The Search for New Odorants: Synthesis of Animalic Fragrant and Musky/Ambery Compounds

by **Caroline Plessis**

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An overview of the recent research which allowed us to discover novel animalic odorants is presented. The new derivatives were prepared from readily available starting materials *via* easy reaction steps in good yields. They possess very different structures, such as bicyclic pentanols, glycolates, or tricyclic ketones, and all show interesting notes in the animalic fragrant family: from costus, leathery to ambery and musky scents, making them all attractive for different purposes.

Introduction. – Natural animal raw materials can be described as rich and warm, leathery, and with fecal aspects and unique undertones related to their origin (castoreum, civet, musk deer, ambergris). Despite unclean aspects, animal odorants, throughout centuries, have always played important roles in compositions, such as texturing agents (warmness, leathery, powdery) and as fixatives (resulting in long-lasting perfumes). They also give opulence/richness to some accords, notably white flowers [1].

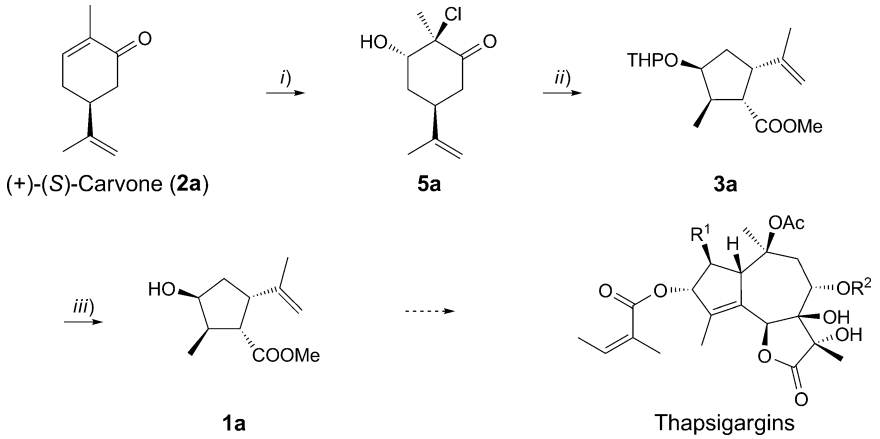
Natural animal raw materials were, therefore, studied in detail to unveil the active principles. Fascinating essential molecules were prepared by highly challenging syntheses mainly in two important olfactory families: Musk and Amber [2].

Found in leathery Chypre perfumes with Castoreum undertones late 1980s, animalic notes regained interest recently, in luxury niche perfume houses, notably in Arabian oud fragrances.

Ambery or musky proprietary molecules are important for our portfolio. Nevertheless, the molecules presented here, belonging to the broad animalic family, were discovered rather by serendipity while working on 'non-ambery'-oriented projects, demonstrating again how amazing and exciting fragrance chemistry can be. The first part deals with new cyclopentanols obtained from both (+)-(*S*)- and (−)-(*R*)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone ((*S*)- and (*R*)-carvone), the second part describes new glycolates, and the last part is about a new tricyclic ambery odorant.

Cyclopentanol Derivatives. – Hydroxy ester **1a** was prepared by *Ley* and co-workers [3] as a starting material for thapsigargins (*Scheme 1*). *Ley*'s group emphasized the effectiveness of their first steps on large scale, using cheap reagents and starting from easily available (*S*)-carvone (**2**). With its interesting structure, obtained stereospecifically, this small molecule was appealing as a synthon.

Scheme 1



i) *a*) H_2O_2, NaOH, MeOH, 10°; 88%. *b*) LiCl, CF_3COOH, THF, r.t.; 95%. *ii*) *a*) Dihydropyran, cat. pyridinium *p*-toluenesulfonate (PPTS), CH_2Cl_2, r.t.; 87%. *b*) MeONa, MeOH, 0°; 95%; dr >95:5. *iii*) Cat. PPTS, MeOH, 40°; 84%.

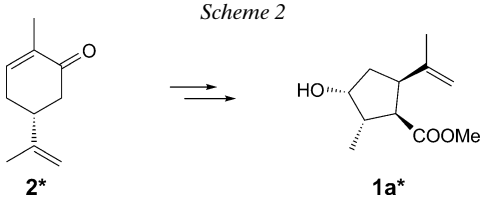
Its enantiomer **1a*** (*Scheme 2*) was reported earlier by another group, starting from also available (*R*)-carvone (**2***), by similar chemistry in the synthesis of iridomyrmecins, also pointing out the good stereoselectivity of the sequence [4].

For clarity and easier understanding, in the following, the * indicates that the molecule is the enantiomer of the correspondingly numbered compound. As outlined above, therefore, this indicates that the **1a*** is prepared *via* a sequence starting from **2***, whereas **1a** is synthesized from **2**.

Actually, both enantiomers, **1a** and **1a***, were since reported as starting material for various natural products synthesis by other groups [5]. As chirality can be important in olfaction, and since olfactory properties of these compounds and derivatives were not described, we prepared both isomers following the procedure of *Ley* and co-workers. The only modification we made was using EtOH instead of MeOH in the first step for the synthesis of the carvone epoxide. We obtained alcohols **1a** and **1a*** in 48 and 38% yields, respectively, over five steps (86% average yield per step, 82% resp.), *via* their corresponding THP derivatives **3a** and **3a*** (*cf.* S*cheme 1*). Unfortunately, the odors of compounds **1a** and **1a*** were only slightly floral.

However, given the easy preparation of the THP intermediates **3a** and **3a*** from inexpensive carvones **2** and **2***, respectively, we focused on the preparation of **3**, as a

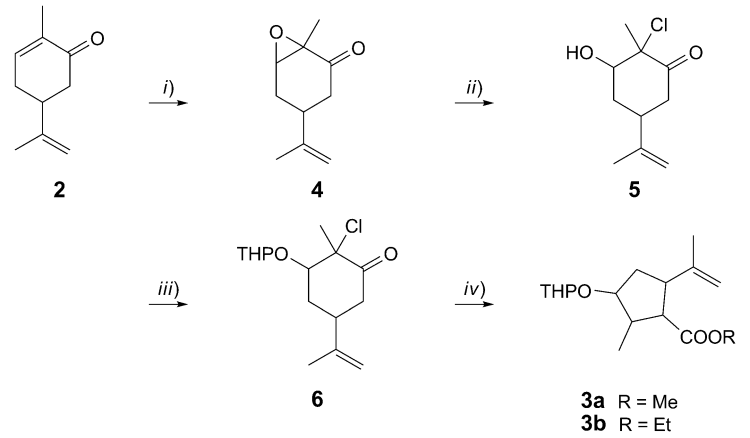
Scheme 2



source of other new derivatives. For industrial purposes, it was important to replace MeOH and CH_2Cl_2 for toxicity and environmental reasons, and THF for recovery purposes.

Based on previous experience [6], the epoxidation was directly carried out in EtOH, instead of MeOH, without influencing the overall yields. Thus epoxides **4** and **4***(*Scheme 3*) were prepared in 83% yield from both carvones (average yield reported by *Ley* and co-workers: 88.6%).

Scheme 3



i) H_2O_2, NaOH, EtOH, 10°. *ii*) LiCl, CF_3COOH, r.t. *iii*) Dihydropyran, cat. PPTS, r.t. *iv*) Na, ROH, 0°.

The opening of the epoxides to the chlorhydrins **5** and **5*** was then performed in 2-MeTHF with similar yield as in THF (*Table 1*).

The THP (tetrahydropyran-2-yl) protection step carried out in toluene instead of CH_2Cl_2 proceeded with very good yields to afford compounds **6** and **6*** (*Table 2*).

Table 1. *Chlorhydrins* **5** *Obtained in 2-MeTHF* vs. *THF*

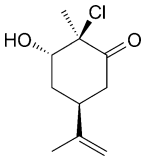
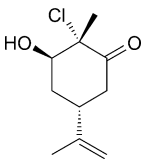
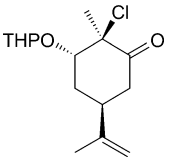
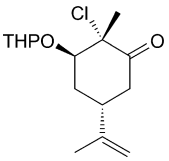
Compound		Solvent	Crude yield [%]
	**5**	THF	75
		2-MeTHF	85
	**5***	THF	80
		2-MeTHF	100

Table 2. *Protected Chlorhydrins* **6** *Obtained in Toluene* vs. CH_2Cl_2

Compound		Solvent	Crude yield [%]
	**6**	CH_2Cl_2	87
		Toluene	83
	**6***	CH_2Cl_2	84
		Toluene	quant.

The *Favorskii* rearrangement was performed in EtOH and afforded the so far unknown ethyl esters **3b** and **3b*** instead of the methyl derivatives **3a** or **3a***, however, in lower yields (*Table 3*).

Performing the reaction sequences in different solvent systems (*Scheme 3*, and *Table 4*) led to **3** in quite similar overall yields.

From the ethyl esters **3b** and **3b***, corresponding alcohols **1b** and **1b*** were prepared to evaluate their olfactory properties. The deprotection was either performed in MeOH as described, or in EtOH for safer use. The yields were almost quantitative. However, again, these compounds showed no interesting odors.

The new structures that were further envisaged were obtained by simple transformations (*Scheme 4*).

Table 3. *Esters* **3** *Obtained* via Favorskii *Rearrangement in EtOH or MeOH*

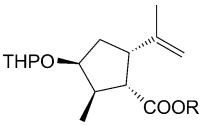
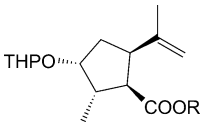
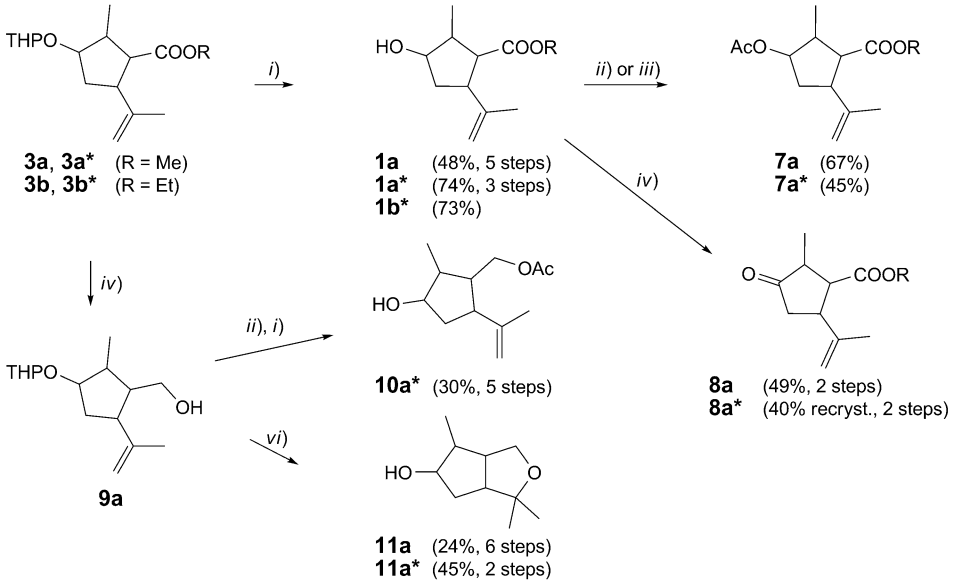
Compound	Solvent	Crude yield [%]	Compound	Solvent	Crude yield [%]
					
3a R = Me	MeOH	62	**3a*** R = Me	MeOH	68
3b R = Et	EtOH	33	**3b*** R = Et	EtOH	52

Table 4. *Sequence Yields to Obtain* **3** *from* **2** *Using Different Solvents* (*Scheme 3*)

Entry	Compound	Step *ii*	Step *iii*	Step *iv*	Yield [%]
1	**3a**	THF	CH_2Cl_2	MeOH	48
2	**3a***	THF	CH_2Cl_2	MeOH	52
3	**3a***	2-MeTHF	Toluene	MeOH	39
4	**3b**	2-MeTHF	Toluene	EtOH	28
5	**3b***	2-MeTHF	Toluene	EtOH	39

Scheme 4



i) cat. PPTS, MeOH. *ii*) Ac_2O, cat. 4-(dimethylamino)pyridine (DMAP). *iii*) AcCl, Et_3N, cat. TsOH, ^{t}BuOMe. *iv*) Pyridinium dichromate (PDC)/SiO_2, CH_2Cl_2. *v*) $LiAlH_4$, Et_2O. *vi*) Cat. PPTS, MeOH, then TfOH, toluene.

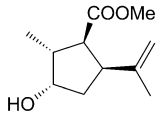
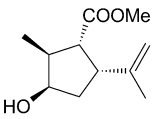
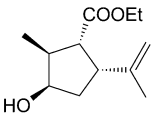
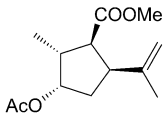
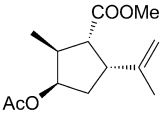
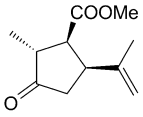
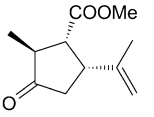
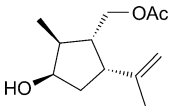
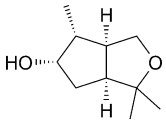
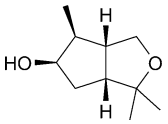
After deprotection of derivatives **3** to yield alcohols **1**, the corresponding acetates **7** were prepared in good yields. From alcohols **1**, also the corresponding cyclopentanones **8** were obtained. Then, the ester **3** was further transformed to the corresponding alcohol **9a**, which was then esterified and deprotected to afford compounds **10**. Alcohols **9a** also underwent cyclization with the isopropenyl group, and the THP group was removed to furnish the bicyclic compounds **11a**. All the obtained compounds were evaluated by a perfumer panel as compiled in *Table 5*.

