Synthesis of [4.3.3]Propellanes by Carbenium-Ion Rearrangement and Their Olfactory Characterization

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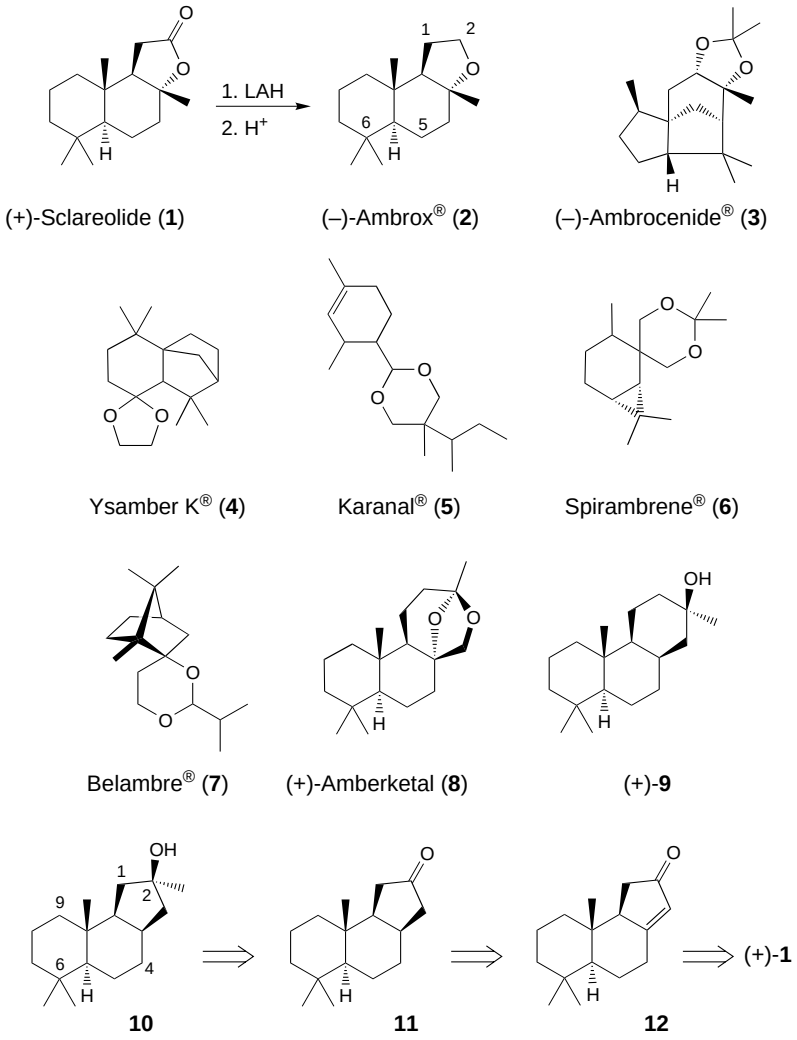
Treatment of (+)-sclareolide (**1**) with polyphosphoric acid or *Eaton*'s reagent furnished, besides the anticipated cyclopentenone (−)-**12** and its isomer (−)-**15**, two diastereoisomeric [4.3.3]propellanes (−)-**13** and (−)-**14**, which possess interesting woody-ambery odors. The hydrogenated derivative (−)-**17** possessed an even more-powerful odor reminiscent of natural ambergris tincture. Mechanistic insight into this rearrangement was provided by a by-product **24** of the reaction of sclareolide (**1**) with *Eaton*'s reagent. The carbenium ion rearrangement was then employed in the synthesis of four related [4.3.3]propellanes **40**–**43**, illustrating the utility and scope of this reaction. The olfactory properties of the synthesized [4.3.3]propellanes as well as of the original target structures **10**, **33**, and **34**, prepared from (−)-**12** and (−)-**15**, are discussed. Especially the pronounced ambra odor of (−)-**17** vividly contradicts the *'triaxial rule of amber sensation'* and provides new insight into the structural requirements for ambra odorants.

Introduction. – (+)-Sclareolide (**1**), a degradation product of ambrein [1–3], sclareol [4], and manool [5], was isolated from the resin of *Cistus labdaniferus* L. (Cistaceae) [6] and also occurs in tobacco [7]. It is a central intermediate in the commercial synthesis of *(−)-Ambrox*® (**2**) [8][9], which is still the most typical and most important amber odorant in perfumery. Besides **2**, a number of acetals and ketals of amber tonality with more or less pronounced woody facets found their way into perfumery. These include *Ambrocenide*® (**3**) and *Ysamber K*® (**4**) of *Dragoco*, *Karanal*® (**5**) of *Quest*, *Spirambrene*® (**6**) as well as *Belambre*® (**7**) of *Givaudan*, and amberketal (**8**) (*Scheme 1*). Amberketal (**8**), possesses the most pronounced ambery character and the least woody aspects of these acetals and ketals. Already in 1978, *Ohloff* and *Vial* [10] synthesized the tertiary alcohol **9**, and reported it to emanate an '*exceptionally strong ambery odor, recalling acetal'* **8**.

Considering the structural similarity of **9** with *Ambrox*® (**2**), we were curious about **10**, the ring-contracted *A*-nor-**9**. As depicted in *Scheme 1*, retrosynthetic analysis of **10** led *via* **11** to the enone **12**, which we planned to synthesize from (+)-sclareolide (**1**) in analogy to other known γ-lactone–cyclopentenone rearrangements [11–14][1]). When we heated (+)-sclareolide (**1**) with polyphosphoric acid (PPA) at 100° for 1 h, we obtained the [4.3.3]propellanes (−)-**13**/(−)-**14** (ratio 1:3) as the main products, besides the projected cyclopentenones (−)-**12** and (−)-**15** (*Scheme 2*). We have already

[1]) This reaction is sometimes accompanied by skeletal rearrangements, for instance, a ketone with brexane skeleton was obtained by treatment of a bicyclic lactone with PPA [13], and the formation of tricyclo[6.3.0.$0^{4,8}$]undec-3-en-2-one from the reaction of bicyclo[4.3.0]non-1(9)-en-6-acetic acid with PPA was also reported [14].

