 70.4/76.9 (2 d, C-1′′), 130.6/131.2 (2 s, C-2′′), 135.5/136.6 (2 d, C-3′′), 167.0/167.1 (s, C-1′), 173.6/173.6 (s, C-1) ppm. MS (70 eV): m/z = 242 (1) [M$^+$], 128 (4) [C$_8$H$_{16}$O$^+$], 115 (80) [C$_5$H$_7$O$^+$], 110 (54) [C$_8$H$_{14}$$^+$], 95 (86) [C$_8H_{14}$$^+$ − CH$_3$], 87 (39) [C$_4$H$_7$O$_2$$^+$], 81 (16) [C$_8H_{14}$$^+$ − C$_2$H$_5$], 67 (39) [C$_8$H$_{14}$$^+$ − C$_3$H$_7$], 57 (100) [C$_4$H$_9$$^+$]. Odor: Green, fruity, slightly musky. Odor threshold (2′′*E*/*Z* mixture): 16 ng/L air.

(2′*E*/*Z*)-6-Methyl-6-(1′,2′,4′-trimethylpent-2-enyloxy)heptan-3-one (29): A solution of pyridinium chlorochromate (PCC, 43.3 g, 201 mmol) in CH$_2$Cl$_2$ (350 mL) was added in one portion to a stirred slurry of Celite® (50 g) in CH$_2$Cl$_2$ (900 mL). Stirring was continued for 15 min before 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propan-1-ol (**27**, 11.8 g, 58.9 mmol) in CH$_2$Cl$_2$ (350 mL) was added dropwise over the course of 20 min. The reaction mixture was stirred at room temp. for 1 day, with a further portion of PCC (4.30 g, 20.0 mmol) being added after the first 5 h, and then it was filtered by suction over a pad of Celite®. The filtrate was concentrated in a rotary evaporator, and the resulting residue purified by FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.57) to furnish 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propionaldehyde (9.97 g, 85%). A solution of diethyl (2-oxobutyl)phosphonate (5.25 g, 25.2 mmol) in DME (5 mL) was added dropwise to a stirred suspension of 95% NaH (640 mg, 25.2 mmol) in DME (15 mL). The reaction mixture was heated under reflux for 15 min prior to the dropwise addition of 2-methyl-2-(1′,2′,4′-trimethylpent-2′-enyloxy)propionaldehyde (5.00 g, 25.2 mmol). After a further 2 h under reflux, the reaction mixture was poured into ice/water (1:1, 100 mL), acidified with AcOH, and extracted with Et$_2$O (2 × 50 mL). The combined ethereal extracts were washed with water (50 mL) and brine (25 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.22) of the resulting residue provided (4*E*,2′-*E*/*Z*)-6-methyl-6-(1′,2′,4′-trimethylpent-2′-enyloxy)hept-4-en-3-one (**28**, 2.11 g, 33%), which possesses a relatively weak green, floral, and cinnamic odor without musk character. [(PPh$_3$)CuH]$_6$ (5.83 g, 2.97 mmol) was dissolved in deoxygenated benzene under an atmosphere of N$_2$. After stirring for 5 min, **28** (2.05 g, 8.12 mmol) was added dropwise over 5 min, and then the reaction mixture was stirred for 5 h at room temp. under an atmosphere of N$_2$. The inert gas supply was then removed and the dark-red suspension was stirred under humid air for 30 min, during which time the color of the reaction mixture turned dark brown. The insoluble material was removed by vacuum filtration through a pad of Celite® and washed with toluene, and the combined organic solutions were evaporated using a rotary evaporator. The resulting residue was purified by FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.14) to furnish the odoriferous title compound (1.68 g, 81%). IR (ATR): ṽ = 1112 (s, νC−O), 1716 (s, νC=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.90/0.91/0.91/0.93 (4 d, J = 7.0 Hz, 6 H, 4′-Me$_2$), 1.05/1.06 (2 t, J = 7.0 Hz, 3 H, 1-H$_3$), 1.11/1.12 (2 d, J = 6.5 Hz, 3 H, 1′-Me), 1.11/1.14 (2 s, 6 H, 6-Me$_2$), 1.16−1.77 (m, 2 H, 5-H$_2$), 1.58/1.67 (2 d, J = 1.5 Hz, 3 H, 2′-Me), 2.41−2.63 (m, 5 H, 2-,4-H$_2$, 4′-H), 3.92/4.49 (2 q, J = 6.5 Hz, 1 H, 1′-H), 4.83/5.10 (2 br. d, J = 9.5 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 7.85/7.87 (2 q, C-1), 11.3/17.9 (2 q, 2′-Me), 22.5/22.6/22.8/22.9/23.5/26.0 (6 q, 1′-,4′-Me$_2$), 26.5/26.6 (2 d, C-4′), 34.9/35.0/35.8/35.9/37.2/37.3 (6t, C-2,-4,-5), 65.4/74.7 (2 d, C-1′), 72.9/74.6 (2 s, C-6), 131.6/131.9 (2 s, C-2′), 136.7/136.9 (2 d, C-3′), 211.8 (s, C-3) ppm. MS (70 eV): m/z = 254 (1) [M$^+$], 211 (1) [M$^+$ − C$_3$H$_7$], 145 (2) [C$_8$H$_{17}$O$_2$$^+$], 127 (89) [C$_8H_{15}O^+$], 111 (42) [C$_8H_{15}$$^+$], 110 (32) [C$_8H_{14}$$^+$], 95 (36) [C$_8H_{14}$$^+$ − CH$_3$], 85 (7) [C$_8$H$_{15}$O$^+$ − C$_3$H$_6$], 69 (44) [C$_8$H$_{14}$$^+$ − C$_3$H$_5$], 57 (100) [C$_4$H$_9$$^+$]. C$_{16}H_{30}O_2$ (254.41): calcd. C 75.54, H 11.89; found C 75.65, H 12.06. Odor: Musky, sweet, fruity. Odor threshold: 0.55 ng/L air.