The only rather interesting compounds were bicyclic derivatives **11a**. So, we prepared new, differently substituted bicycles. This could be easily performed by condensing a *Grignard* reagent onto the ester **3** instead of hydride reduction. Thus, the obtained alcohols **9b** and **9c**, with dimethyl and diethyl substituents, respectively, were obtained. Compounds **9b** and **9c** were further cyclized to afford **11b** and **11c**, respectively, in good yields (*Scheme 5*). To obtain bicyclic compound **11d***, a *Kulinkowich* reaction was performed on **3***, leading to cyclopropyl alcohol **9d*** [7], reacting the ester with EtMgCl in the presence of $(^i PrO)_4Ti$. Enantiomer **11b*** was obtained in 59% yield from alcohol **9b***, by using EtOH to remove the THP group in the one-pot cyclization/deprotection step.

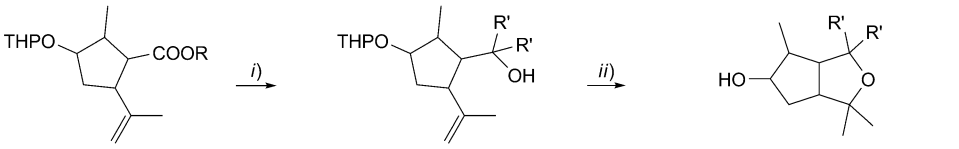
Then, acetates **12** as well as the corresponding cyclopentanones **13** (*Scheme 6*) were prepared from **11**.

Acetates **12** were easily obtained by treating bicyclic alcohols **11** with Ac_2O in good yields (average yields 60–70%), whereas ketone **13a*** was prepared from oxo-ester **8a***

Table 5. *Odor Descriptions of the Carvone Derivatives*

Compound		Odor	Compound		Odor
	**1a**	Slightly floral, a bit smokey		**1a***	Slightly floral
				**1b***	Lactonic, powdery, musky, weak
	**7a**	Weak		**7a***	Spearmint, Carvone, chlorophylle, «cédrat confit»
	**8a**	Very weak		**8a***	Very weak
				**10***	Carnation, eugenol, weak
	**11a**	Fishy, fish flesh		**11a***	Leathery, animal, phenolic, indolic, smokey

Scheme 5



3a, **3a*** (R = Me)
3b, **3b*** (R = Et)

9b, **9b*** (R' = Me)
9c* (R' = Et)
9d* (R',R' = –CH_2CH_2–)

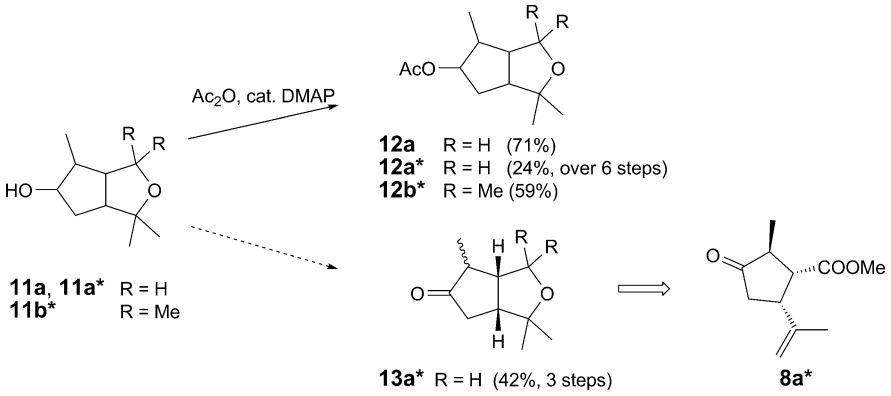
11b (R' = Me; 18%, over 6 steps)
11b* (R' = Me; 59%[a]))
11c* (R' = Et; 36%)
11d* (R',R' = –CH_2CH_2– ; 10%)

i) *a*) R′MgX, THF, 0–10°; or *b*) EtMgCl, (^{i}PrO)$_4$Ti, Et_2O. *ii*) Cat. PPTS, 2 equiv. MeOH ([a]) or EtOH) then TfOH, toluene.

by reducing the ester and performing the one-pot deprotection-cyclization sequence, in overall good yield. However, some epimerization occurred at the α-C-atom.

All the new bicyclic derivatives were also evaluated by a perfumer panel (*Table 6*). Despite interesting tonalities, compounds **12** and **13** were too weak, only the bicyclic alcohols **11** showed attractive notes, **11a*** being the outstanding molecule.

Scheme 6



The final steps of the preparation of compound **11a*** had to be improved from an industrial point of view. Some improvements were already performed along the different syntheses of the compounds **11**, notably the way the one-pot cyclization-deprotection was carried out. Finally, we found that the yield was improved and the process was cleaner, by performing the deprotection first at 60° in toluene in the presence of TsOH and 2 equiv. of MeOH or EtOH, and only then adding trifluoromethylsulfonic acid (triflic acid, TfOH) to perform the cyclization at 80°. We then tried to avoid the use of $LiAlH_4$ industrially. Literature survey revealed that $NaBH_4$ by adding catalysts in different solvents is a convenient alternative [8]. The conditions that were evaluated are compiled in *Table 7* (*Entries 1–4*). Other possibilities were aluminum hydrides such as *Synhydrid®* (*Entry 5*) or DIBAl-H (*Entry 6*). Only the latter gave a good conversion.

Finally, we achieved a better overall yield of **11a*** from ester **3a*** (*Scheme 7*), by performing the THP removal, followed by cyclization in the presence of TfOH in one pot (*Table 8*, *Entry 2*). Using DIBAl-H instead of $LiAlH_4$ also gave better results, and the resulting toluene solution after hydrolysis can be directly used in the subsequent cyclization step (*Entry 3*).

New cyclopentanol derivatives were prepared in good yields *via* simple steps, starting from inexpensive and available carvones (**2** and **2***). Among the different structures, an interesting bicyclic compound **11a***, prepared in 27% yield over six steps (average yield: 80.4%) from (+)-(*R*)-enantiomer **2***, was found as a nice leathery and animalic odorant.

Scheme 7

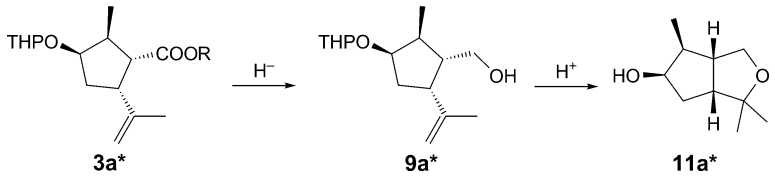


Table 6. *Odor Descriptions of the Bicyclic Derivatives*

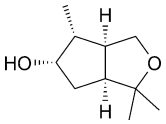
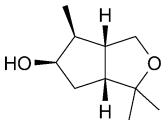
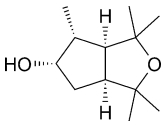
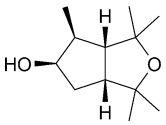
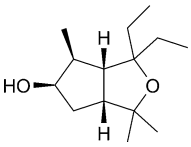
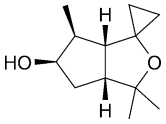
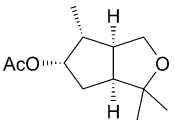
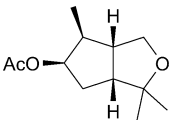
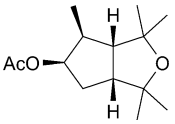
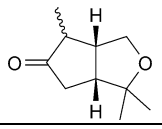
Compound		Odor description	Compound		Odor description
	**11a**	Fishy, fish flesh		**11a***	Leathery, animal, phenolic, indolic, smokey
	**11b**	Green, metallic, raw vegetables, earthy		**11b***	Woody, leathery, sligthly honey, animal
				**11c***	Marine, oyster, weak
				**11d***	Spicy, pepper, a bit Carvone, weak
	**12a**	Slightly plastic, weak		**12a***	Woody, vetiver, weak
				**12b***	Marine, aqueous, algae, weak
				**13a***	Musky, lactonic, powdery, weak

Table 7. *Reduction Conditions to Obtain Alcohol* **9a***

Entry	Reducing agent	Catalyst	Solvent	Yield of **9a*** [%]	Reaction time
1	$NaBH_4$	MeOH	*t*-AmOH[a])	Only isomers	1 week
2	$NaBH_4$	MeOH	THF	–	5 h
3	$NaBH_4 + ZnCl_2$	Me_2NPh	THF	–	4 h
4	$Ca(BH_4)_2$	–	THF	–	1 h
5	$NaAl(MeOC_2H_4O)_2H_2$	–	Toluene	–	0.5 h
6	DIBAl-H	–	Toluene	88	2.5 h

[a]) *tert*-Amyl alcohol (2-methylbutan-2-ol).

Table 8. *Sequence Yields to Obtain* **11a*** *from* **3a*** *Using Different Conditions* (*Scheme 7*)

Entry	Reducing agent (*Step 1*)	Cyclization/Deprotection (*Step 2*)	Yield [%]
1	$LiAlH_4$	TfOH/Toluene then MeOH	34%
2	$LiAlH_4$	PPTS/MeOH/Toluene then TfOH	45%
3	DIBAl-H	PPTS/MeOH/Toluene[a]) then TfOH	53%

[a]) Toluene from the *Step 1*.

Glycolate Derivatives. – Finding a new great galbanum-type green note to be added to our captives portfolio is not easy, the reference being the very powerful *Dynascone*® (**14**; *Fig.*). On alkyl butenyl ketones and intensities, a tremendous work has been accomplished by *Bajgrowicz* and co-workers [9] in association with structure–activity relationships (SARs) for a green/galbanum olfactophore model. The study also dealt with some allyl glycolates, which are also well known in the galbanum family, such as *Cyclogalbanate*® (**15**), allyl amyl glycolate (**16**) or allyl phenoxyacetate (**17**; *Fig.*). These compounds have a more fruity pineapple-type aspect than *Dynascone*®, but they are an attractive class of compounds because of their potentially facile industrial preparation.

We prepared new aryl derivatives of the Acetate PA type (allyl phenoxyacetate), as well as new allyl alkoxyacetates [10]. Both syntheses are trivial. In the case of alkoxyacetates **18** and **19**, the chosen alkyl alcohol **20** was deprotonated with NaH and the obtained alcoholate was condensed onto $ClCH_2COONa$. The allyl derivatives **18** or **19** are then simply obtained by esterification of the acid with allylic alcohol or (*Z*)-hex-3-enol, respectively (*Scheme 8*, *Table 9*).

Concerning the 2-(aryloxy)acetates **21** and **22**, the synthesis is even simpler: the corresponding phenol **23** was reacted with allyl chloroacetate or (*Z*)-hex-3-enyl chloroacetate, respectively, in the presence of K_2CO_3 in refluxing acetone (*Scheme 9* and *Table 10*).

All the target compounds were obtained in fair unoptimized yields (35–55%). Among all the prepared derivatives, only compounds **18a** and **19a** belong to the green family, which is not surprising due to the (*Z*)-hex-3-en-1-ol moiety. However, **18a** and

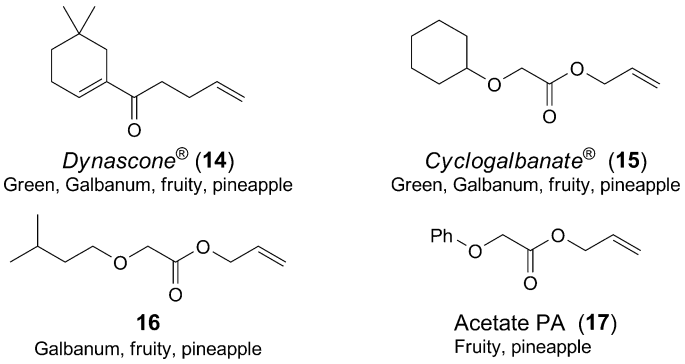


Figure. *Synthetic galbanum-type raw materials*

Scheme 8

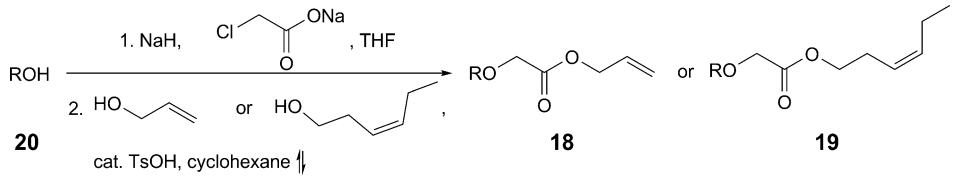
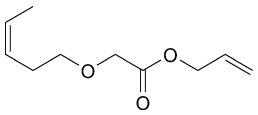
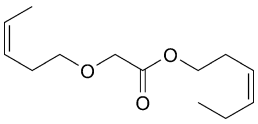
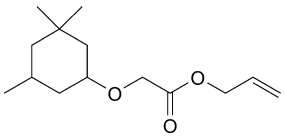
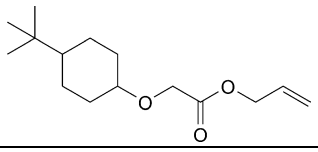


Table 9. *Odor Descriptions of the Glycolate Derivatives* **18** *and* **19** (*Scheme 8*)