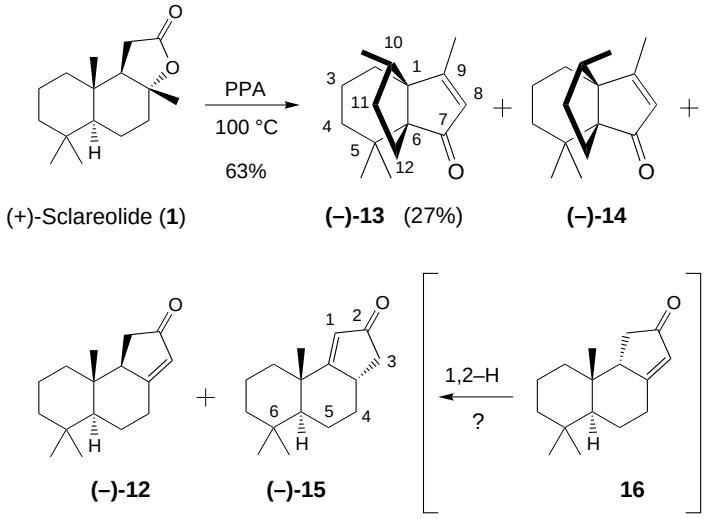
Scheme 1. *Amber Odorants and Our Original Target Structure* **10**



reported these results in a preliminary communication in 1992 [15]. Here, we give a detailed account of this carbenium ion rearrangement with experimental and mechanistic details as well as spectroscopic data; furthermore, the original target structures, the utility and scope of the reaction, as well as the olfactory properties of the products are discussed.

Structural Assignments. – The propellane skeleta of (−)-**13** and (−)-**14** were unambiguously deduced from their $^{13}C,^{13}C$-INADEQUATE NMR spectra; the relative configuration of Me−C(10) is apparent from the ^{13}C-NMR shift of C(2), which is δ 26.3 ppm in (−)-**14** and 23.0 ppm in (−)-**13**. This upfield shift in (−)-**13** is due to the γ-

Scheme 2. *PPA-Mediated Rearrangement of Sclareolide* (**1**)



effect of Me–C(10) (*cf. Scheme 2*). Accordingly, the γ-effect of Me–C(10) causes an upfield shift of C(9) in (–)-**14**, from δ 182.9 in (–)-**13** to 181.2 ppm for (–)-**14**.

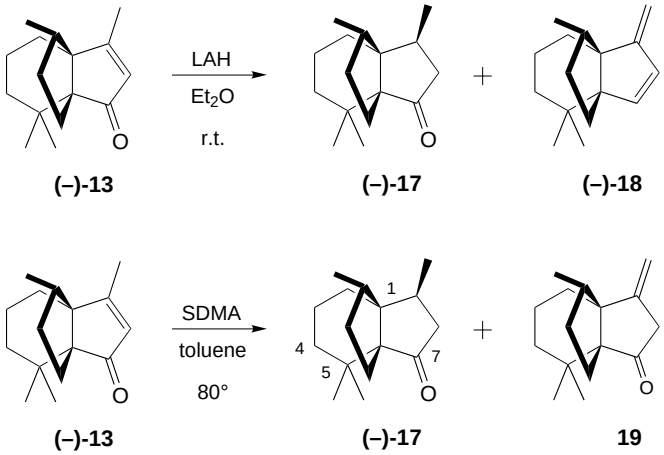
Though in minor quantity, the formation of (–)-**15** is quite surprising, and, most probably, it derives *via* a 1,2-H shift from **16** (after isomerization of **1** to episclareolide (**20**); *cf. Scheme 4*); however, we could not isolate **16**. The structure of (–)-**15** was deduced from 2D NMR experiments, its configuration was determined by NOE-difference spectroscopy. Substantial was the irradiation of H–C(3a) at 2.92 ppm, which led to enhanced intensity of the signals of Me–C(9a) at 1.18 ppm, of H_α–C(3) at 2.55 ppm, and of H_α–C(4) at 2.25 ppm.

The structure and configuration of the originally intended enone (–)-**12** was established by ^{13}C,^{13}C-INADEQUATE, ^{1}H,^{13}C-COSY, and NOE-DIFF experiments. Irradiation of H–C(9b) at 2.48 ppm enhanced the intensity of H–C(5a) at 1.27 ppm and H_β–C(1) at 2.23 ppm. Irradiation of Me–C(9a) at 0.67 ppm enhanced the signals of Me_{ax}–C(6) at 0.86 and of H_α–C(1) at 2.15 ppm.

Reduction of Propellane (–)-13 (*Scheme 3*). – On reduction of (–)-**13** with $LiAlH_4$ (LAH) at room temperature, we obtained a mixture of the ketone (–)-**17** and the diene **18**, the latter resulting most likely from the dehydration of the corresponding intermediary allylic alcohol. We could avoid the formation of **18** by replacing LAH with sodium dihydro bis(2-methoxyethoxy)aluminate (SDMA, *Red-Al*®). As a by-product of this hydride reduction, we isolated in minor amounts the β,γ-unsaturated ketone **19**.

The formation of the saturated ketone instead of the allylic alcohols upon hydride reduction is quite surprising at first sight. However, even LAH reduction of *endo*-5,6-dihydrodicyclopentadien-1-one in THF at 0° proceeds exclusively *via* 1,4-addition [16],

Scheme 3. *Hydride Reduction of the Propellane* (−)-**13**



NOE: Me_{ax}–C(5) / H_{eq}–C(4),
H–C(8), H–C(9).
Me_{eq}–C(5) / H_2–C(4),
H_2–C(12).
Me–C(9) / H–C(8), H–C(9).

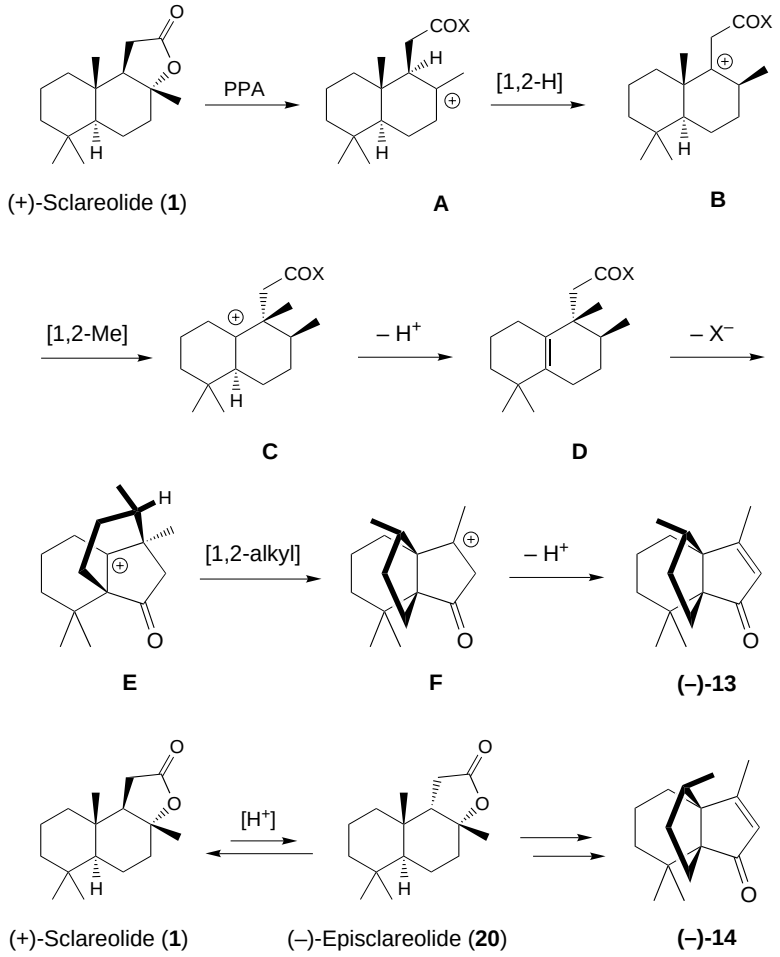
and the steric bulk of the geminal dimethyl group in (−)-**13** probably hinders 1,2-addition.