6-Methyl-6-(1′,2′,4′-trimethylpentyloxy)heptan-3-one (30): Following the procedure for the preparation of **25**, compound **29** (1.07 g, 4.21 mmol) was hydrogenated in the presence of 10% Pd/C (100 mg, 0.09 mmol) to provide, after purification by bulb-to-bulb distillation (125 °C, 0.9 mbar), the odoriferous title compound (750 mg, 70%). IR (ATR): ṽ = 1108 (s, νC−O), 1716 (s, νC=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.80/0.83 (2 br. d, J = 7.0 Hz, 6 H, 4′-Me$_2$), 0.89/0.90/0.95/0.99 (4 d, J = 6.5 Hz, 6 H, 1′-,2′-Me), 1.06/1.06 (2 t, J = 7.5 Hz, 3 H, 1-H$_3$), 1.10/1.11/1.14/1.14 (4 s, 6 H, 6-Me$_2$), 1.22−1.79 (m, 6 H, 5-,3′-H$_2$, 2′-,4′-H), 2.42−2.54 (m, 4 H, 2-,4-H$_2$), 3.44/3.47 (2 q, J = 6.5, 4.5 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 7.88/7.88 (2 q, C-1), 13.9/16.0/17.1/18.4 (4 q, 1′-,2′-Me), 21.7/22.1/23.6/24.1/25.6/25.7/26.2/26.4 (8 q, 6-,4′-Me$_2$), 25.2/25.3 (2 d, C-4′), 35.8/35.8/35.9/36.1/37.2/37.3 (6t, C-2,-4,-5), 36.8/37.1 (2 d, C-2′), 40.7/43.2 (2 t, C-3′), 70.0/70.6 (2 d, C-1′), 73.8/73.9 (2 s, C-6), 211.8/211.9 (2 s, C-3) ppm. MS (70 eV): m/z = 241 (1) [M$^+$ − CH$_3$], 171 (2) [C$_{11}$H$_{23}$O$^+$], 127 (100) [C$_8$H$_{15}$O$^+$], 113 (7) [C$_8$H$_{17}$$^+$], 109 (14) [C$_8H_{15}O^+$ − H$_2$O], 97 (6) [C$_7$H$_{13}$$^+$], 71 (11)

$[C_5H_{11}^+]$, 57 (85) $[C_4H_9^+]$. Odor: Musky, slightly fruity-floral. Odor threshold: 0.87 ng/L air.