Starting alcohol	Compound		Odor
20a R = (*Z*)-Hex-3-en-1-yl		**18a**	Green, cut grass, watery, clean (Ironed linen), powerful
20a		**19a**	Clean (Ironed linen), green
20b R = 3,3,5-Trimethylcyclohexyl		**18b**	Leathery, burnt, green
20c R = 4-(*tert*-Butyl)cyclohexyl		**18c**	Costus, musky

Scheme 9

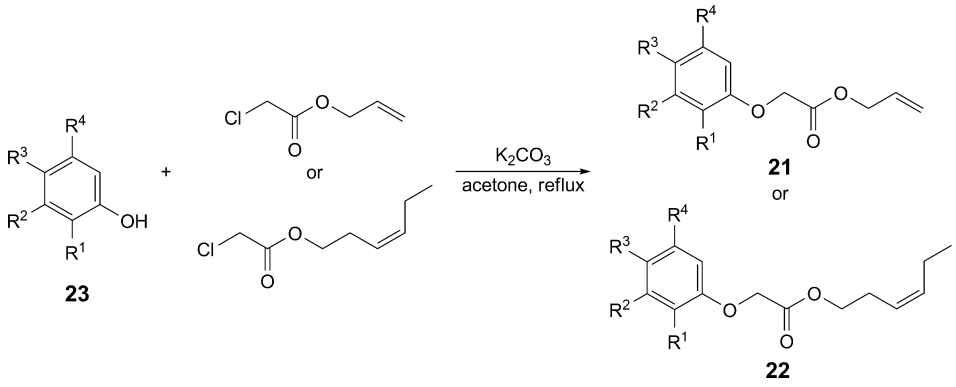
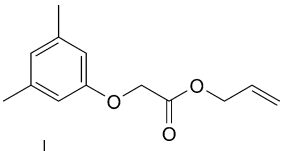
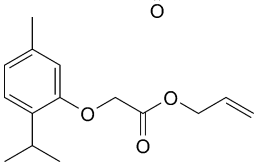
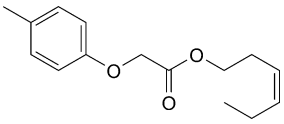
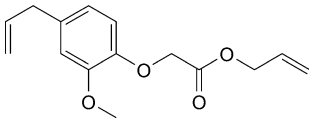
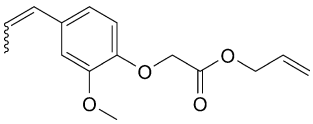
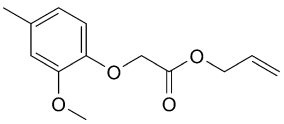
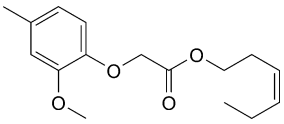
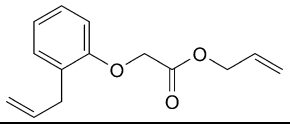


Table 10. *Odor Descriptions of the Glycolate Derivatives* **21** *and* **22** (*Scheme 9*)

Starting Phenol	Product		Odor
23a $R^1=R^3=H$; $R^2=R^4=Me$		**21a**	Musky, hot iron, not powerful
23b $R^1={}^{i}Pr$; $R^2=R^3=H$; $R^4=Me$		**21b**	Costus
23c $R^1=R^2=R^4=H$; $R^3=Me$		**22c**	Animal, leathery
23d $R^1=MeO$; $R^2=R^4=H$; $R^3=$allyl		**21d**	Eugenol, carnation-type, woody
23e $R^1=MeO$; $R^2=R^4=H$; $R^3=$prop-2-enyl		**21e**	Spicy (isoeugenol), leathery, carnation, saffron, fruity (plums, dried plums), woody (vetiver), sweet
23f $R^1=MeO$; $R^2=R^4=H$; $R^3=Me$		**21f**	Vanilla, spicy (isoeugenol)
23f		**22f**	Vanilla, smokey
23g $R^1=$allyl; $R^2=R^3=R^4=H$		**22g**	Vanilla, plastic

19a are far from galbanum-type odorants, but with a nice clean effect and an enhanced substantivity; their green notes are very interesting as such, in regard to (*Z*)-hex-3-en-1-ol. None of the (cyclohexyl)oxy or phenoxy derivatives exhibited the expected green or fruity odor. Further, nice spicy notes, with carnation or vanilla aspects, were found

for alkoxy- and/or allyl-substituted phenoxy compounds, whereas interesting animal notes, such as costus, leathery, and musky (the latter being, however, quite weak), were observed for alkyl-substituted cyclohexyl or phenoxy derivatives.

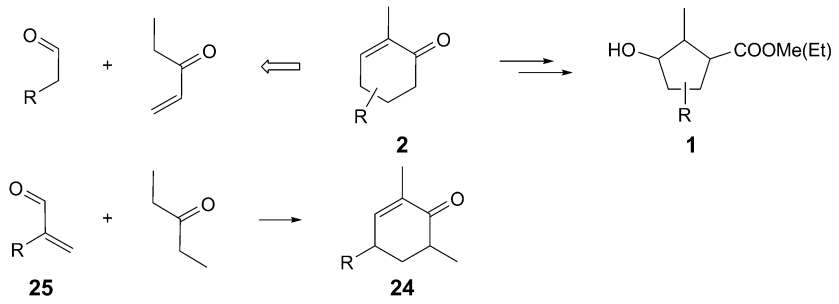
In the easily accessible glycolate family, different new molecules were synthesized in good yields, all showing interesting notes. The most interesting compound in the animalic family was the thymol-derived glycolate **21b**.

New Ambery Odorants. – Since we had an easy access to cyclopentanols **1** from α-methylcyclohex-2-enones **2** (see above), we had a look at other starting materials. We first prepared new compounds **2** from aldehydes and ethyl vinyl ketones (*Scheme 10*), but ethyl vinyl ketone is neither inexpensive, nor easy to prepare and handle. Then, we envisaged the reverse way and developed a method to prepare novel α-methylcyclohex-2-enones **24** from pentan-3-one and different methylidene aldehydes **25** [11].

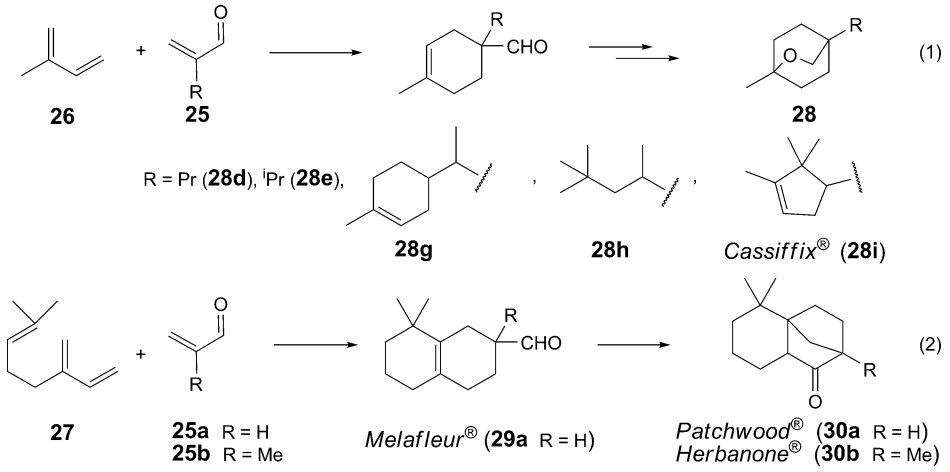
The chemistry of methylidene aldehydes is well-known and documented in the perfumery [12]; they are mostly used in *Diels–Alder* reactions with isoprene (**26**) or myrcene (**27**) to access to very interesting molecules such as *Cassiffix*® (**28i**) [13], or *Melafleur*® (**29a**) [14] (*Scheme 11*). The *Diels–Alder* reactions with isoprene were carried out with high-molecular-weight methylidene aldehydes (*Reaction 1*), whereas, in the case of myrcene, the reactions were performed with the simplest ones: acrolein (**25a**) or methacrolein (**25b**; *Reaction 2*). Among the different structures prepared from pentanal, limonenal, *Vandor B*®, *etc.*, bicyclic ethers **28d**–**28i** were further obtained by reduction of the *Diels–Alder* adduct, followed by cyclization. *Cassiffix*® (**28i**), a compound with a nice substantive camphoraceous cassis note, was thus prepared from isoprene and methylidene-campholenaldehyde. The work on myrcene (**27**), leading to bicyclic and further tricyclic structures by acidic rearrangements, was aimed at molecules in the ambery family. However, even with a nice intense green fruity scent, *Melafleur* (**29a**; from acrolein) is neither woody nor ambery. Of the further cyclized compounds, neither *Patchwood* (**30a**) [14] nor *Herbanone* (**30b**) [14][15], obtained from acrolein and methacrolein, respectively, showed the desired ambery character. They are described as woody, camphoraceous.

We prepared several methylidene aldehydes **25** [11] and applied our tandem *Michael*–aldol reaction to the corresponding cyclohexenones **24** in good yields. The

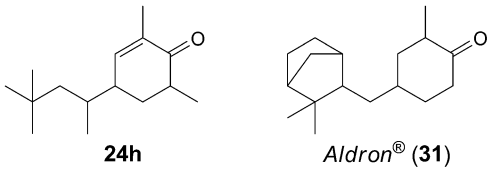
Scheme 10



Scheme 11



compounds obtained had interesting odors with citrus-aldehydic or woody notes, however, no real animalic ones. Only compound **24h**, obtained from *Vandor B*®, could be considered in that direction with sweaty, urinous aspects. As *Aldron*® (**31**) is concerned, it was controversial, some perfumers were really disgusted by the powerful note, whereas others perceived it very light, dry, woody, and somehow ambery.



With many different methylidene aldehydes in hand, we were interested again in the work of *Sprecker* and co-workers [14], since some derivatives were not examplified, and the structures are still appealing as potential ambery notes, even if *Patchwood* and *Herbanone* are not ambery. Contrary to the work we have performed with pentan-3-one [11], we mainly focused on the smallest aldehydes **25a**–**25f** (*Scheme 12* and *Table 11*) [16].

Scheme 12

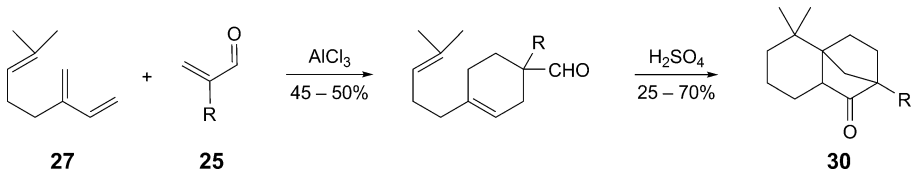
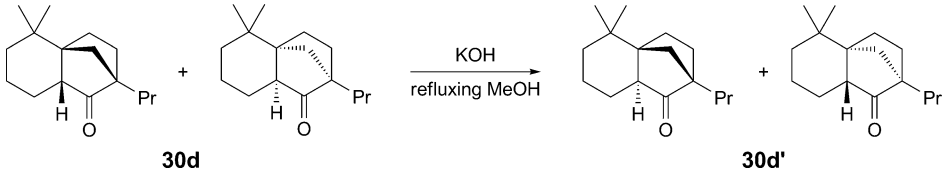


Table 11. *Preparation and Odor Description of Tricyclic Ketones* **30** (*Scheme 12*)

Aldehyde	R	Compound	Yield (two steps) [%]	Odor
25a	H	**30a**	40 (one step from myrac aldehyde)	Camphoraceous, aromatic
25b	Me	**30b**	16	Camphoraceous, aqueous, woody, fatty
25c	Et	**30c**	12	Camphoraceous, slightly ambery, weak
25d	Pr	**30d**	35	Ambery, woody
25e	^{i}Pr	**30e**	38	Woody, dry, weak
25f	Bu	**30f**	13	Weak, fatty

We prepared derivatives **30** including *Patchwood* (**30a**) and *Herbanone* (**30b**) (for comparison). Actually, being heavier, the new compounds exhibited less and less camphoraceous aspects, and the Pr derivative **30d** turned out to be a nice ambery odorant. Obtained as a racemate in *cis*-decaline configuration (confirmed by X-ray crystallography), we also prepared the *trans*-decaline racemate **30d′** by heating **30d** in MeOH in the presence of KOH (*Scheme 13*). Compound **30d′** exhibited, however, a less powerful odor than the *cis* isomer.

Scheme 13



30d **30d'**

On the route to original cyclohexenones and their derivatives, we prepared new bridged tricyclic compounds *via* a *Diels–Alder* reaction, followed by cyclization. A novel ambery odorant **30d** with subtle fruity undertones was thus discovered, easily synthesized in good yields from inexpensive and available myrcene and 2-methylidenepentanal (**25d**).

In conclusion, new interesting structures were found in the leathery-animal family while working on completely different topics. It was all the more fascinating as some of the structures were designed to be green, pineapple odorants. We discovered **11a***, a bicyclic cyclopentanol, **21b**, a thymol-derived glycolate, and **30d**, a tricyclic ketone. All the new derivatives were prepared in good yields *via* simple steps, from inexpensive and readily available starting materials. Finally, it allowed us to add a fine ambery compound, filling a gap in our captives portfolio.