The structure of (−)-**17** was assigned by INADEQUATE and NOE-DIFF experiments: irradiation of Me_{ax}−C(5) at 0.95 ppm enhanced the signals of H−C(9) at 2.56, of H−C(8) at 2.43, and of H_{eq}−C(4) at 1.18 ppm. Irradiation of Me_{eq}−C(5) at 0.85 ppm enhanced the signals of CH_2(12) at 1.68 and 1.94, as well as of CH_2(4) at 1.18 and 1.33 ppm. Furthermore, irradiation of Me−C(9) at 1.60 ppm enhanced the signals of H−C(9) at 2.56 ppm and of H−C(8) (*cf. Scheme 3*).

The nucleophile, thus, attacks (−)-**13** from its *si*-face. When the *re*-face is additionally blocked by a Me substituent as in (−)-**14**, the attack of the H-nucleophile itself should be hindered as this increases the steric hindrance in the product. Indeed, (−)-**14** is not reduced under these reaction conditions. Accordingly, treatment of a mixture (−)-**13**/(−)-**14** with SDMA at 80° furnished a mixture (−)-**17**/(−)-**14** diastereoselectively; no diastereoisomer derived from (−)-**14** was detectable.

Discussion of the Rearrangement. – The formation of the propellanes (−)-**13** and (−)-**14** from treatment of (+)-sclareolide (**1**) with PPA can be rationalized by the mechanism depicted in *Scheme 4*. By a *syn*-[1,2-H] shift and a *syn*-[1,2-Me] shift, the carbenium ion **A** is transformed to **C**. Subsequently, a proton is eliminated, and the resulting alkene **D** is acylated intramolecularly to furnish the carbenium ion **E**, which is then transformed by a *Wagner–Meerwein* rearrangement and deprotonation of **F** to the [4.3.3]propellane (−)-**13** (*Scheme 4*). The formation of the diastereoisomer (−)-**14** is due to the isomerization of sclareolide (**1**) to episclareolide (**20**) [17–19] prior to the

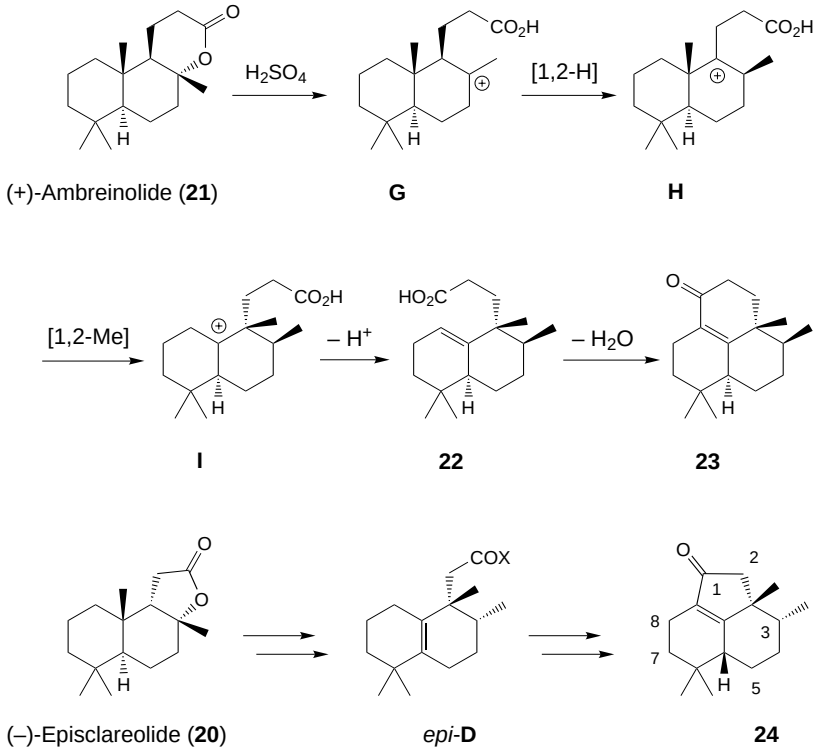
Scheme 4. *Mechanistic Considerations*



rearrangement (*Scheme 5*). When **20** was treated directly with PPA at 100° the propellanes (−)-**13**/(−)-**14** were isolated in 13% as a 1:1 mixture, while the cyclopentenones (−)-**12**/(−)-**15** (87:13) were obtained in 6% yield. Reaction of (−)-isosclareolide [19][20] under the same conditions gave 20% of the propellanes (−)-**13**/(−)-**14** (6:1) and 10% of (−)-**12**/(−)-**15** (92:8).

Similar with respect to the first steps is the rearrangement of ambreinolide (**21**) upon treatment with H_2SO_4 in dioxane [21]. *Büchi*, *Saar*, and *Eschenmoser* proposed the mechanism outlined in *Scheme 5*, consisting as well of a *syn*-[1,2-H] shift followed by a *syn*-[1,2-Me] shift leading from carbenium ion **G** → **I**. This is transformed to enone **23** *via* the alkene **22**. A related sequence of *syn*-[1,2-H] with subsequent [1,2-Me] shift was also proposed by *Vlad* and co-workers [22] for the formation of an oxacyclopenta[*d*]naphthalene by-product upon treatment of a (hydroxyethyl)decahydronaphtha-

Scheme 5. *Related Rearrangement Reported by* Büchi, Saar, *and* Eschenmoser [21]