(2′′*E*)-2′-Methyl-2′-(1′′,4′′,4′′-trimethylpent-2′′-enyloxy)propyl Propionate (31): Following the procedure for the preparation of **8**, (3*E*)-5,5-dimethylhex-3-en-2-ol (29.4 g, 229 mmol) was etherified with isobutylene oxide (19.8 g, 275 mmol) to provide, after FC (silica gel; pentane/Et$_2$O, 9:1; R_f = 0.27), 2-methyl-2-(1′,4′,4′-trimethylpent-2′-enyloxy)propan-1-ol (4.21 g, 8%). According to the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,4′,4′-trimethylpent-2′-enyloxy)propan-1-ol (1.30 g, 6.49 mmol) with propionic acid (480 mg, 6.49 mmol) and FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.14) furnished the odoriferous title compound (1.37 g, 82%). IR (ATR): ṽ = 1169/1063 (s, νC−O), 1741 (s, νO−C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.99 (s, 9 H, 4′′-Me$_3$), 1.16 (t, *J* = 7.0 Hz, 3 H, 3-H$_3$), 1.17 (d, *J* = 6.5 Hz, 3 H, 1′′-Me), 1.19 (s, 6 H, 2′-Me$_2$), 2.37 (q, *J* = 7.0 Hz, 2 H, 2-H$_2$), 3.94 (d, *J* = 11.0 Hz, 1 H, 1′-H$_b$), 4.00 (d, *J* = 11.0 Hz, 1 H, 1′-H$_a$), 4.14 (quint. d, *J* = 6.5, 1.0 Hz, 1 H, 1′′-H), 5.34 (dd, *J* = 15.5, 6.5 Hz, 1 H, 2′′-H), 5.54 (dd, *J* = 15.5, 1.0 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 9.09 (q, C-3), 23.8/23.9/23.9 (3 q, 2′-,1′′-Me), 27.6 (t, C-2), 29.4 (3 q, 4′′-Me$_3$), 32.5 (s, C-4′′), 69.1 (d, C-1′′), 69.8 (t, C-1′), 74.4 (s, C-2′), 129.3 (d, C-2′′), 140.3 (d, C-3′′), 174.2 (s, C-1) ppm. MS (70 eV): *m*/*z* = 241 (1) $[M^+ - CH_3]$, 129 (20) $[C_8H_{17}O^+]$, 127 (9) $[C_8H_{15}O^+]$, 111 (100) $[C_8H_{15}^+]$, 95 (16) $[C_7H_{11}^+]$, 69 (43) $[C_8H_{14}^+ - C_3H_5]$, 57 (92) $[C_4H_9^+]$. Odor: Green, grapefruit, slightly musky.