Experimental Part

General. All the reagents and solvents were commercially available, and were used without any further purification, unless otherwise mentioned. Spectral data of compounds **1a**, **3a**, **4**–**6**, and **1a***, **3a***, **4***–**6***, prepared from *(+)-(*S*)-carvone* (**2**) and *(−)-(*R*)-carvone* (**2***), resp., have already been reported [3][4]. GC: *HP 6890* with a polar *DBWAX-FF* column. Optical rotations: *Bellingham+ ADP 220*. IR Spectra: *Nicolet iS5 ATR* diamond spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker* 200-MHz or *Fourier*

300 instrument; in $CDCl_3$; δ in ppm rel. to Me_4Si as internal standard; *J* in Hz. MS: *Agilent 5975 MSD* quadrupole EI spectrometer; in *m*/*z*.

*Ethyl (1*R,*2*S,*3*R,*5*R*)-2-Methyl-5-(prop-1-en-2-yl)-3-(tetrahydro-2*H*-pyran-2-yloxy)cyclopentanecarboxylate* (**3b***). To a freshly prepared 2.25M EtONa soln. (52 g, (2.26 mol) of Na in 1 l of abs. EtOH) was added dropwise at 10° chlorhydrin **6*** (637 g, 2.22 mol; prepared from **2***). After completion of the reaction (monitored by GC), the mixture was poured onto 1 l H_2O/^{t}BuOMe 1:1 soln. The aq. phase was extracted three times with ^{t}BuOMe (200 ml), and the combined org. layers were washed with a sat. aq. $NaHCO_3$ soln. (250 ml) and brine (250 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude oil was purified by distillation to give THP derivative **3b*** as a 53:47 ratio of diastereoisomers (482 g, 45% over the 4 steps). B.p. 135°/1.3 Torr. Major isomer: ^{1}H-NMR (200 MHz): 1.05 (*d*, *J* = 7, 3 H); 1.14 (*t*, *J* = 7.2, 3 H); 1.25–1.59 (*m*, 4 H); 1.67 (*s*, 3 H); 1.60–1.87 (*m*, 3 H); 1.93 (*dd*, *J* = 2.81, *J* = 8.81, 1 H); 2.37–2.63 (*m*, 1 H); 2.63–2.84 (*m*, 1 H); 2.94–3.28 (*m*, 1 H); 3.36–3.52 (*m*, 1 H); 3.73–3.89 (*m*, 1 H); 3.89–4.10 (*m*, 2 H); 4.10–4.21 (*m*, 1 H); 4.48–4.58 (*m*, 1 H); 4.64 (*s*, 1 H); 4.70 (*s*, 1 H). MS: 296 (< 1, M^+), 195 (10), 194 (14), 149 (11), 121 (51), 85 (100), 67 (10), 41 (10). Minor isomer: ^{1}H-NMR (200 MHz, selected data): 0.94 (*d*, *J* = 7.0, 3 H); 3.89–4.10 (*m*, 1 H); 4.58–4.68 (*m*, 1 H). MS: 296 (< 1, M^+), 194 (20), 149 (12), 121 (64), 85 (100), 67 (12), 41 (12).

*Ethyl (1*S,*2*R,*3*S,*5*S*)-2-Methyl-5-(prop-1-en-2-yl)-3-(tetrahydro-2*H*-pyran-2-yloxy)cyclopentanecarboxylate* (**3b**). Starting from **2**, **3b** was obtained in 33% yield over the 4 steps as a 58:42 ratio of diastereoisomers, as described for **3b***. Major isomer: ^{1}H-NMR (200 MHz): 1.05 (*d*, *J* = 6.9, 3 H); 1.14 (*t*, *J* = 7.2, 3 H); 1.30–1.60 (*m*, 4 H); 1.67 (*s*, 3 H); 1.61–1.89 (*m*, 3 H); 1.94 (*dd*, *J* = 3.0, 9.0, 1 H); 2.30–2.63 (*m*, 1 H); 2.63–2.90 (*m*, 1 H); 2.90–3.32 (*m*, 1 H); 3.36–3.52 (*m*, 1 H); 3.74–3.90 (*m*, 1 H); 3.90–4.12 (*m*, 2 H); 4.12–4.23 (*m*, 1 H); 4.50–4.59 (*m*, 1 H); 4.64 (*s*, 1 H); 4.70 (*s*, 1 H). MS: 296 (< 1, M^+), 194 (18), 121 (52), 85 (100), 67 (12), 41 (12). Minor isomer: ^{1}H-NMR (200 MHz; selected data): 0.95 (*d*, *J* = 7.0, 3 H); 3.90–4.11 (*m*, 1 H); 4.58–4.70 (*m*, 1 H). MS: 296 (< 1, M^+), 194 (17), 149 (11), 121 (64), 85 (100), 67 (12), 41 (14).

*Ethyl (1*R,*2*S,*3*R,*5*R*)-3-Hydroxy-2-methyl-5-(prop-1-en-2-yl)cyclopentanecarboxylate* (**1b***). A soln. of **3b*** (20 g, 67.5 mmol) in MeOH (35 ml) with cat. amount of PPTS (0.1 g, 0.5 wt-%) was heated under reflux until completion of the reaction (monitored by GC). The mixture was poured into H_2O/^{t}BuOMe 1:1 (50 ml), and the aq. phase was extracted once with ^{t}BuOMe (15 ml). The combined org. layers were washed with a sat. aq. $NaHCO_3$ soln. (15 ml) and brine (15 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude oil was purified by distillation to give **1b*** (11.4 g, 73%). B.p. 97°/1 Torr. IR: 889*m*, 1014*m*, 1030*m*, 1138*m*, 1176*s*, 1375*m*, 1713*m*, 1728*m*, 2936*w*, 2967*w*, 3447*w*. ^{1}H-NMR (200 MHz): 1.03 (*d*, *J* = 7, 3 H); 1.18 (*t*, *J* = 7.2, 3 H); 1.70 (*s*, 3 H); 1.66–1.89 (*m*, 1 H); 2.01 (*ddd*, *J* = 4.2, *J* = 11.0, 14.8, 1 H); 2.35–2.55 (*m*, 1 H); 2.77 (*dd*, *J* = 8.6, 10.2, 1 H); 3.20 (*td*, *J* = 7.2, 10.4, 1 H); 4.02 (*qd*, *J* = 3.6, 7.2, 2 H); 4.16–4.28 (*m*, 1 H); 4.68 (*s*, 1 H); 4.75 (*s*, 1 H). ^{13}C-NMR (50 MHz): 13.55; 14.12; 22.58; 39.32; 42.39; 46.57; 52.90; 60.05; 74.92; 111.39; 145.0; 174.49. MS: 212 (1, M^+), 122 (10), 121 (100), 120 (19), 115 (21), 105 (14), 95 (10), 93 (14), 87 (26), 79 (12), 69 (14), 41 (13). Odor description: Lactonic, powdery, musky, weak.

*Methyl (1*S,*2*R,*3*S,*5*S*)-3-Acetoxy-2-methyl-5-(prop-1-en-2-yl)cyclopentanecarboxylate* (**7a**). Alcohol **1a** (33.6 g, 171 mmol) was heated with Ac_2O (100 g, 980 mmol) and cat. amount of DMAP. AcOH and excess Ac_2O were removed from the mixture. After cooling, the mixture was poured into H_2O/^{t}BuOMe (1:1; 150 ml), and the org. phase was washed with a sat. aq. $NaHCO_3$ soln. (4 × 50 ml) and brine (50 ml), dried ($MgSO_4$), filtered, and concentrated *in vacuo*. The crude oil was purified by distillation to give **7a** (27.3 g, 67%). B.p. 90°/0.4 Torr. IR: 891*m*, 993*m*, 1018*s*, 1142*m*, 1171*s*, 1193*s*, 1237*s*, 1371*m*, 1435*m*, 1732*s*, 2950*w*, 2970*w*. ^{1}H-NMR (300 MHz): 0.97 (*d*, *J* = 7.0, 3 H); 1.71 (*m*, 3 H); 1.81–1.90 (*m*, 1 H); 2.01–2.17 (*m*, 1 H); 2.03 (*s*, 3 H); 2.57–2.71 (*m*, 1 H); 2.82 (*dd*, *J* = 8.9, 9.2, 1 H); 3.05–3.17 (*m*, 1 H); 3.59 (*s*, 3 H); 4.66–4.69 (*m*, 1 H); 4.77–4.80 (*m*, 1 H); 5.30 (br. *t*, *J* = 4.9, 1 H). ^{13}C-NMR (75 MHz): 13.78; 21.02; 22.36; 36.87; 41.01; 46.67; 51.29; 53.70; 77.58; 111.64; 144.49; 170.54; 174.29. MS: 180 (9), 122 (10), 121 (100), 120 (13), 105 (19), 93 (13), 91 (10), 79 (11), 43 (23). Odor description: Very weak.

*Methyl (1*R,*2*S,*3*R,*5*R*)-3-Acetoxy-2-methyl-5-(prop-1-en-2-yl)cyclopentanecarboxylate* (**7a***). A soln. of **1a*** (19 g, 96 mmol) and Et_3N (11.6 g, 115 mmol) in ^{t}BuOMe (100 ml) was cooled to 5°, and AcCl (9 g, 115 mmol) in ^{t}BuOMe (20 ml) was added dropwise. The mixture was further stirred to r.t. for 14 h and then poured into a cold 10% aq. HCl soln. (100 ml). The separated org. phase was washed with

sat. aq. $NaHCO_3$ (50 ml) and twice with brine (50 ml), dried ($MgSO_4$), filtered, and the solvents were evaporated. The crude product was purified by distillation to give **7a*** (10.4 g, 45%). B.p. 80°/0.15 Torr. IR: 891*m*, 993*m*, 1017*s*, 1142*m*, 1171*s*, 1193*s*, 1237*s*, 1371*m*, 1435*m*, 1732*s*, 2950*w*, 2970*w*. ^{1}H-NMR (300 MHz): 0.97 (*d*, *J* = 7.0, 3 H); 1.71 (*m*, 3 H); 1.82–1.91 (*m*, 1 H); 2.01–2.18 (*m*, 1 H); 2.04 (*s*, 3 H); 2.58–2.71 (*m*, 1 H); 2.82 (*dd*, *J* = 8.3, 9.9, 1 H); 3.11 (*td*, *J* = 7.1, 10.2, 1 H); 3.59 (*s*, 3 H); 4.67–4.70 (*m*, 1 H); 4.77–4.81 (*m*, 1 H); 5.30 (br. *t*, *J* = 4.9, 1 H). ^{13}C-NMR (75 MHz): 13.80; 21.04; 22.37; 36.89; 41.03; 46.68; 51.31; 53.71; 77.61; 111.65; 144.50; 170.57; 174.32. MS: 180 (9), 122 (11), 121 (100), 120 (14), 105 (17), 93 (12), 79 (10), 43 (24). Odor description: spearmint, carvone, chlorophylle, 'cédrat confit'.

*Methyl (1*S*,2*R*,5*S*)-2-Methyl-3-oxo-5-(prop-1-en-2-yl)cyclopentanecarboxylate* (**8a**). Compound **3a** (80 g, 283 mmol) was deprotected as described for **1a*** to give crude **1a** quantitatively. To a suspension of PDC (69 g, 182 mmol) and silica gel (60 g) in CH_2Cl_2 (200 ml) was added a soln. of **1a** (30 g, 151 mmol) in CH_2Cl_2 (50 ml). The mixture was further stirred overnight and filtered over a pad of *Clarcel*®. The org. soln. was washed with a 10% aq. $Na_2S_2O_3$ soln. and with brine, and dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The crude oil was purified by distillation to give **8a** (14.4 g, 49%), which was crystalline and could be crystallized from hexane. M.p. 65°. B.p. 75°/0.5 Torr. IR: 869*m*, 892*s*, 1043*m*, 1071*m*, 1156*s*, 1175*s*, 1238*m*, 1375*m*, 1443*m*, 1723*s*, 2875*w*, 2919*w*, 2952*w*, 2969*w*, 2981*w*. ^{1}H-NMR (200 MHz): 1.14 (*d*, *J* = 7.4, 3); 1.76 (*s*, 3 H); 2.36 (*dd*, *J* = 8.1, 18.3, 1 H); 2.64 (*ddd*, *J* = 1.6, 7.7, 18.3, 1 H); 2.65–2.83 (*m*, 1 H); 3.01 (*dd*, *J* = 6.1, 7.3, 1 H); 3.19 (*q*, *J* = 7.7, 1 H); 3.65 (*s*, 3 H); 4.71–4.74 (*m*, 1 H); 4.84–4.89 (*m*, 1 H). ^{13}C-NMR (50 MHz): 15.16; 21.77; 41.18; 43.18; 45.20; 51.60; 52.68; 112.32; 143.48; 173.04; 218.31. MS: 196 (25, M^+), 137 (51), 136 (18), 128 (15), 127 (18), 12), 109 (24), 108 (14), 101 (21), 100 (14), 96 (43), 95 (54), 94 (12), 93 (37), 91 (14), 85 (17), 81 (12), 79 (24), 77 (18), 69 (83), 68 (100), 67 (76), 65 (12), 59 (13), 55 (15), 53 (27), 41 (38), 39 (31). Odor description: very weak.

*Methyl (1*R*,2*S*,5*R*)-2-Methyl-3-oxo-5-(prop-1-en-2-yl)cyclopentanecarboxylate* (**8a***). Obtained from **1a*** (35 g, 176 mmol) as described for **8a**. Recrystallization from hexane (40% yield). M.p. 65°. ^{1}H-NMR (200 MHz): 1.08 (*d*, *J* = 7.4, 3 H); 1.70 (*s*, 3 H); 2.30 (*dd*, *J* = 8.1, 18.3, 1 H); 2.57 (*ddd*, *J* = 1.6, 7.7, 18.3, 1 H); 2.62–2.76 (*m*, 1 H); 2.96 (*dd*, *J* = 6.1, 7.3, 1 H); 3.14 (*q*, *J* = 7.7, 1 H); 3.59 (*s*, 3 H); 4.64–4.69 (*m*, 1 H); 4.77–4.83 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.99; 21.63; 41.03; 43.04; 45.04; 51.42; 52.50; 112.13; 143.40; 172.90; 218.05. Odor description: weak.