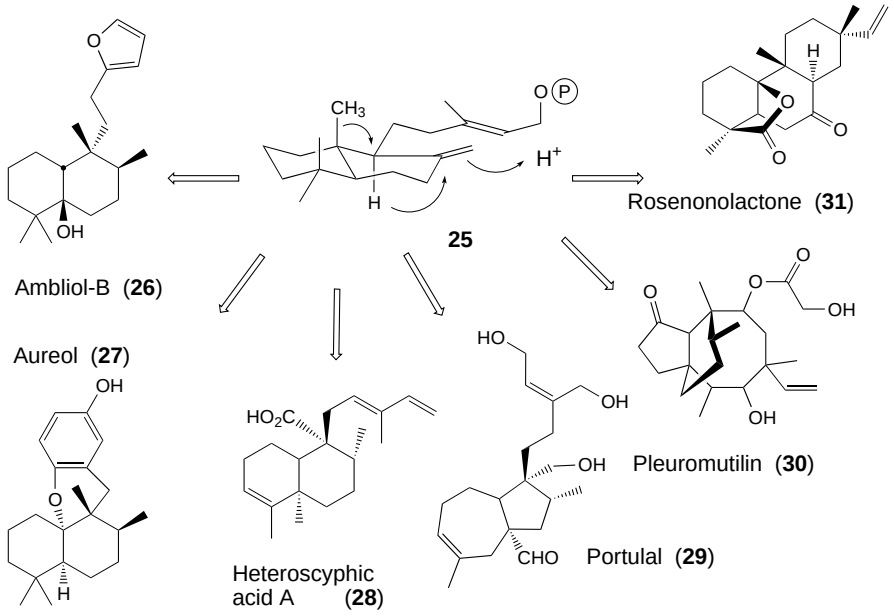


lenol with the cationic ion-exchange resin *KG-23*. And of course, this type of rearrangement is involved in the biogenesis of numerous terpenoids, like, for instance, ambliol-B (**26**) [23], aureol (**27**) [24], heteroscyphic acid A (**28**) [25], portulal (**29**) [26], pleuromutilin (**30**) [27][28], and rosenonolactone (**31**) [29][30] *ex* labdanoid precursors (**25**) (*Scheme 6*).

Though *via* different mechanisms, we should mention that some other syntheses of propellanes made use of acid-catalyzed rearrangements, too. For instance, *Cargill et al.* [31] synthesized dispiro[3.3.3.0]undecanones from tricyclo[6.3.0.$0^{1,6}$]undecan-2-one. Especially elegant in this respect are some works of *Fitjer et al.* [32–35], *e.g.*, the preparation of modheptene by acid-catalyzed rearrangement of dispiro[3.0.4.2]undecane [35]. Treatment of tricyclo[6.2.1.$0^{2,7}$]undecane with trifluoromethanesulfonic acid also led to a propellane [36].

Upon treatment of (+)-sclareolide (**1**) with *Eaton*'s reagent [37] (P_2O_5 in MsOH, 1 h at 105°), the cyclopentenone mixture (–)-**12**/(–)-**15** (8:3) became the main product (48%), and the propellanes (–)-**13**/(–)-**14** (5:1) were only formed as by-products (5%). Under these conditions, we observed the formation of another by-product (<2%). This compound was isolated and assigned structure **24** (*Scheme 5*) by INADEQUATE experiments; the configuration was again derived from NOE-DIFF spectra. Irradiation of the signal of Me–C(2a) at 1.32 ppm enhanced the signals of

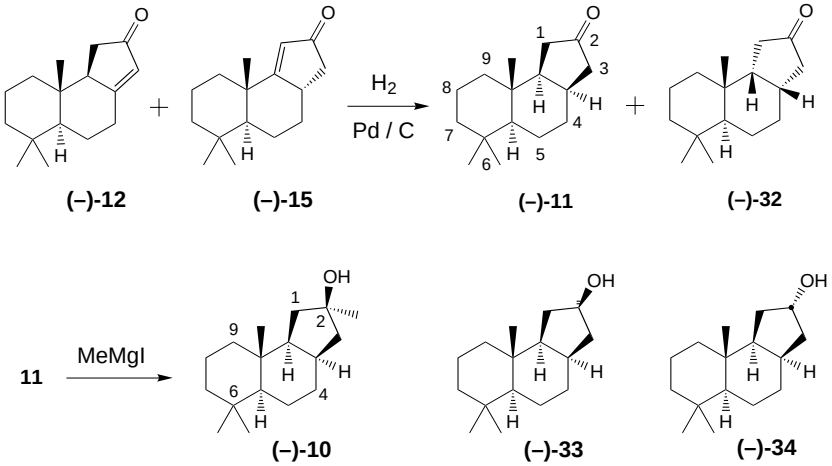
Scheme 6. *Examples from the Biogenesis of Diterpenoids*



H_α–C(2) and H–C(5a) at 1.99 ppm as well as of H–C(3) at 2.16 ppm, while the intensity of the signal of Me–C(3) at 0.78 ppm remained unaltered; we, thus, concluded that the Me groups are *trans*-configured. On irradiation of Me–C(3) at 0.78 ppm, one observed enhancement of the signals of H–C(3) (2.16 ppm), H_{eq}–C(4) (1.51 ppm), H_{ax}–C(5) (1.36 ppm), and H_β–C(2) (2.51 ppm). This minor by-product **24** is mechanistically important, as, in analogy to the formation of **23**, it indicates the existence of *epi*-**D**, and, thus, supports the mechanistic proposal put forward above. The basic skeleton of **24** was known in the literature [38][39].

Synthesis of the Original Target (–)-10. – Not losing sight of our original target structure, the decahydro-2,6,6,9a-tetramethyl-1*H*-benz[*e*]inden-2-ol (**10**), we seized the chance of having the cyclopentenones (–)-**12**/(–)-**15** (8:3) as main product from the reaction of (+)-sclareolide (**1**) with *Eaton*'s reagent. Catalytic hydrogenation of the mixture (–)-**12**/(–)-**15** in the presence of Pd/C (5%) provided (–)-**11** and (–)-**32** (*Scheme 7*), which were separated by chromatography. The configuration was assigned by NOE-DIFF experiments (*cf. Exper. Part*). *Grignard* reaction with MeMgI then furnished **10**, the nucleophile attacking selectively from the convex face. As expected, LAH reduction proceeded with the same selectivity to provide **33**, while *Bouveault–Blanc* reduction with Li metal in liquid NH_3 in the presence of EtOH furnished the *exo*-alcohol **34**. The original target molecule (–)-**10** possesses only a relatively weak ambery-woody tonality, and was found far less interesting than the propellanes (–)-**13**, (–)-**14**, and (–)-**17**. The ketone **11** also showed some ambery tonality, but was mainly

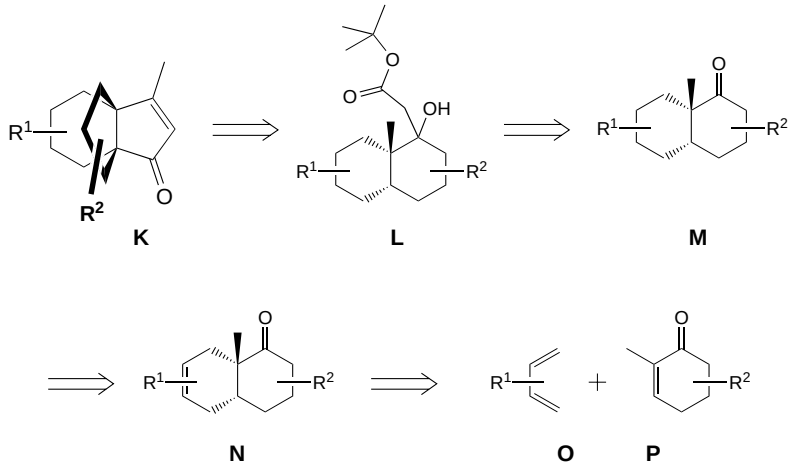
Scheme 7. *Synthesis of the Original Lead Compound (–)*-**10** and Related Compounds



woody, even sandalwood-like. The alcohols **33** and **34** were very weak to odorless without any distinct character.