(2′′*E*)-2′-Methyl-2′-(1′′,4′′,4′′-trimethylpent-2′′-enyloxy)propyl Cyclopropanecarboxylate (32): According to the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,4′,4′-trimethylpent-2′-enyloxy)propan-1-ol (1.30 g, 6.49 mmol) with cyclopropanecarboxylic acid (590 mg, 6.49 mmol) and FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.29) furnished the odoriferous title compound (1.46 g, 84%). IR (ATR): ṽ = 1163/1063 cm^{-1} (s, νC−O), 1731 cm^{-1} (s, νO−C=O). ^{1}H NMR (CDCl$_3$): δ = 0.86 (m$_c$, 2 H, 3-,4-H$_b$), 0.99 (s, 9 H, 4′′-Me$_3$), 1.02 (m$_c$, 2 H, 3-,4-H$_a$), 1.17 (d, *J* = 6.5 Hz, 3 H, 1′′-Me), 1.20 (s, 6 H, 2′-Me$_2$), 1.66 (m$_c$, 1 H, 2-H), 3.93 (d, *J* = 11.5 Hz, 1 H, 1′-H$_b$), 3.99 (d, *J* = 11.5 Hz, 1 H, 1′-H$_a$), 4.13 (quint. d, *J* = 6.5, 1.0 Hz, 1 H, 1′′-H), 5.35 (dd, *J* = 15.5, 6.5 Hz, 1 H, 2′′-H), 5.54 (dd, *J* = 15.5, 1.0 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 8.33 (2 t, C-3,-4), 12.9 (d, C-2), 23.9/23.9/24.0 (3 q, 2′-,1′′-Me), 29.4 (3 q, 4′′-Me$_3$), 32.5 (s, C-4′′), 69.1 (d, C-1′′), 69.8 (t, C-1′), 74.4 (s, C-2′), 129.3 (d, C-2′′), 140.3 (d, C-3′′), 174.6 (s, C-1) ppm. MS (70 eV): *m*/*z* = 253 (1) $[M^+ - CH_3]$, 141 (13) $[C_8H_{13}O_2^+]$, 127 (9) $[C_8H_{15}O^+]$, 111 (78) $[C_8H_{15}^+]$, 95 (14) $[C_7H_{11}^+]$, 69 (100) $[C_8H_{14}^+ - C_3H_5]$, 41 (33) $[C_3H_5^+]$. Odor: Fruity, musky, powdery, anisic.

(2′′*E*)-2′-Methyl-2′-(1′′,4′′,4′′-trimethylpent-2′′-enyloxy)propyl Butyrate (33): According to the synthesis of **17**, Steglich esterification of 2-methyl-2-(1′,4′,4′-trimethylpent-2′-enyloxy)propan-1-ol (1.30 g, 6.49 mmol) with butyric acid (570 mg, 6.49 mmol) and FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.26) furnished the odoriferous title compound (1.45 g, 83%). IR (ATR): ṽ = 1168/1062 (s, νC−O), 1738 (s, νO−C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.96 (t, *J* = 7.5 Hz, 3 H, 4-H$_3$), 0.99 (s, 9 H, 4′′-Me$_3$), 1.16 (d, *J* = 6.5 Hz, 3 H, 1′′-Me), 1.20 (s, 6 H, 2′-Me$_2$), 1.68 (sext, *J* = 7.5 Hz, 2 H, 3-H$_2$), 2.33 (t, *J* = 7.5 Hz, 2 H, 2-H$_2$), 3.94 (d, *J* = 11.5 Hz, 1 H, 1′-H$_b$), 4.02 (d, *J* = 11.0 Hz, 1 H, 1′-H$_a$), 4.13 (quint. d, *J* = 6.5, 1.0 Hz, 1 H, 1′′-H), 5.35 (dd, *J* = 15.5, 6.5 Hz, 1 H, 2′′-H), 5.54 (dd, *J* = 15.5, 1.0 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.7 (q, C-4), 18.4 (t, C-3), 23.8/23.9/24.0 (3 q, 2′-,1′′-Me), 29.4 (3 q, 4′′-Me$_3$), 32.5 (s, C-4′′), 36.2 (t, C-2), 69.1 (d, C-1′′), 69.7 (t, C-1′), 74.4 (s, C-2′), 129.3 (d, C-2′′), 140.3 (d, C-3′′), 173.4 (s, C-1) ppm. MS (70 eV): *m*/*z* = 143 (15) $[C_8H_{15}O_2^+]$, 127 (10) $[C_8H_{15}O^+]$, 111 (100) $[C_8H_{15}^+]$, 95 (16) $[C_7H_{11}^+]$, 71 (66) $[C_4H_7O^+]$, 69 (39) $[C_8H_{14}^+ - C_3H_5]$, 55 (29) $[C_4H_7^+]$, 43 (41) $[C_3H_7^+]$. Odor: Fruity, musky.