*[(1*R*,2*S*,3*R*,5*R*)-2-Methyl-5-(prop-1-en-2-yl)-3-(tetrahydro-2*H*-pyran-2-yloxy)cyclopentyl]methanol* (**9***). To a soln. of **3a*** (100 g, 0.337 mol) [3] in toluene (150 ml) was added dropwise at r.t. a 1M soln. of DIBAl-H in toluene (680 ml, 0.680 mol). After completion of the reaction (followed by GC), the mixture was poured into ice/AcOH (800 g/120 g). The aq. phase (pH 5–6) was extracted three times with toluene (150 ml), and the combined org. layers were washed with a sat. aq. $NaHCO_3$ soln. (200 ml) and then with brine (200 ml). The org. phase was dried ($MgSO_4$), filtered, and evaporated *in vacuo* to give crude **9*** (96% purity) as a 50:50 mixture of diastereoisomers (72.4 g, 81%).

*[(1*R*,2*S*,3*R*,5*R*)-3-Hydroxy-2-methyl-5-(prop-1-en-2-yl)cyclopentyl]methyl Acetate* (**10***). Alcohol **9*** was converted to its acetate as described for **7a**, and **10*** was obtained after removal of the THP group as described for **1b***. Yield: 30% over five steps from **5***. B.p. 85°/0.04 Torr. IR: 555*m*, 606*m*, 888*m*, 970*m*, 1030*s*, 1085*w*, 1231*s*, 1367*m*, 1452*w*, 1646*w*, 1716*m*, 1738*s*, 2937*w*, 2961*w*, 3436*w*. ^{1}H-NMR (300 MHz): 1.05 (*d*, *J* = 7.1, 3 H); 1.73 (*s*, 3 H); 1.79–1.88 (*m*, 2 H); 1.98 (*s*, 3 H); 2.04–2.15 (*m*, 2 H); 2.95–3.06 (*m*, 1 H); 3.78 (*dd*, *J* = 7.4, 11.0, 1 H); 3.92 (*dd*, *J* = 6.5, 11.1, 1 H); 4.15 (br. *t*, *J* = 4.1, 1 H); 4.63–4.66 (*m*, 1 H); 4.77–4.81 (*m*, 1 H). ^{13}C-NMR (75 MHz): 14.13; 20.81; 23.60; 38.68; 42.81; 44.11; 44.62; 65.85; 74.24; 110.80; 144.55; 171.21. MS: 152 (23), 137 (17), 134 (47), 123 (14), 121 (59), 120 (10), 119 (100), 114 (20), 109 (23), 107 (16), 106 (12), 105 (25), 99 (13), 95 (26), 94 (13), 93 (45), 92 (16), 91 (45), 83 (40), 82 (10), 81 (38), 79 (41), 77 (26), 72 (10), 71 (22), 70 (12), 69 (28), 68 (16), 67 (30), 65 (10), 55 (41), 53 (19), 43 (100), 41 (31), 39 (20). Odor description: carnation, eugenol, weak.

*(3a*S*,4*S*,5*R*,6a*R*)-Hexahydro-1,1,4-trimethyl-1*H*-cyclopenta[*c*]furan-5-ol* (**11a***). A mixture of **9*** (72.4 g, 0.284 mol), PPTS (1.5 g, 2 wt-%) and MeOH (67 g, 2.1 mol) in toluene (150 ml) was heated to 60°, and the conversion was monitored by GC. After 2 h, TfOH was added (0.38 g, 0.5% (*w*/*w*)), and the mixture was further stirred at 80°. After completion of the reaction (GC), the mixture was poured into a sat. aq. $NaHCO_3$ soln. (100 ml). The aq. phase was extracted twice with toluene (50 ml), and the combined org. layers were washed with brine (50 ml), dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The residue was purified by distillation to give **11a*** (21 g, 43%). B.p. 123°/0.9 Torr. $[\alpha]_D = -67.6$. IR:

1134*m*, 1180–1237*m*, 2870*m*, 2929*m*, 2967*m*, 3425*w*. ^{1}H-NMR (200 MHz): 1.01 (*d*, *J* = 7, 3 H); 1.13 (*s*, 3 H); 1.19 (*s*, 3 H); 1.53–1.85 (*m*, 3 H); 2.40 (*m*, 1 H); 2.59 (*td*, *J* = 8.4, 9.2, 1 H); 3.51 (*dd*, *J* = 2.4, 9.15, 1 H); 3.88 (*dd*, *J* = 7.2, 9.1, 1 H); 4.08–4.17 (*m*, 1 H). ^{13}C-NMR (50 MHz): 13.72; 23.78; 26.68; 36.52; 46.67; 50.13; 51.43; 70.64; 77.97; 81.43. MS: 170 (< 1, M^+), 155 (100), 109 (17), 95 (29), 71 (21), 67 (16), 59 (31), 57 (17), 55 (22), 43 (48), 41 (20). Odor description: leathery, animal, phenolic, indolic, smokey.

*(3a*R*,4*R*,5*S*,6a*S*)-1,1,4-Trimethylhexahydro-1*H*-cyclopenta[*c*]furan-5-ol* (**11a**). Obtained in 24% yield over six steps from **2** *via* **3**, as described for **11a***. B.p. 70°/0.06 Torr. $[\alpha]_D = +61.9$. IR: 917*m*, 964*m*, 998*m*, 1018*m*, 1035*m*, 1058*m*, 1134*m*, 1365*m*, 2870*w*, 2929*m*, 2966*m*, 3419*w*. ^{1}H-NMR (200 MHz): 1.02 (*d*, *J* = 7, 3 H); 1.14 (*s*, 3 H); 1.20 (*s*, 3 H); 1.55–1.82 (*m*, 3 H); 2.42 (*m*, 1 H); 2.61 (*td*, *J* = 8.4, 9.2, 1 H); 3.53 (*dd*, *J* = 2.2, 9.2, 1 H); 3.90 (*dd*, *J* = 7.2, 9.1, 1 H); 4.13–4.20 (*m*, 1 H). ^{13}C-NMR (50 MHz): 13.74; 23.84; 26.72; 36.60; 46.71; 50.20; 51.50; 70.69; 78.16; 81.43. MS: 170 (< 1, M^+), 156 (10), 155 (100), 115 (10), 109 (16), 107 (19), 97 (13), 95 (31), 94 (13), 93 (12), 91 (12), 83 (12), 81 (10), 79 (30), 77 (12), 71 (21), 67 (20), 59 (33), 57 (16), 55 (21), 53 (11), 43 (47), 41 (18), 39 (13). Odor description: fishy, fish flesh.

*(3a*R*,4*R*,5*S*,6a*S*)-Hexahydro-1,1,3,3,4-pentamethyl-1*H*-cyclopenta[*c*]furan-5-ol* (**11b**). To a soln. of crude **3a** (40 g, 0.142 mol) in THF (150 ml) was added dropwise at 10° a 3M soln. of MeMgCl in THF (100ml). When the reaction was complete (GC), the mixture was poured into ice-cold ^{t}BuOMe/10% aq. HCl 1:1. The aq. phase was extracted twice with ^{t}BuOMe (100 ml), and the combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (100 ml), brine (100 ml) and dried ($MgSO_4$). The solvents were filtered and evaporated *in vacuo*. The residue was further cyclized as described for **11a*** to give **11b** (14.7 g, 36% over two steps). B.p 80°/0.05 Torr. IR: 830*m*, 890*m*, 978*s*, 1139*m*, 1262*m*, 1365*m*, 2931*w*, 2968*m*, 3420*w*. ^{1}H-NMR (200 MHz): 1.02 (*d*, *J* = 6.8, 3 H); 1.18 (*s*, 3 H); 1.20 (*s*, 3 H); 1.27 (*s*, 3 H); 1.29 (*s*, 3 H); 1.60–1.85 (*m*, 2 H); 1.92–2.08 (*m*, 1 H); 2.30 (*t*, *J* = 9.2, 1 H); 2.90 (*td*, *J* = 8.7, 9.2, 1 H); 4.19–4.27 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.45; 26.83; 27.20; 32.37; 33.08; 36.51; 40.84; 54.11; 60.51; 78.88; 80.51; 80.62. MS: 198 (< 1, M^+), 184 (13), 183 (100), 123 (53), 122 (25), 121 (21), 111 (12), 107 (68), 97 (28), 95 (14), 91 (16), 83 (12), 81 (28), 79 (18), 69 (16), 67 (16), 59 (10), 55 (22), 53 (10), 43 (59), 41 (23), 39 (10). Odor description: green, metallic, raw vegetables, earthy.

*(3a*S*,4*S*,5*R*,6a*R*)-Hexahydro-1,1,3,3,4-pentamethyl-1*H*-cyclopenta[*c*]furan-5-ol* (**11b***). Obtained from **3a*** in 51% yield over the two steps, as described for **11b**. B.p. 76°/0.06 Torr. IR: 831*m*, 889*m*, 977*m*, 1139*m*, 1262*w*, 1365*m*, 2930*w*, 2968*m*, 3406*w*. ^{1}H-NMR (200 MHz): 1.03 (*d*, *J* = 6.8, 3 H); 1.13 (*s*, 3 H); 1.21 (*s*, 3 H); 1.28 (*s*, 3 H); 1.30 (*s*, 3 H); 1.55–1.90 (*m*, 2 H); 1.94–2.11 (*m*, 1 H); 2.31 (*t*, *J* = 9.3, 1 H); 2.91 (*td*, *J* = 8.6, 9.2, 1 H); 4.21–4.28 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.45; 26.86; 27.23; 32.40; 33.12; 36.54; 40.87; 54.16; 60.57; 78.99; 80.53; 80.64. MS: 198 (< 1, M^+), 184 (13), 183 (100), 123 (48), 122 (24), 121 (20), 111 (10), 107 (68), 97 (26), 95 (13), 91 (16), 83 (11), 81 (26), 79 (17), 77 (10), 69 (14), 67 (16), 59 (10), 55 (18), 43 (51), 41 (21). Odor description: woody, leathery, sligthly honey, animal.

*(3a*S*,4*S*,5*R*,6a*R*)-3,3-Diethylhexahydro-1,1,4-trimethyl-1*H*-cyclopenta[*c*]furan-5-ol* (**11c***). Obtained from **3a*** and EtMgCl as described for **11b**. B.p. 90°/0.02 Torr. IR: 982*m*, 1048*w*, 1142*m*, 1456*w*, 2878*w*, 2937*m*, 2965*m*, 3409*w*. ^{1}H-NMR (200 MHz): 0.78 (*t*, *J* = 7.4, 3 H); 0.75 (*t*, *J* = 7.3, 3 H); 0.99 (*d*, *J* = 6.8, 3 H); 1.09 (*s*, 3 H); 1.21 (*s*, 3 H); 1.36–1.77 (*m*, 7 H); 2.35 (*t*, *J* = 9.9, 1 H); 2.83 (*td*, *J* = 8.6, 9.9, 1 H); 4.18–4.27 (*m*, 1 H). ^{13}C-NMR (50 MHz): 8.69; 8.71; 14.57; 27.08; 27.78; 32.21; 32.61; 36.24; 39.75; 54.06; 58.93; 79.45; 80.11; 85.36. MS: 226 (< 1, M^+), 198 (12), 197 (100), 123 (67), 122 (22), 121 (32), 107 (42), 97 (16), 95 (13), 91 (15), 81 (27), 79 (16), 77 (11), 69 (15), 67 (11), 57 (84), 55 (17), 43 (19), 41 (18). Odor description: marine, oyster, weak.

*(3a*R*,5*R*,6*S*,6a*S*)-Hexahydro-3,3,6-trimethylspiro[cyclopenta[*c*]furan-1,1′-cyclopropan]-5-ol* (**11d***). To a soln. of **3a*** (103 g, 0.365 mol) in Et_2O (300 ml) was added (^{i}PrO)$_4$Ti (10.3 g, 0.036 mol). After stirring for 10 min, a 25 wt-% EtMgCl soln. in Et_2O (270 ml, 0.767 mol) was added dropwise at 10°. After completion of the (GC), conc. H_2SO_4 (37 g, 0.377 mol) was added carefully. The org. phase was washed with sat. aq. $NaHCO_3$ soln. (100 ml) and brine (100 ml), and dried ($MgSO_4$). The solvents were filtered and evaporated *in vacuo*. The residue was further cyclized as described for **11a*** to give **11d*** (10.3 g, 10%). B.p. 66°/0.02 Torr. IR: 835*m*, 865*m*, 902*m*, 970*s*, 1002*m*, 1136*m*, 1170*m*, 1191*m*, 1266*w*, 1365*w*, 1455*w*, 2874*w*, 2929*w*, 2968*w*, 3426*w*. ^{1}H-NMR (200 MHz): 0.46–0.90 (*m*, 4 H); 0.95 (*d*, *J* = 7.0, 3 H); 1.20 (*s*, 3 H); 1.32 (*s*, 3 H); 1.68–1.77 (*m*, 2 H); 1.90–2.09 (*m*, 1 H); 2.19 (*dd*, *J* = 7.4, 9.0, 1 H); 2.85 (*q*, *J* = 9.0, 1 H); 4.19 (br. *q*, *J* = 3.1, 1 H). ^{13}C-NMR (50 MHz): 4.47; 14.54; 16.52; 23.77; 28.21; 36.39;

45.04; 53.71; 54.07; 65.56; 77.99; 81.54. MS: 196 (8, M^+), 181 (10), 167 (16), 163 (11), 153 (14), 152 (44), 139 (32), 137 (48), 128 (24), 127 (19), 126 (10), 125 (80), 124 (12), 123 (36), 122 (39), 121 (49), 111 (26), 110 (12), 109 (33), 108 (14), 107 (100), 105 (27), 99 (16), 98 (22), 97 (79), 96 (20), 95 (42), 93 (33), 91 (39), 83 (32), 82 (13), 81 (72), 80 (14), 79 (59), 77 (35), 71 (20), 70 (27), 69 (68), 67 (37), 65 (15), 59 (16), 57 (56), 56 (19), 55 (61), 53 (27), 43 (70), 41 (61), 39 (28). Odor description: spicy, pepper, a bit carvone, weak.