Syntheses of Related Propellanes. – On account of the mechanistic considerations detailed in *Scheme 4*, the related [4.3.3]propellane systems **K** should be accessible by treatment of β-hydroxy esters **L** (*Scheme 8*) with polyphosphoric acid (PPA), because the *Reformatsky* products **L** should be direct precursors to carbenium ions of type **B**. The pivotal intermediates **L** should in turn be accessible, for instance, by reaction of ketones **M** with the lithio ester enolate of *tert*-butyl acetate [40]. Retrosynthetic introduction of a double bond, reveals *Diels–Alder* adducts **N** as suitable starting

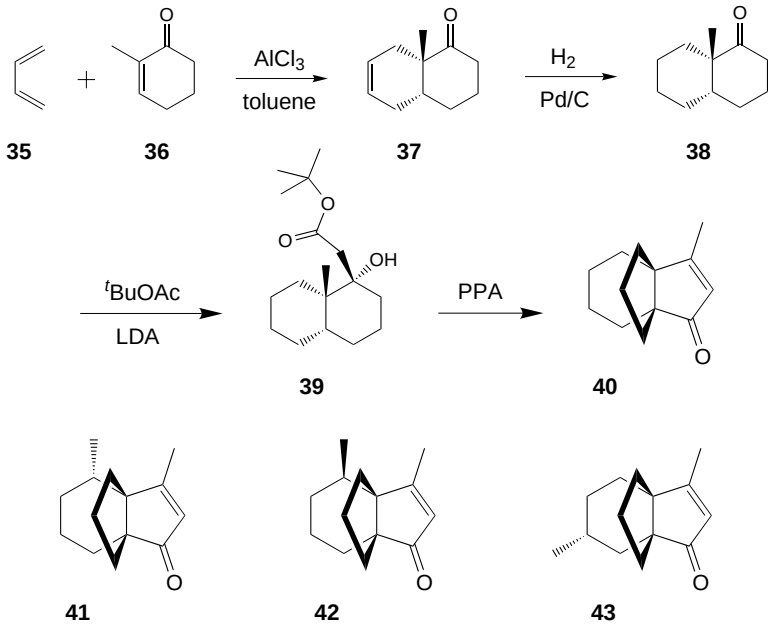
Scheme 8. *Retrosynthesis of Related [4.3.3]Propellanes*



materials – easily available by reaction of substituted butadienes **O** with optionally substituted 2-methylcyclohexenones **P**. A vast variety of *Diels–Alder* adducts of type **N** has been described by *Nerdel* and *Dahl* [41], *Kitahara* and co-workers [42], and *Wenkert, Fringuelli*, and co-workers [43–47][2]).

For the synthesis of the parent skeleton 9-methyltricyclo[4.3.3.$0^{1,6}$]dodec-8-en-7-one (**40**; *Scheme 9*), buta-1,3-diene (**35**) was reacted with 2-methylcyclohex-2-enone (**36**) at 70° in the presence of $AlCl_3$ [40][41]. The corresponding *endo*-adduct **37** [40–43][49][50] was isolated by distillation in 65% yield. Subsequent hydrogenation of the *cis*-Δ^6-octalone **37** at 10 bar in the presence of Pd/C furnished the *cis*-decalone **38** [51] in 95% yield. Treatment of decalone **38** with ^{t}BuOAc/LDA in toluene at 0° provided the desired β-hydroxy ester **39** in 84% yield. The configuration was established by NOE-DIFF spectroscopy, and is in accord with the nucleophile attacking **38** from the convex face. Submitting **39** to the elaborated rearrangement conditions in polyphosphoric acid (PPA) at 100°, the projected target molecule **40** was obtained in 52% yield.

Scheme 9. *Further [4.3.3]Propellanes Synthesized*



Following the same sequence, we also synthesized the related [4.3.3]propellane ketones **41**, **42**, and **43** (*cf. Exper. Part*; the corresponding cycloadducts [44–46][52–54] and hydrogenated analoga [44][55–60] are known in the literature). The diastereoisomeric ketones **41** and **42** resulted from the *Diels–Alder* reaction of **36** with (*E*/*Z*)-isomeric piperylene, and were separated by flash chromatography (FC) only after the

[2]) The corresponding ketones **M** may also be obtained in optically active form, for instance, both enantiomers of **38** were prepared from *cis*-decahydro-8a-methylnaphthalene-1,8-dione *via* enantiotopically differentiating monoacetalization [48].

final rearrangement step. Other *Diels–Alder* adducts, *e.g.*, with carvone as dienophile [41], would, for example, lead to derivatives substituted in the cyclopentyl ring; thus, the presented sequence should offer a flexible route to differently substituted propellanes. However, the 8a-Me substitution in **M** is indispensible, since (octahydronaphthalen-1-yl)acetic acid rearranges in PPA at 120° to 2a,3,4,5,5a,6,7,8-octahydro-1(2*H*)-acenaphthylenone, as was already reported by *Cargill et al.* [38]. We, indeed, obtained the same product submitting *tert*-butyl *rac*-[(1β,4aβ,8aα)-decahydro-1-hydroxynaphthalen-1-yl]acetate to our rearrangement conditions.

Olfactory Evaluation. – Neither **40**, nor **41**, **42**, and **43** showed any amber tonality: **40** was woody-camphoraceous in smell, with resinous and cognac-like facets, **41** and **42** were mainly camphoraceous with a woody-aromatic background, and in **43** the camphoraceous character of **41** and **42** changed to a fresh, eucalyptus-like odor with reminiscence to buchu leaf oil, while the woody-aromatic tonality was still present. Bearing their globular overall shape in mind, which after all is not so far from camphoraceous-smelling molecules like adamantane or even camphor, these odor characteristics are rather in line with what one would expect for propellane structures.

However, both propellanes (−)-**13** and (−)-**14** possess fruity, ambery odor characteristics, besides a woody, cedar-type tonality, with (−)-**14** being slightly more intense than (−)-**13**. The ambra note is most pronounced in the saturated propellane (−)-**17**, which possesses a very natural scent, typical for that of ambergris tincture and *(−)-Ambrox*® (**2**). When our patent claiming (−)-**17** as ambergris odorant was filed in 1990 [61], (−)-**17** constituted the first striking exception to the *'triaxial rule of ambra odorants'* [62].