1′,4′,4′-Trimethylpent-2-enyl (2′*E*)-4-Oxopentanoate (34): Steglich esterification of (3*E*)-5,5-dimethylhex-3-en-2-ol (760 mg, 5.93 mmol) with 4-oxopentanoic acid (690 mg, 5.93 mmol) provided, after the usual workup and purification by FC (silica gel; pentane/Et$_2$O, 9:1; R_f = 0.14), the odoriferous title compound (1.21 g, 90%). IR (ATR): ṽ = 1721 (s, νC=O), 1159 (s, νC−O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 1.00 (s, 9 H, 4′-Me$_3$), 1.28 (d, *J* = 6.0 Hz, 3 H, 1′-Me), 2.19 (s, 3 H, 5-H$_3$), 2.56 (t, *J* = 7.0 Hz, 2 H, 2-H$_2$), 2.74 (td, *J* = 7.0, 2.5 Hz, 2 H, 3-H$_2$), 5.28−5.38 (m, 2 H, 1′-,2′-H), 5.69 (d, *J* = 14.5 Hz, 1 H, 3′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 20.4 (q, 1′-Me), 28.4 (t, C-2), 29.3 (3 q, 4′-Me$_3$), 29.8 (q, C-5), 32.7 (s, C-4), 37.9 (t, C-3), 71.6 (d, C-1′), 124.2 (d, C-2′), 143.9 (d, C-3′), 171.9 (s, C-1), 206.6 (s, C-4) ppm. MS (70 eV): *m*/*z* = 208 (1) $[M^+ - H_2O]$, 170 (5) $[M^+ - C_4H_8]$, 152 (1) $[M^+ - C_4H_8 - H_2O]$, 127 (11) $[C_8H_{15}O^+]$, 110 (16) $[C_8H_{15}^+]$, 99 (100) $[C_5H_7O_2^+]$, 95 (55) $[C_8H_{15}^+ - CH_3]$, 81 (9) $[C_5H_7O_2^+ - H_2O]$, 67 (25) $[C_5H_7^+]$, 55 (30) $[C_4H_7^+]$, 43 (37) $[C_2H_3O^+]$. Odor: Musky, fruity, pear, ambrette seed oil.

(2′′*E*)-2′-(1′′,4′′-Dimethylpent-2′′-enyloxy)-2′-methylpropyl Propionate (35): Following the procedure for the preparation of **8**, (3*E*)-5-dimethylhex-3-en-2-ol (108 g, 946 mmol) was etherified with isobutylene oxide (81.8 g, 1.14 mmol) to provide, after FC (silica gel; pentane/Et$_2$O, 9:1; R_f = 0.17), 2-methyl-2-(1′,4′-dimethylpent-2′-enyloxy)propan-1-ol (24.8 g, 14%). Steglich esterification of 2-methyl-2-(1′,4′-dimethylpent-2′-enyloxy)propan-1-ol (1.80 g, 9.66 mmol) with propionic acid (1.19 g, 16.1 mmol) and the usual workup with FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.31) furnished the odoriferous title compound (1.00 g, 43%). IR (ATR): ṽ = 1168/1057 (s, νC−O), 1741 (s, νO−C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.96/0.97 (2 d, *J* = 7.0 Hz, 6 H, 4′′-Me$_2$), 1.16 (t, *J* = 7.5 Hz, 3 H, 3-H$_3$), 1.17 (d, *J* = 6.5 Hz, 3 H, 1′′-Me), 1.20 (s, 6 H, 2′-Me$_2$), 2.24 (br. oct., *J* = 7.0 Hz, 1 H, 4′′-H), 2.37 (q, *J* = 7.5 Hz, 2 H, 2-H$_2$), 3.95 (d, *J* = 11.5 Hz, 1 H, 1′-H$_b$), 3.99 (d, *J* = 11.5 Hz, 1 H, 1′-H$_a$), 4.12 (br. quint., *J* = 6.5 Hz, 1 H, 1′′-H), 5.38 (ddd, *J* = 15.5, 6.5, 1.0 Hz, 1 H, 2′′-H), 5.50 (ddd, *J* = 15.5, 6.5, 1.0 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 9.09 (q, C-3), 21.2/22.2 (2 q, 4′′-Me), 23.7/23.8/23.9 (3 q, 2′-,1′′-Me), 27.6 (t, C-2), 30.5 (d, C-4′′), 68.8 (d, C-1′′), 69.7 (t, C-1′), 74.4 (s, C-2′), 131.5 (d, C-2′′), 136.4 (d, C-3′′), 174.2 (s, C-1) ppm. MS (70 eV): *m*/*z* = 227 (1) $[M^+ - CH_3]$, 146 (1) $[C_7H_{14}O_3^+]$, 129 (15) $[C_8H_{17}O^+]$, 113 (8) $[C_7H_{13}O^+]$, 97 (100) $[C_7H_{13}^+]$, 57 (80) $[C_4H_9^+]$, 55 (56) $[C_7H_{13}^+ - C_3H_6]$. Odor: Earthy, green, slightly musky.