*(3a*R*,4R,5*S*,6a*S*)-Hexahydro-1,1,4-trimethyl-1*H*-cyclopenta[*c*]furan-5-yl Acetate* (**12a**). Obtained in 71% yield from **11a** as described for **7a**. B.p. 60°/0.04 Torr. IR: 843*w*, 961*m*, 969*m*, 996*m*, 1019*s*, 1043*m*, 1059*m*, 1138*m*, 1172*m*, 1237*s*, 1366*m*, 1734*s*, 2873*w*, 2933*w*, 2968*w*. ^{1}H-NMR (300 MHz): 0.94 (*d*, *J* = 6.9, 3 H); 1.14 (*s*, 3 H); 1.19 (*s*, 3 H); 1.64–1.92 (*m*, 3 H); 2.01 (*s*, 3 H); 2.37–2.58 (*m*, 2 H); 3.53 (*dd*, *J* = 2.2, 9.2, 1 H); 3.88 (*dd*, *J* = 7.0, 9.2, 1 H); 5.14–5.20 (*m*, 1 H). ^{13}C-NMR (75 MHz): 13.92; 21.07; 23.71; 26.56; 34.17; 45.22; 50.77; 51.33; 70.52; 81.0; 81.31. MS: 212 (< 1, M^+), 198 (11), 197 (100), 155 (15), 154 (11), 137 (16), 109 (11), 107 (30), 95 (46), 94 (61), 93 (16), 91 (18), 79 (62), 77 (15), 67 (14), 55 (18), 43 (90), 41 (17), 39 (10). Odor description: slightly plastic, weak.

*(3a*S*,4*S*,5*R*,6a*R*)-Hexahydro-1,1,4-trimethyl-1*H*-cyclopenta[*c*]furan-5-yl Acetate* (**12a***). Obtained from **11a*** as described for **7a** in 24% yield over six steps from **5b**. B.p. 60°/0.04 Torr. IR: 843*w*, 961*m*, 969*m*, 996*m*, 1019*s*, 1043*m*, 1059*m*, 1138*m*, 1172*m*, 1237*s*, 1366*m*, 1734*s*, 2873*w*, 2933*w*, 2968*w*. ^{1}H-NMR (300 MHz): 0.96 (*d*, *J* = 6.9, 3 H); 1.15 (*s*, 3 H); 1.20 (*s*, 3 H); 1.65–1.93 (*m*, 3 H); 2.03 (*s*, 3 H); 2.38–2.60 (*m*, 2 H); 3.54 (*dd*, *J* = 2.2, 9.2, 1 H); 3.90 (*dd*, *J* = 7.2, 9.2, 1 H); 5.15–5.21 (*m*, 1 H). ^{13}C-NMR (75 MHz): 13.94; 21.10; 23.73; 26.58; 34.19; 45.24; 50.79; 51.35; 70.54; 81.04; 81.34. MS: 212 (< 1, M^+), 198 (12), 197 (100), 155 (15), 154 (10), 137 (17), 109 (11), 107 (33), 95 (47), 94 (64), 93 (17), 91 (19), 81 (10), 79 (65), 77 (16), 67 (13), 55 (19), 43 (93), 41 (17), 39 (10). Odor description: woody, vetiver, weak.

*(3a*S*,4*S*,5*R*,6a*R*)-Hexahydro-1,1,3,3,4-pentamethyl-1*H*-cyclopenta[*c*]furan-5-yl Acetate* (**12b***). Obtained in 59% yield from **11b*** as described for **7a**. B.p. 65°/0.05 Torr. IR: 832*w*, 987*s*, 1017*m*, 1046*m*, 1142*m*, 1174*m*, 1186*m*, 1237*ss*, 1365*m*, 1735*s*, 2933*w*, 2970*m*. ^{1}H-NMR (200 MHz): 0.95 (*d*, *J* = 6.7, 3 H); 1.13 (*s*, 3 H); 1.21 (*s*, 3 H); 1.28 (*s*, 3 H); 1.30 (*s*, 3 H); 1.65–1.97 (*m*, 3 H); 2.04 (*s*, 3 H); 2.31 (*t*, *J* = 9.1, 1 H); 2.84 (*q*, *J* = 8.7, 1 H); 5.28 (*td*, *J* = 1.7, 4.7, 1 H). ^{13}C-NMR (50 MHz): 14.68; 21.10; 26.80; 27.15; 32.30; 32.97; 34.33; 39.58; 54.13; 61.34; 80.46; 80.59; 81.50. MS: 240 (< 1, M^+), 225 (32), 165 (27), 123 (41), 122 (32), 121 (17), 107 (100), 91 (17), 81 (10), 79 (14), 43 (46), 41 (10). Odor description: marine, aqueous, algae, weak.

*(3a*R*,6a*R*)-Tetrahydro-1,1,4-trimethyl-1*H*-cyclopenta[*c*]furan-5(3*H*)-one* (**13a***). A soln. of **8a*** (10 g, 50 mmol), ethylene glycol (30 g, 483 mmol), $HC(OEt)_3$ (14 g, 100 mmol) and a cat. amount of TsOH (0.1 g) was stirred at r.t. After completion of the reaction, the mixture was poured into H_2O/^{t}BuOMe 1:1 (100 ml). The org. layer was washed with a sat. aq. $NaHCO_3$ soln. (50 ml) and then with brine (50 ml). The org. phase was dried ($MgSO_4$), filtered, and evaporated *in vacuo*. The crude oil was further converted as described for **11a***, MeOH being replaced by acetone in the one-pot deprotection/cyclization step. Crude compound was purified by column chromatography (CC; SiO_2; AcOEt/hexane 10:90) to give pure **13a*** (3.7 g, 42%) as a 75:25 mixture of diastereoisomers. IR: 826*m*, 1038*m*, 1065*m*, 1170*m*, 1366*w*, 1737*s*, 2872*w*, 2933*w*, 2970*w*. Major isomer: ^{1}H-NMR (200 MHz): 1.07 (*d*, *J* = 7.3, 3 H); 1.16 (*s*, 3 H); 1.23 (*s*, 3 H); 2.14–2.24 (*m*, 1 H); 2.29–2.33 (*m*, 1 H); 2.35 (*s*, 1 H); 2.42–2.68 (*m*, 2 H); 3.63 (*dd*, *J* = 3.4, 9.2, 1 H); 4.03 (*dd*, *J* = 6.6, 9.3, 1 H). ^{13}C-NMR (50 MHz): 15.01; 24.71; 27.82; 39.17; 46.41; 47.43; 49.54; 70.19; 81.74; 220.7. MS: 168 (1, M^+), 153 (93), 111 (27), 110 (38), 95 (16), 82 (65), 81 (15), 68 (12), 67 (100), 59 (15), 55 (24), 53 (15), 43 (53), 41 (34), 39 (18). Minor isomer: ^{1}H-NMR (200 MHz): 1.01 (*d*, *J* = 7.2, 3 H); 1.20 (*s*, 3 H); 1.25 (*s*, 3 H); 1.96–2.01 (*m*, 1 H); 2.07–2.14 (*m*, 1 H); 2.42–2.68 (*m*, 2 H); 3.16–3.34 (*m*, 1 H); 3.49 (*dd*, *J* = 8.6, 9.3, 1 H); 3.91 (*t*, *J* = 9.1, 1 H). ^{13}C-NMR (50 MHz): 10.61; 24.17; 27.74; 37.87; 45.50; 46.73; 46.80; 66.54; 82.03; 221.1. MS: 168 (< 1, M^+), 154 (11), 153 (100), 111 (21), 110 (26), 95 (15), 82 (41), 81 (13), 67 (78), 59 (10), 55 (19), 53 (12), 43 (45), 41 (20), 39 (14). Odor description: musky, lactonic, powdery, weak.

Representative Procedure for the Synthesis of Alkyl Glycolates **18** *or* **19**: *Prop-2-enyl (3*Z*)-(Hex-3-enyloxy)-acetate* (**18a**). *Step 1.* (*Z*)-Hex-3-enol (50 g, 0.5 mol) was added dropwise to a suspension of NaH (21 g, 0.55 mol) in THF (500 ml), and the mixture was further stirred under reflux for 3 h. After cooling to r.t., $ClCH_2COONa$ (58 g, 0.5 mol) was added portionwise, and the mixture was further reacted under reflux overnight. It was then poured into H_2O/^{t}BuOMe 1:1 (500 ml), and the aq. phase was

acidified and extracted three times with *t*BuOMe (150 ml). The extracted layers were washed with H_2O and brine, and dried ($MgSO_4$). The solvents were evaporated to give crude (*3Z*)-(hex-3-enyloxy)acetic acid.

Step 2. A soln. of *(3Z)*-2-(hex-3-enyloxy)acetic acid in cyclohexane (300 ml) with a cat. amount of TsOH (0.5 g) was heated at 80°, and allyl alcohol (35 g, 0.6 mol) was added dropwise. After removal of the formed H_2O using a *Dean–Stark* apparatus, the soln. was cooled, washed with a sat. aq. $NaHCO_3$ soln. and with brine, and dried ($MgSO_4$). The solvents were evaporated, and the crude product was purified by distillation to give **18a** (48 g, 48%). B.p. 65°/0.67 Torr. IR: 723*w*, 930*w*, 993*w*, 1136*s*, 1197*s*, 1274*m*, 1429*w*, 1460*w*, 1738*m*, 1758*s*, 2876*m*, 2936*m*, 2965*m*, 3012*w*. ^{1}H-NMR (200 MHz): 0.95 (*t*, *J* = 7.5, 3 H); 1.94–2.13 (*m*, 2 H); 2.24–2.46 (*m*, 2 H); 3.53 (*t*, *J* = 7.1, 1 H); 4.06 (*s*, 2 H); 4.08–4.12 (*m*, 2 H); 4.14 (*t*, *J* = 7.0, 1 H); 5.15–5.37 (*m*, 3 H); 5.37–5.60 (*m*, 1 H); 5.79–6.02 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.13; 20.53; 26.63; 64.23; 67.04; 72.29; 118.10; 123.29; 133.69; 134.73; 170.34. MS: 198 (< 1, M^+), 82 (86), 71 (20), 67 (83), 55 (57), 41 (100), 39 (30). Odor description: green, cut grass, watery, clean (ironed linen), powerful.

(3Z)-Hex-3-enyl (3Z)-2-(Hex-3-enyloxy)acetate (**19a**). It was prepared as described for **18a** using (*Z*)-hex-3-enol in *Steps 1* and *2*. Yield: 36%. B.p. 107°/1.2 Torr. IR: 723*w*, 995*w*, 1045*w*, 1070*w*, 1137*s*, 1195*s*, 1283*m*, 1430*w*, 1461*w*, 1738*m*, 1758*s*, 2876*m*, 2935*m*, 2965*s*, 3012*m*. ^{1}H-NMR (200 MHz): 0.95 (*t*, *J* = 7.5, 6 H); 1.95–2.14 (*m*, 4 H); 2.26–2.46 (*m*, 4 H); 3.52 (*t*, *J* = 7.1, 2 H); 4.07 (*s*, 2 H); 4.14 (*t*, *J* = 7.0, 2 H); 5.20–5.60 (*m*, 4 H). ^{13}C-NMR (50 MHz): 14.18; 14.26; 20.55; 20.59; 26.65; 27.62; 64.21; 68.24; 71.40; 123.33; 124.27; 133.94; 134.73; 170.47. MS: 240 (< 1, M^+), 83 (44), 82 (90), 67 (74), 55 (100), 41 (46). Odor description: clean (ironed linen), green.