Evaluating numerous ambra odorants, *Ohloff 'found that the characteristic ambergris odor* or *any of its individual component qualities arise* exclusively *in compounds having a* decalin *ring system of strictly determined stereochemistry […]. The only requirement, which each molecule has to fulfill is the 1,2,4-triaxial arrangement of the substituents in the decalin ring system'* [62] (*Fig. 1*). Thus, ambergris odorants had to possess a *trans*-fused decalin partial structure, according to this rule.

The features of the triaxial rule can be best illustrated on *(−)-Ambrox*® (**2**; *Fig. 1*) as the most typical ambra odorant (for locants of **2**, *cf. Scheme 1*): the 1,2,4-triaxial arrangement is formed by H−C(5a), Me−C(3a), and Me−C(9a), while the geminal dimethyl group at C(6) was reported to intensify the amber odor [19]. In contrary, the intensive and distinctively amber-smelling [4.3.3]propellane (−)-**17** does not possess a decalin ring system, and all rings in (−)-**17** are obviously *cis*-fused (*Fig. 1*); and even trying to superimpose the electron-density clouds, there is as little shape similarity between (−)-*Ambrox*® (**2**) and propellane (−)-**17**, as is with the skeleton of (−)-**17** and the basic core structure of the triaxial rule. Apparently, the immediate vicinity of the functional groups (*i.e.*, Me−C(3a) in **2**) is much more important for the ambergris odor than the overall electronic shape or the skeleton it is based on.

Fig. 2 presents an overlay analysis of (−)-**17** and *Ambrocenide*® (**3**) on *(−)-Ambrox*® (**2**), aligned on their oxygen functionalities. Now the importance of the Me−C(3a) group in **2** becomes apparent, and in all three molecules hydrophobic elements are accumulated around here. In this superposition, also Me−C(10) of (−)-**17** lies in quite close proximity to Me−C(9a) of **2**, and these two features may account for

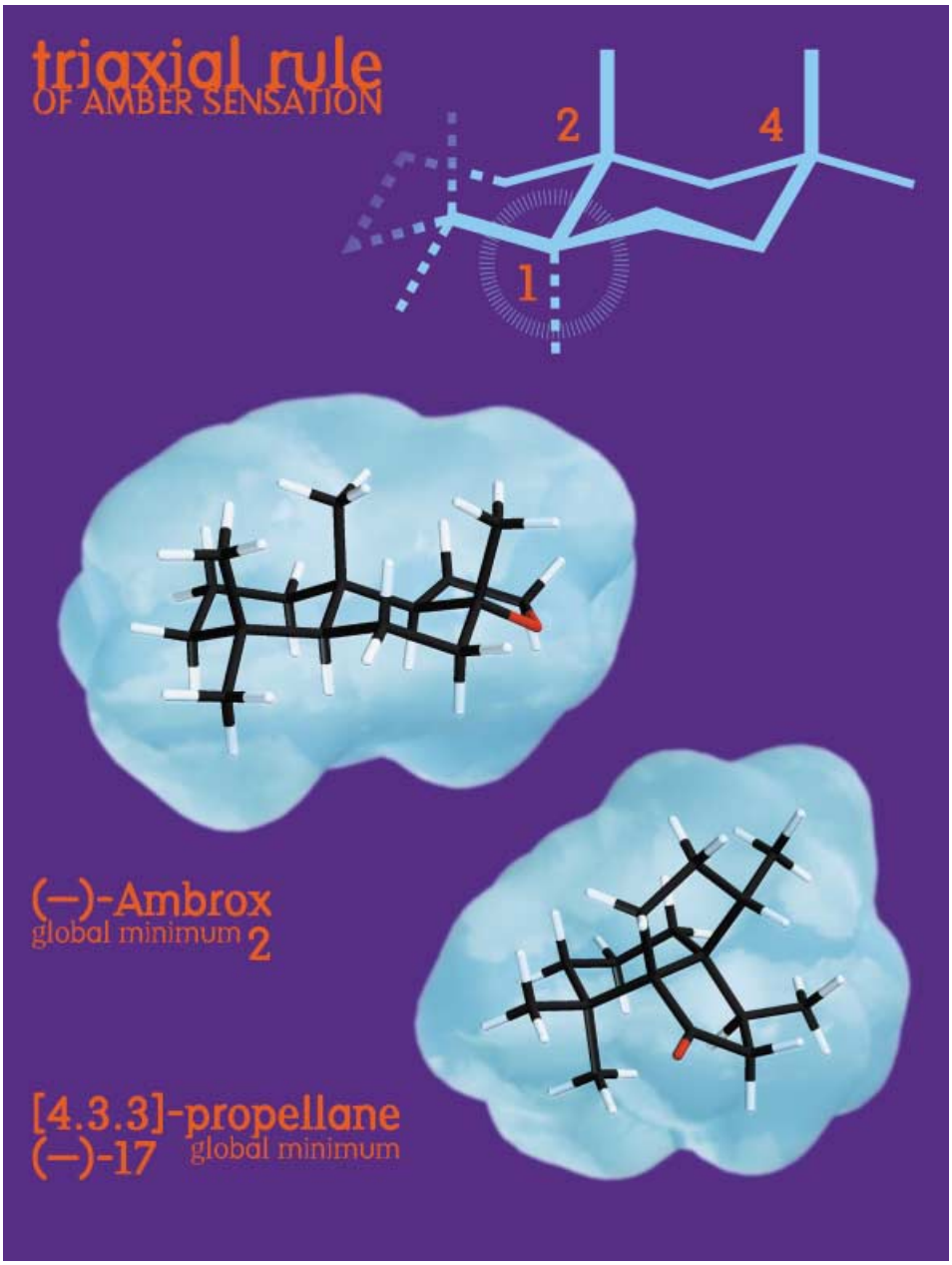


Fig. 1. *Rebuttal of the* 'triaxial rule of amber sensation'