(2′′*E*)-2′-(1′′,4′′-Dimethylpent-2′′-enyloxy)-2′-methylpropyl Cyclopropanecarboxylate (36): Steglich esterification of 2-methyl-2-(1′,4′-dimethylpent-2′-enyloxy)propan-1-ol (1.80 g, 9.66 mmol) with cyclopropanecarboxylic acid (1.40 g, 16.1 mmol) and the usual workup with FC (silica gel; pentane/Et$_2$O, 19:1; R_f = 0.28) provided the odoriferous title compound (900 mg, 37%). IR (ATR): ṽ = 1162 (s, νC−O), 1730 (s, νO−C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ = 0.86 (m$_c$, 2 H, 3-,4-H$_b$), 0.96/0.97 (2 d, *J* = 7.0 Hz, 6 H, 4′′-Me$_2$), 1.02 (m$_c$, 2 H, 3-,4-H$_a$), 1.17 (d, *J* = 6.5 Hz, 3 H, 1′′-Me), 1.21 (s, 6 H, 2′-Me$_2$), 1.65 (m$_c$, 1 H, 2-H), 2.24 (br. oct., *J* = 7.0 Hz, 1 H, 4′′-H), 3.94 (d, *J* = 11.0 Hz, 1 H, 1′-H$_b$), 3.98 (d, *J* = 11.0 Hz, 1 H, 1′-H$_a$), 4.12 (br. quint., *J* = 6.5 Hz, 1 H, 1′′-H), 5.39 (ddd, *J* = 15.5, 6.5, 1.0 Hz, 1 H, 2′′-H), 5.51 (ddd, *J* = 15.5, 6.5, 1.0 Hz, 1 H, 3′′-H) ppm. ^{13}C NMR (CDCl$_3$): δ = 8.29/8.30 (2 t, C-3,-4), 12.9 (d, C-2), 22.1/22.2 (2 q, 4′′-Me$_2$), 23.7/23.8/23.9 (3 q, 2′-,1′′-Me), 30.5 (d, C-4′′), 68.8 (d, C-1′′), 69.7 (t, C-1′), 74.4 (s, C-2′), 131.5 (d, C-2′′), 136.4 (d, C-3′′), 174.6 (s, C-1) ppm. MS (70 eV):

m/*z* = 239 (1) [$M^+ - CH_3$], 158 (1) [$C_8H_{14}O_3^+$], 141 (13) [$C_8H_{13}O_2^+$], 127 (1) [$C_8H_{15}O^+$], 110 (12) [$C_8H_{14}^+$], 97 (100) [$C_7H_{13}^+$], 69 (100) [$C_4H_5O^+$], 55 (57) [$C_7H_{13}^+ - C_3H_6$], 41 (36) [$C_3H_5^+$]. Odor: Fruity, floral, musky.

Acknowledgments

We are grateful to Katarina Grman for the GC-threshold determinations, and to Dr. Gerhard Brunner, Dr. Joachim Schmid, and Annette Rahn for the spectroscopic data. Thanks are also due to Dr. Markus Gautschi for proofreading, to Caroline Denis, Anne-Sylvie Selezneff and Jean Jacques Rouge for the odor descriptions, and to Ursula Wandel and Jean Guichard, who created and evaluated numerous perfumery trials with these new musks.

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Received September 15, 2003