Prop-2-enyl 2-(3,3,5-Trimethylcyclohexyloxy)acetate (**18b**). It was prepared was described for **18a** using 3,3,5-trimethylcyclohexanol in *Step 1* (obtained from the reduction of isophorone) and allyl alcohol in *Step 2*. It consisted of a 93 : 7 *cis*/*trans* mixture. Yield: 53%. B.p. 93°/1.2 Torr. IR: 931*m*, 987*m*, 1129*s*, 1183*s*, 1193*s*, 1275*m*, 1365*w*, 1388*w*, 1430*w*, 1457*m*, 1738*m*, 1761*s*, 2838*w*, 2870*m*, 2914*m*, 2951*s*, 2992*w*. *cis*-Isomer: ^{1}H-NMR (200 MHz): 0.71–1.14 (*m*, 3 H); 0.85 (*d*, *J* = 6.4, 3 H); 0.85 (*s*, 3 H); 1.39 (*ddd*, *J* = 2.2, 5.2, 12.9, 1 H); 1.72 (*qd*, *J* = 2.3, 14.4, 1 H); 1.80–2.07 (*m*, 2 H); 3.71 (*quint*, *J* = 2.8, 1 H); 4.06 (*dd*, *J* = 16.4, 21.4, 2 H); 4.62 (*td*, *J* = 1.3, 5.7, 2 H); 5.18–5.38 (*m*, 2 H); 5.91 (*tdd*, *J* = 5.7, 10.3, 17.1, 1 H). ^{13}C-NMR (50 MHz): 22.99; 23.46; 27.67; 31.15; 34.47; 39.08; 40.72; 48.97; 65.64; 66.07; 76.63; 118.94; 132.25; 171.11. MS: 240 (< 1, M^+), 141 (81), 125 (18), 109 (35), 83 (91), 69 (86), 67 (26), 57 (23), 55 (55), 43 (23), 41 (100), 39 (26). *trans*-Isomer: ^{1}H-NMR (200 MHz, selected data): 1.46–1.63 (*m*, 1 H); 3.48 (*tt*, *J* = 4.3, 11.4, 1 H); 4.12 (*s*, 2 H). ^{13}C-NMR (50 MHz, selected data): 22.80; 26.13; 27.55; 33.54; 41.14; 44.92; 48.10; 65.73; 66.03; 76.98; 119.10. MS: 240 (< 1, M^+), 141 (58), 125 (24), 109 (22), 83 (73), 69 (100), 67 (18), 57 (25), 55 (48), 43 (19), 41 (80), 39 (19). Odor description: Costus, musky.

*Prop-2-enyl 2-(4-(*tert*-Butyl)cyclohexyloxy)acetate* (**18c**). It was prepared as described for **18a** using 4-(*tert*-butyl)cyclohexanol in *Step 1* and allyl alcohol in *Step 2*. Yield: 35%. B.p. 110°/0.8 Torr. It consisted of a 10 : 90 *cis*/*trans*-mixture. IR: 929*w*, 987*w*, 1133*s*, 1190*s*, 1276*w*, 1366*w*, 1451*w*, 1737*m*, 1760*s*, 2865*m*, 2946*s*. *trans*-Isomer: ^{1}H-NMR (200 MHz): 0.82 (*s*, 9 H); 0.88–1.10 (*m*, 3 H); 1.10–1.40 (*m*, 2 H); 1.70–1.87 (*m*, 2 H); 2.10–2.16 (*m*, 2 H); 3.24 (*tt*, *J* = 4.3, 10.9, 1 H); 4.13 (*s*, 2 H); 4.63 (*td*, *J* = 1.3, 5.8, 2 H); 5.19–5.37 (*m*, 2 H); 5.91 (*tdd*, *J* = 5.8, 10.3, 17.1, 1 H). ^{13}C-NMR (50 MHz): 25.47 (2 C); 27.55 (3 C); 32.23 (3 C); 47.23; 65.29; 65.49; 79.44; 118.63; 131.76; 170.65. MS: 254 (< 1, M^+), 155 (49), 83 (31), 81 (36), 67 (26), 57 (100), 55 (24), 41 (63). *cis*-Isomer: ^{1}H-NMR (200 MHz, selected data): 3.57–3.65 (*m*, 1 H); 4.08 (*s*, 2 H). ^{13}C-NMR (50 MHz, selected data): 21.29 (2 C); 27.45 (3 C); 30.27 (2 C); 47.88; 65.20; 65.55; 74.26; 118.51; 131.80. MS: 254 (< 1, M^+), 155 (48), 117 (21), 83 (29), 81 (44), 67 (44), 57 (100), 55 (28), 41 (71). Odor description: leathery, burnt, green.

Representative Procedure for the Synthesis of Phenoxyglycolates **21** *or* **22**: *Prop-2-enyl 2-(3,5-dimethylphenoxy)acetate* (**21a**). A soln. of 3,5-dimethylphenol (20 g, 163 mmol) in refluxing acetone (150 ml) was treated overnight with prop-2-enyl 2-chloroacetate (22 g, 163 mmol) and K_2CO_3 (22.5 g, 163 mmol). The mixture was then poured into H_2O/*t*BuOMe 1 : 1 (200 ml), and the aq. phase was extracted twice with *t*BuOMe (50 ml). The combined org. phases were washed with brine and dried ($MgSO_4$). The solvents were evaporated, and the crude product was purified by distillation to give **21a** (12.5 g, 35%). B.p. 93°/0.02 Torr. IR: 687*m*, 830*m*, 929*m*, 987*m*, 1032*w*, 1096*m*, 1157*s*, 1171*s*, 1200*s*, 1277*m*, 1299*m*, 1324*s*, 1383*w*, 1442*m*, 1473*m*, 1596*s*, 1615*m*, 1739*m*, 1764*s*, 2922*m*, 3020*w*. ^{1}H-NMR (200 MHz): 2.26 (*s*, 3 H); 2.29 (*s*, 3 H); 4.63 (*s*, 2 H); 4.71 (*td*, *J* = 1.2, 5.8, 2 H); 5.22–5.42 (*m*, 2 H); 5.94 (*tdd*, *J* = 5.8,

10.3, 17.0, 1 H); 6.55 (br. *s*, 2 H); 6.65 (br. *s*, 1 H). ^{13}C-NMR (50 MHz): 21.35; 65.20; 65.67; 112.34; 118.89; 123.48; 131.45; 139.26; 157.75; 168.75. MS: 220 (99, M^+), 135 (69), 105 (100), 103 (17), 91 (16), 79 (29), 77 (36), 41 (25), 39 (19). Odor description: musky, hot iron, not powerful.

Prop-2-enyl 2-(2-Isopropyl-5-methylphenoxy)acetate (**21b**). It was prepared from thymol as described for **21a**. Yield: 43%. B.p. 90°/0.03 Torr. IR: 813*m*, 932*m*, 986*m*, 1071*m*, 1102*m*, 1120*m*, 1167*s*, 1194*s*, 1279*m*, 1416*m*, 1445*m*, 1507*m*, 1614*w*, 1740*m*, 1765*s*, 2871*w*, 2962*m*. ^{1}H-NMR (200 MHz): 1.25 (*d*, J = 6.9, 6 H); 2.32 (*s*, 3 H); 3.40 (*sept.*, J = 6.9, 1 H); 4.68 (*s*, 2 H); 4.73 (*td*, J = 1.3, 5.8, 2 H); 5.22–5.42 (*m*, 2 H); 5.95 (*tdd*, J = 5.7, 10.4, 17.1, 1 H); 6.57 (br. *s*, 1 H); 6.81 (br. *d*, J = 7.7, 1 H); 7.14 (br. *d*, J = 7.7, 1 H). ^{13}C-NMR (50 MHz): 21.72; 23.22; 27.03; 66.07; 112.77; 119.21; 122.75; 126.71; 131.99; 135.02; 136.71; 155.39; 169.31. MS: 248 (100, M^+), 233 (68), 207 (18), 187 (12), 179 (23), 149 (59), 147 (22), 121 (53), 105 (50), 91 (42), 77 (21), 41 (62), 39 (30). Odor description: costus.

Hex-3-enyl 2-(4-Methylphenoxy)acetate (**22c**). It was prepared from *p*-cresol and (*Z*)-hex-3-enyl 2-chloroacetate as described for **21a**. Yield: 49%. B.p. 116°/0.2 Torr. IR: 724*m*, 818*m*, 996*m*, 1086*s*, 1191*s*, 1290*s*, 1391*w*, 1443*m*, 1458*m*, 1512*s*, 1589*w*, 1391*m*, 1737*s*, 1762*s*, 2874*m*, 2932*m*, 2964*s*, 3012*m*. ^{1}H-NMR (200 MHz): 0.97 (*t*, J = 7.5, 3 H); 2.05 (br. *quint.*, J = 7.6, 2 H); 2.29 (*s*, 3 H); 2.41 (br. *q*, J = 7.0, 2 H); 4.20 (*t*, J = 6.9, 2 H); 4.59 (*s*, 2 H); 5.21–5.37 (*m*, 1 H); 5.44–5.60 (*m*, 1 H); 6.76–6.85 (*m*, 2 H); 7.04–7.13 (*m*, 2 H). ^{13}C-NMR (50 MHz): 14.15; 20.42; 20.55; 26.61; 64.62; 65.52; 114.50 (2 C); 123.89; 129.92 (2 C); 130.96; 134.84; 155.71; 169.09. MS: 248 (38, M^+), 166 (100), 121 (35), 108 (14), 107 (12), 91 (54), 82 (22), 77 (14), 67 (36), 65 (21), 55 (35), 41 (28). Odor description: animal, leathery.

Prop-2-enyl 2-[4-(Prop-2-enyl)-2-methoxyphenoxy]acetate (**21d**). It was prepared from eugenol as described for **21a**. Yield: 39%. B.p. 110°/0.02 Torr. IR: 749*w*, 805*m*, 851*w*, 919*m*, 991*m*, 1036*s*, 1072*m*, 1148*s*, 1189*s*, 1262*s*, 1420*m*, 1464*m*, 1512*s*, 1593*m*, 1639*w*, 1738*s*, 1762*s*, 2836*w*, 2939*m*, 2977*w*, 3003*w*, 3079*w*. ^{1}H-NMR (200 MHz): 3.32 (br. *d*, J = 6.7, 2 H); 3.85 (*s*, 3 H); 4.64–4.70 (*m*, 2 H); 4.68 (*s*, 2 H); 5.00–5.05 (*m*, 1 H); 5.05–5.13 (*m*, 1 H); 5.19–5.37 (*m*, 2 H); 5.80–6.03 (*m*, 2 H); 6.64–6.80 (*m*, 3 H). ^{13}C-NMR (50 MHz): 39.69; 55.72; 65.55; 66.60; 112.47; 114.63; 115.65; 118.76; 120.28; 131.43; 134.43; 137.30; 145.46; 149.47; 168.72. MS: 262 (100, M^+), 163 (25), 115 (14), 109 (9), 103 (17), 91 (17), 77 (10), 41 (22). Odor description: eugenol, carnation-type, woody; not as powerful as eugenol, isoeugenol, or methyl-*Diantilis*®.

Prop-2-enyl 2-[2-Methoxy-4-(prop-2-enyl)phenoxy]acetate (**21e**). It was prepared from isoeugenol as described for **21a**. It consisted of a 30:70 (*Z*)/(*E*) mixture. Yield: 41%. B.p. 126°/0.05 Torr. IR: 784*w*, 816*w*, 859*w*, 933*w*, 966*m*, 985*m*, 1036*m*, 1071*m*, 1144*s*, 1191*s*, 1259*s*, 1272*s*, 1259*s*, 1272*s*, 1298*m*, 1416*m*, 1463*m*, 1512*s*, 1585*w*, 1602*w*, 1738*m*, 1762*s*, 2916*w*, 2938*w*, 3019*w*. (*Z*)-Isomer: ^{1}H-NMR (200 MHz): 1.89 (*dd*, J = 1.6, 7.3, 3 H); 3.87 (*s*, 3 H); 4.64–4.73 (*m*, 2 H); 4.69 (*s*, 2 H); 5.18–5.38 (*m*, 2 H); 5.72 (*ddd*, J = 8.1, 12.5, 14.4, 1 H); 6.07 (*q*, J = 6.4, 1 H); 6.34–6.40 (*m*, 1 H); 6.72 (br. *s*, 1 H); 6.77–6.82 (*m*, 1 H); 6.82–6.86 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.55; 55.80; 65.64; 66.49; 112.84; 114.10; 118.36; 121.15; 125.87; 129.27; 131.44; 132.33; 145.77; 149.15; 168.65. MS: 262 (100, M^+), 163 (47), 162 (16), 115 (16), 107 (29), 103 (13), 91 (21), 77 (10), 41 (19), 39 (10). (*E*)-Isomer: ^{1}H-NMR (200 MHz): 1.85 (*dd*, J = 1.4, 6.4, 3 H); 3.87 (*s*, 3 H); 4.64–4.73 (*m*, 2 H); 4.69 (*s*, 2 H); 5.18–5.38 (*m*, 2 H); 5.91 (*tdd*, J = 5.8, 10.4, 17.3, 1 H); 6.14 (*q*, J = 6.3, 1 H); 6.26–6.31 (*m*, 1 H); 6.77 (br. *s*, 1 H); 6.77–6.82 (*m*, 1 H); 6.88–6.91 (*m*, 1 H). ^{13}C-NMR (50 MHz): 18.29; 55.75; 65.64; 66.55; 109.26; 114.49; 118.36; 118.85; 124.46; 130.36; 131.44; 132.80; 146.22; 149.58; 168.65. MS: 262 (100, M^+), 163 (43), 162 (16), 115 (13), 107 (24), 103 (11), 91 (17), 77 (8), 41 (16), 39 (9). Odor description: spicy (isoeugenol), leathery, carnation, saffron, fruity (plums, dried plums), woody (vetiver), sweet; not as powerful as eugenol, isoeugenol, or methyl-*Diantilis*®.