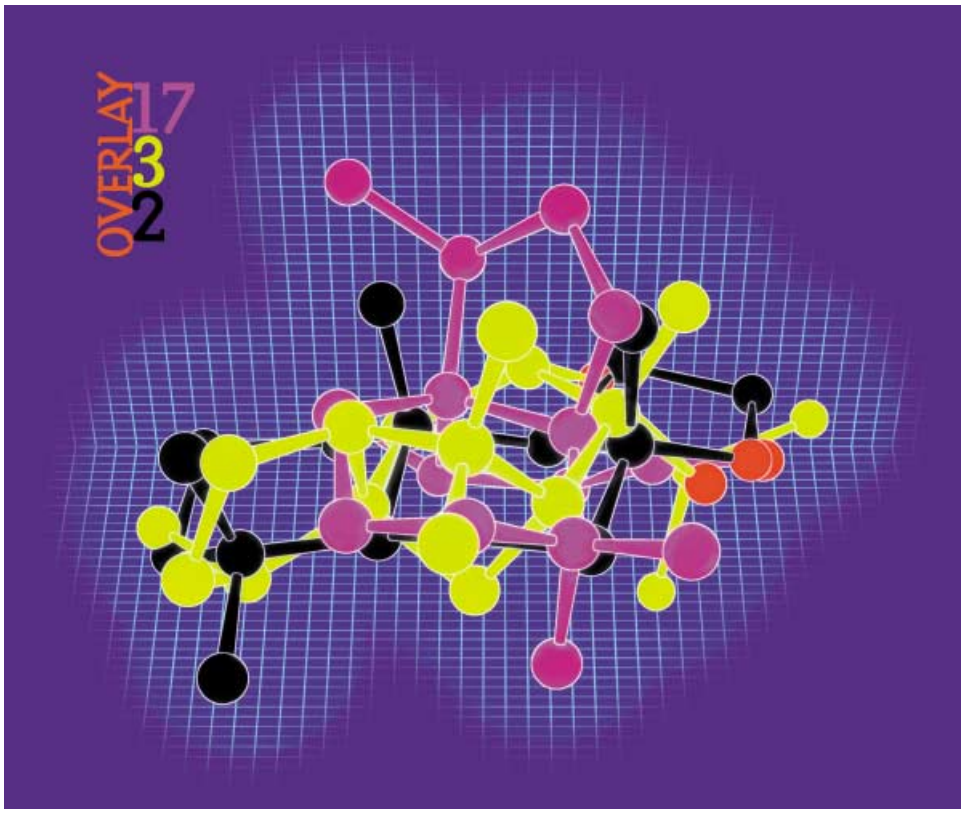


Fig. 2. *Overlay analysis of* **2** (black), **3** (yellow), *and* **17** (magenta)

the surprising and outstanding odor characteristics of (−)-**17**, as well as of (−)-**13** and (−)-**14**.

The *trans*-fused decalin skeleton of *Ambrox*® (**2**) is in this superposition of very little importance for the common spatial arrangement of the hydrophobic elements of **2**, **3**, and **17**. The importance of Me−C(3a) and, to a lesser extent, of Me−C(9a) was of course already been discovered by *Ohloff*; yet, 1,2,4-triaxially substituted decalin skeleta are just one way to fill these hydrophobic cavities at the receptor site. Other exceptions to the triaxial rule of amber sensation, as well as alternative olfactophore models for ambra odorants, can be found in a recent review [63].

The olfactory characteristics of the original target structures were less interesting. Compound (−)-**12** is weak, woody, and (−)-**15** is weak, camphoraceous, and woody. The compounds (−)-**10**, (−)-**11**, and (−)-**32** are weak woody; (−)-**10** and (−)-**11** possess in addition an ambra note, but far less distinct than that of the propellanes (−)-**13**, (−)-**14**, and (−)-**17**.

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Experimental Part

General. Reagents and solvents: *Fluka (puriss.* or *purum)*, used without further purification. IR: *Perkin-Elmer 681* and *Nicolet 510 FT-IR* spectrometer, $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR: *Bruker AM-400* and *Bruker AC-F-200* spectrometer, resp., δ in ppm rel. to Me_4Si, J in Hz. MS: *Finnigan MAT 212* and *Varian MAT-CH-5* instrument, rel. int. in % of the base peak.

*(−)-(1*S*,6*R*,10*S*)-5,5,9,10-Tetramethyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* ((−)-**13**), *(−)-(1*S*,6*R*,10*R*)-5,5,9,10-Tetramethyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* ((−)-**14**), *(−)-(5a*S*,5aβ,9aα,9bβ)-1,4,5,5a,6,7,8,9,9a,9b-Decahydro-6,6,9a-trimethylbenz[e]inden-2-one* ((−)-**12**), and *(−)-(5a*S*,3aα,5aβ,9bα)-3,3a,4,5,5a,6,7,8,9,9a-Decahydro-6,6,9a-trimethylbenz[e]inden-2-one* ((−)-**15**). At 100°, *(+)-sclareolide* (**1**; 80.0 g, 320 mmol) was added portionwise into stirred polyphosphoric acid (PPA; 300 g), and stirring was continued at this temp. for 1 h. The mixture was allowed to cool down, and, at 70°, H_2O (400 ml) and hexane (300 ml) were added, and the mixture was stirred for another 75 min. The org. layer was separated, and the aq. one extracted with Et_2O. The combined org. extracts were washed with sat. aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and concentrated in a rotary evaporator. GC Analysis of the resulting residue (63.3 g) indicated 42% of (−)-**13**, 13% of (−)-**14**, 26% of (−)-**12**, and 5% of (−)-**15**. Distillation at 70–75°/10^{-5} mbar provided a mixture (−)-**13**/(−)-**14** (3:1, 27.9 g, 37%) and at 85–90°/10^{-5} mbar a mixture (−)-**12**/(−)-**15** (27:5, 20.2 g, 27%). Pure samples for characterization were obtained by FC (silica gel; hexane/Et_2O 4:1).

*Data of (−)-***13**. $[\alpha]_D^{20} = -145.6$ ($c = 1.0$, $CHCl_3$). CD: (dioxane) λ_{max} 228 ($\Delta\varepsilon = -3.70$), 205 ($\Delta\varepsilon = +2.46$). IR (neat): 1690*s* (C=O), 1620*m* (C=C). ^1H-NMR ($CDCl_3$): 0.84 (*s*, Me_{ax}−C(5)); 1.00 (*d*, $J = 7.0$, Me−C(10)); 1.05 (*s*, Me_{eq}−C(5)); 1.20 (*m*, H_{ax}−C(4)); 1.34 (*m*, H_{ax}−C(11)); 1.40–1.72 (*m*, CH_2(3)); 1.46 (*m*, H_{eq}−C(4)); 1.54 (*m*, H_{eq}−C(11)); 1.72 (*m*, CH_2(2)); 1.85 (*m*, H−C(10)); 1.88 (*m*, CH_2(12)); 2.05 (*d*, $J = 1.5$, Me−C(9)); 5.76 (*m*, H−C(8)). NOE-DIFF: Me_{ax}−C(5)/H_{ax}−C(2), H_{ax}−C(4), H−C(3), H−C(8); Me_{eq}−C(5)/CH_2(12). ^{13}C-NMR ($CDCl_3$): 15.4 (*q*, *Me*−C(9)); 15.8 (*q*, *Me*−C(10)); 17.9 (*t*, C(3)); 22.9 (*t*, C(2)); 26.3 (*q*, Me_{ax}−C(5)); 26.9 (*q*, Me_{eq}−C(5)); 28.4 (*t*, C(12)); 31.8 (*t*, C(11)); 33.8 (*t*, C(4)); 34.8 (*s*, C(5)); 44.1 (*d*, C(10)); 58.9 (*s*, C(1)); 65.5 (*s*, C(6)); 129.1 (*d*, C(8)); 182.0 (*s*, C(9)); 213.8 (*s*, C(7)). MS (70 eV): 232 (34, M^+), 217 (11, $[M-Me]^+$), 204 (6, $[M-CO]^+$), 189 (6, $[M-CO-Me]^+$), 175 (16, $[M-CO-C_2H_5]^+$), 161 (15, $[M-CO-C_3H_7]^+$), 150 (100, $C_{11}H_{18}^+$), 122 (37, $C_9H_{14}^+$), 28 (52, CO^+). Odor: Woody, cedar, fruity, ambery.