Prop-2-enyl (2-Methoxy-4-methylphenoxy)acetate (**21f**). It was prepared from 2-methoxy-4-methylphenol as described for **21a**. Yield: 53%. B.p. 100°/0.04 Torr. IR: 800*w*, 929*w*, 987*w*, 1037*m*, 1071*w*, 1148*s*, 1156*s*, 1191*s*, 1269*s*, 1465*w*, 1513*s*, 1593*w*, 1737*m*, 1762*s*, 2939*w*. ^{1}H-NMR (200 MHz): 2.29 (*s*, 3 H); 3.85 (*s*, 3 H); 4.65–4.71 (*m*, 2 H); 4.66 (*s*, 2 H); 5.20–5.38 (*m*, 2 H); 5.91 (*tdd*, J = 5.8, 10.3, 17.1, 1 H); 6.62–6.79 (*m*, 3 H). ^{13}C-NMR (50 MHz): 20.99; 55.73; 65.59; 66.76; 113.10; 114.81; 118.80; 120.73; 131.49; 132.34; 144.99; 149.38; 168.84. MS: 236 (100, M^+), 151 (11), 137 (46), 136 (39), 109 (20), 91 (40), 77 (16), 65 (15), 41 (21), 39 (17). Odor description: vanilla, spicy (isoeugenol).

Hex-3-enyl 2-(2-Methoxy-4-methylphenoxy)acetate (**22f**). It was prepared from 2-methoxy-4-methylphenol and (*Z*)-hex-3-enyl 2-chloroacetate as described for **21a**. Yield: 50%. B.p. 114°/0.02 Torr. IR: 798*w*, 817*w*, 997*w*, 1038*s*, 1075*m*, 1148*s*, 1156*s*, 1191*s*, 1268*s*, 1414*w*, 1465*m*, 1513*s*, 1593*w*, 1735*m*, 1762*s*,

2874*w*, 2935*m*, 2963*m*, 3010*w*. ^{1}H-NMR (200 MHz): 0.95 (*t*, *J* = 7.5, 3 H); 2.03 (br. *quint.*, *J* = 7.6, 2 H); 2.29 (*s*, 3 H); 2.39 (br. *q*, *J* = 7.1, 2 H); 3.85 (*s*, 3 H); 4.18 (*t*, *J* = 7.0, 2 H); 4.64 (*s*, 2 H); 5.27 (*m*, 1 H); 5.49 (*m*, 1 H); 6.61–6.77 (*m*, 3 H). ^{13}C-NMR (50 MHz): 14.13; 20.52; 21.0; 26.6; 55.75; 64.50; 66.74; 113.09; 114.71; 120.73; 123.22; 132.26; 134.74; 145.07; 149.38; 169.17. MS: 278 (100, M^+), 196 (55), 151 (11), 137 (44), 136 (27), 109 (15), 91 (26), 77 (12), 67 (17), 65 (11), 55 (28), 41 (22). Odor description: vanilla, smokey.

Prop-2-enyl 2-[2-(Prop-2-enyl)-phenoxy]acetate (**22g**). It was prepared from 2-allylphenol as described for **21a**. Yield: 50%. B.p. 100°/0.02 Torr. IR: 754*s*, 919*m*, 989*m*, 1072*m*, 1092*m*, 1129*m*, 1194*s*, 1276*m*, 1296*m*, 1441*m*, 1455*m*, 1493*s*, 1589*m*, 1601*w*, 1639*w*, 1739*s*, 1764*s*, 2980*w*, 3079*w*. ^{1}H-NMR (200 MHz): 3.48 (br. *d*, *J* = 6.6, 2 H); 4.68 (*s*, 2 H); 4.71 (*dt*, *J* = 1.2, 5.9, 2 H); 5.02–5.07 (*m*, 1 H); 5.07–5.15 (*m*, 1 H); 5.23–5.40 (*m*, 2 H); 6.04 (*ddt*, *J* = 5.8, 9.2, 15.1, 1 H); 5.94 (*tdd*, *J* = 5.7, 10.4, 17.1, 1 H); 6.7–6.8 (*m*, 1 H); 6.91–7.01 (*m*, 1 H); 7.12–7.23 (*m*, 2 H). ^{13}C-NMR (50 MHz): 34.23; 65.59; 65.67; 111.39; 115.50; 118.88; 121.66; 127.21; 129.26; 130.14; 131.42; 136.76; 155.51; 168.66. MS: 232 (95, M^+), 145 (100), 133 (22), 131 (27), 117 (20), 115 (75), 105 (17), 91 (62), 77 (20), 41 (53), 39 (37). Odor description: vanilla, plastic.

4-(4,4-Dimethylpentan-2-yl)-2,6-dimethylcyclohex-2-enone (**24h**). A mixture of pentan-3-one (64.5 g, 0.75 mol, 1.5 equiv.), 2-methylidene-3,5,5-trimethylhexanal (prepared from 71 g, 0.5 mol, 1 equiv. of. *Vandor B*®) and KOH (5.6 g, 0.1 mol, 0.2 equiv.) in H_2O/EtOH (150 ml/100 ml) was heated at 70° overnight. After completion of the reaction, the mixture was cooled, and AcOH (6 g, 0.1 mol, 0.2 equiv.) was added. The aq. layer was extracted three times with ^{t}BuOMe, and the combined org. layers were washed with brine, dried ($MgSO_4$), and filtered. The solvents were evaporated, and the crude product was purified by distillation to give **24h** as a colourless oil in 56% yield over the two steps. It consisted of a mixture of four detectable isomers in a 23 : 17 : 30 : 30 ratio. B.p. 88–92°/0.4 Torr. IR: 1364*m*, 1453*w*, 1673*s*, 2868*w*, 2954*m*. ^{1}H-NMR (200 MHz): 0.75–1.37 (*m*, 2 H); 0.87–0.95 (*m*, 12 H); 1.12 (*d*, *J* = 7.2, 3 H); 1.37–2.0 (*m*, 3 H); 1.76 (*m*, 3 H); 2.20–2.62 (*m*, 2 H); 6.45–6.57 (*m*, 1 H). ^{13}C-NMR (50 MHz, selected data): 29.89 (3 C); 32.40/31.67/31.02 (C_q); 34.80/34.17 (CH_2); 48.46/47.97/47.92/47.74 (CH_2); 135.75/135.37/134.33 (C_q); 149.06/148.64/148.60/148.20 (CH); 196.52 (CO). MS: 222 (12, M^+), 124 (99), 123 (11), 109 (48), 95 (18), 81 (11), 79 (16), 77 (11), 67 (11), 57 (100), 55 (18), 43 (16), 41 (30). Odor description: woody, ambery, hazelnut, a little bit sandalwood.

Representative Procedure for the Preparation of Compounds **30**. *(2*S*,4a*S*,8a*R*)- and (2*R*,4a*R*,8a*S*)-Hexahydro-5,5-dimethyl-2-propyl-2,4a-methanonaphthalen-1-one* (**30d**). Myrcene (136 g, 1 mol) in toluene (350 ml) was reacted with 2-methylidenepentanal (120 g, 1.22 mol) at r.t. with a cat. amount of $AlCl_3$ (8 g, 0.06 mol) during 16 h. The solvent was removed, and the residue was flash-distilled (107 g; b.p. 100°/1 Torr). The crude oil obtained was further reacted in toluene (600 ml) at 60 ° in the presence of H_2SO_4 (4 g) during 24 h. The crude product was purified by distillation (b.p. 104°/0.8 Torr) to give **30d** (81 g, 35%). The compound was further crystallized from hexane at −28°. M.p. 45°. IR: 1465, 1730, 2870, 2934, 2960. ^{1}H-NMR (200 MHz): 0.89 (*t*, *J* = 7, 3 H); 0.95 (*s*, 3 H); 0.99 (*s*, 3 H); 1.17–1.93 (*m*, 16 H); 2.00–2.06 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.96; 19.47; 21.02; 21.96; 22.54; 23.56; 26.28; 31.55; 32.68; 33.61; 36.77; 41.05; 51.97; 53.84; 59.37; 220.72. MS: 234 (61, M^+), 205 (13), 191 (40), 177 (22), 165 (14), 164 (15), 163 (22), 151 (12), 150 (40), 149 (100), 135 (29), 126 (36), 122 (30), 121 (22), 109 (76), 108 (49), 107 (30), 105 (14), 95 (15), 93 (34), 91 (36), 81 (23), 79 (35), 77 (25), 69 (11), 67 (33), 55 (24), 41 (29). Odor description: nice, linear and longlasting (>2 weeks) ambery note.

*(2*S*,4a*S*,8a*S*)- and (2*R*,4a*R*,8a*R*)-Hexahydro-5,5-dimethyl-2-propyl-2,4a-methano-1-one* (**30d′**). Compound **30d** in MeOH was refluxed in the presence of KOH (10% (*w*/*w*)) until complete conversion to **30d′** (24 h). IR: 1462, 1739, 2869, 2929, 2955. ^{1}H-NMR (200 MHz): 0.89 (*m*, 9 H); 1.12–1.85 (*m*, 16 H); 1.89–2.00 (*m*, 1 H). ^{13}C-NMR (50 MHz): 14.96; 19.37; 20.76; 23.93; 24.11; 25.94; 29.64; 30.90; 31.45; 32.05; 37.90; 38.43; 50.44; 52.21; 58.89; 220.59. MS: 234 (66, M^+), 205 (14), 191 (40), 177 (24), 165 (16), 164 (16), 163 (26), 151 (13), 150 (43), 149 (96), 135 (33), 126 (46), 125 (11), 123 (10), 122 (36), 121 (25), 110 (11), 109 (100), 108 (66), 107 (34), 105 (17), 95 (20), 93 (41), 91 (43), 81 (36), 80 (12), 79 (44), 77 (31), 69 (18), 67 (46), 65 (11), 55 (36), 53 (14), 43 (15), 41 (44), 39 (14).

2-Ethylhexahydro-5,5-dimethyl-2,4a-methanonaphthalen-1-one (**30c**). It was obtained from methylidene butanal and myrcene as described for **30d**. Yield: 12%. B.p. 86°/0.7 Torr. IR: 1366*w*, 1378*w*, 1449*w*, 1460*w*, 1729*s*, 2873*m*, 2931*m*, 2962*m*. ^{1}H-NMR (200 MHz): 0.87 (*t*, *J* = 7, 3 H); 0.97 (*s*, 3 H); 1.01 (*s*, 3 H);

1.15–1.95 (*m*, 14 H); 2.0–2.10 (*m*, 1 H). ^{13}C-NMR (50 MHz): 10.27; 20.92; 21.82; 22.56; 23.57; 26.29; 32.04; 33.51; 36.67; 40.44; 51.89; 53.99; 60.01; 220.75. MS: 220 (47, M^+), 191 (23), 177 (17), 163 (21), 151 (14), 150 (12), 149 (20), 137 (13), 136 (42), 135 (100), 126 (37), 121 (40), 109 (19), 108 (25), 107 (33), 105 (19), 95 (92), 94 (44), 93 (45), 91 (49), 81 (27), 79 (45), 77 (34), 69 (13), 67 (33), 65 (12), 55 (39), 53 (16), 43 (10), 41 (34), 39 (12).

Hexahydro-5,5-dimethyl-2-(propan-2-yl)-2,4a-methanonaphthalen-1-one (**30e**). It was obtained from methylideneisovaleraldehyde and myrcene as described for **30d**. Yield: 38%. B.p. 85°/0.3 Torr. IR: 1365*w*, 1384*w*, 1452*w*, 1463*w*, 1735*s*, 2870*w*, 2931*m*, 2954*m*. ^{1}H-NMR (300 MHz): 0.9 (*d*, *J* = 6.8, 3 H); 0.9 (*d*, *J* = 6.9, 3 H); 0.96 (*s*, 3 H); 1.0 (*s*, 3 H); 1.1–1.8 (*m*, 10 H); 1.84–1.95 (*m*, 1 H); 1.95–2.15 (*m*, 2 H); 2.2–2.37 (*m*, 1 H). ^{13}C-NMR (75 MHz): 18.09; 19.65; 20.78; 21.72; 22.41; 23.51; 26.19; 26.37; 29.62; 33.4; 36.60; 37.55; 51.38; 54.60; 63.39; 220.87. MS: 234 (46, M^+), 191 (30), 177 (13), 165 (11), 164 (11), 163 (17), 151 (10), 150 (38), 149 (100), 135 (31), 126 (24), 122 (20), 121 (22), 109 (85), 108 (57), 107 (40), 105 (20), 95 (18), 93 (42), 91 (46), 81 (28), 79 (36), 77 (28), 69 (22), 67 (35), 65 (11), 55 (32), 53 (13), 43 (19), 41 (38), 39 (11).

2-Butylhexahydro-5,5-dimethyl-2,4a-methanonaphthalen-1-one (**30f**). It was obtained from 2-methylidenehexanal and myrcene as described for **30d**. Yield: 13%. B.p. 96°/0.45 Torr. IR: 1366*w*, 1384*w*, 1450*m*, 1467*m*, 1734*s*, 2861*m*, 2905*m*, 2932*m*, 2954*m*. ^{1}H-NMR (300 MHz): 0.85 (*t*, *J* = 7, 3 H); 0.93 (*s*, 3 H); 0.97 (*s*, 3 H); 1.15–1.75 (*m*, 17 H); 1.82–1.92 (*m*, 1 H); 1.97–2.05 (*m*, 1 H). ^{13}C-NMR (75 MHz): 13.97; 20.79; 21.73; 22.33; 23.32; 23.46; 26.18; 28.24; 28.76; 32.40; 33.38; 36.54; 40.80; 51.84; 53.74; 59.23; 220.61. MS: 248 (41, M^+), 206 (23), 205 (14), 191 (34), 179 (12), 178 (18), 177 (18), 165 (11), 164 (32), 163 (100), 149 (25), 136 (24), 135 (12), 126 (28), 123 (66), 122 (58), 121 (25), 119 (12), 109 (18), 107 (34), 105 (19), 95 (21), 93 (43), 91 (45), 81 (39), 80 (23), 79 (43), 69 (16), 67 (41), 55 (31), 43 (11), 41 (27).

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