*Data of (−)-***14**. $[\alpha]_D^{20} = -178.7$ ($c = 1.1$, $CHCl_3$). CD (dioxane): λ_{max} 230 ($\Delta\varepsilon = -6.89$), 202 ($\Delta\varepsilon = +3.78$). IR (neat): 1690*s* (C=O); 1615*m* (C=C). ^1H-NMR ($CDCl_3$): 0.79 (*s*, Me_{ax}−C(5)); 0.87 (*m*, H_{ax}−C(11)); 0.95 (*d*, $J = 7.0$, Me−C(10)); 1.03 (*s*, Me_{eq}−C(5)); 1.23 (*m*, H_{ax}−C(4)); 1.35 (*m*, H_{eq}−C(4)); 1.45 (*m*, H_{ax}−C(12)); 1.53 (*m*, H_{eq}−C(11)); 1.67 (*m*, CH_2(3)); 1.70 (*m*, H_{ax}−C(2)); 1.78 (*m*, H_{eq}−C(2)); 1.91 (*m*, H_{eq}−C(12)); 1.96 (*m*, H−C(10)); 2.07 (*d*, $J = 1.5$, Me−C(9)); 5.97 (*m*, H−C(8)). ^{13}C-NMR ($CDCl_3$): 16.4 (*q*, *Me*−C(10)); 16.5 (*t*, C(3)); 17.1 (*q*, *Me*−C(2)); 26.3 (*t*, C(2)); 27.4 (*q*, Me_{ax}−C(5)); 28.0 (*q*, Me_{eq}−C(5); 30.9 (*t*, C(12)); 31.2 (*t*, C(11)); 33.0 (*t*, C(4)); 34.9 (*s*, C(5)); 43.1 (*d*, C(10)); 57.6 (*s*, C(1)); 65.3 (*s*, C(6)); 132.6 (*d*, C(8)); 181.2 (*s*, C(9)); 214.1 (*s*, C(7)). MS (70 eV): 232 (40, M^+), 217 (12, $[M-Me]^+$), 204 (2, $[M-CO]^+$), 189 (6, $[M-CO-Me]^+$), 175 (12, $[M-CO-C_2H_5]^+$), 161 (14, $[M-CO-C_3H_7]^+$), 150 (100, $C_{11}H_{18}^+$), 122 (34, $C_9H_{14}^+$), 28 (33, CO^+). Odor: Woody, cedar, fruity, ambery, slightly stronger than (−)-**13**.

*Data of (−)-***12**. $[\alpha]_D^{20} = -103.5$ ($c = 1.0$, $CHCl_3$). IR (neat): 1670*s* (C=O), 1620*m* (C=C). ^1H-NMR ($CDCl_3$): 0.67 (*s*, Me_{ax}−C(6)); 0.86 (*s*, Me_{ax}−C(9a)); 0.95 (*s*, Me_{eq}−C(6)); 1.17 (*m*, H_{ax}−C(9)); 1.27 (*m*, H_{ax}−C(7)); 1.27 (*dd*, $J = 12.5$, 2.5, H_{ax}−C(5a)); 1.45 (*m*, H_{ax}−C(8)); 1.47 (2*m*, H_{ax}−C(5), H_{eq}−C(7)); 1.57 (2*m*, H_{eq}−C(8,9)); 1.91 (*ddd*, $J = 13.5$, 6.5, 2.5, H_{eq}−C(5)); 2.15 (*ddd*, $J = 19.0$, 2.5, 1.0, H_α−C(1)); 2.23 (*ddd*, $J = 19.0$, 6.5, 1.0, H_β−C(1)); 2.30 (*m*, H_{ax}−C(4)); 2.48 (br. *d*, $J = 6.5$, H−C(9b)); 2.85 (*ddd*, $J = 14.5$, 5.0, 1.5, H_{eq}−C(4)); 5.83 (*m*, H−C(3)). NOE-DIFF: Me_{ax}−C(6)/Me_{eq}−C(6), Me−C(9a); Me_{eq}−C(6)/H_{eq}−C(5), H_{ax}−C(5a), Me_{ax}−C(6), H_{ax}−C(7); Me−C(9a)/H_α−C(1), Me_{ax}−C(6), H−C(9b)/H_β−C(1), H−C(5a). ^{13}C-NMR ($CDCl_3$): 12.1 (*q*, Me_{ax}−C(6)); 18.0 (*t*, C(8)); 21.1 (*q*, *Me*−C(9a)); 21.9 (*t*, C(5)); 30.0 (*t*, C(4)); 32.5 (*s*, C(6)); 32.8 (*q*, Me_{eq}−C(6)); 35.4 (*t*, C(1)); 38.3 (*s*, C(9a)); 39.5 (*t*, C(9)); 41.4 (*t*, C(7)); 52.5 (*d*, C(5a)); 54.7 (*d*, C(9b)); 126.7 (*d*, C(3)); 181.7 (*s*, C(3a)); 208.2 (*s*, C(2)). MS (70 eV): 232 (11, M^+), 217 (9, $[M-Me]^+$), 204 (5, $[M-CO]^+$), 189 (6, $[M-C_2H_3O]^+$), 175 (4, $C_{13}H_{19}^+$), 161 (8, $C_{12}H_{17}^+$), 149 (10, $C_{11}H_{17}^+$), 137 (72, $C_{10}H_{17}^+$), 123 (38, $C_9H_{15}^+$), 109 (57, $C_8H_{13}^+$), 96 (100, $C_7H_{12}^+$), 81 (40, $C_6H_9^+$), 69 (34, $C_5H_9^+$), 55 (29, $C_4H_7^+$), 41 (48, $C_3H_5^+$). Odor: weak, woody.

*Data of (−)-***15**. $[\alpha]_D^{20} = -191.8$ ($c = 1.2$, $CHCl_3$). IR (neat): 1680*s* (C=O), 1620*m* (C=C). ^1H-NMR ($CDCl_3$): 0.90 (*s*, Me_{eq}−C(6)); 0.93 (*s*, Me_{ax}−C(6)); 1.04 (*m*, H−C(5a)); 1.10 (*m*, H_{ax}−C(4)); 1.18 (*s*, Me−C(9a)); 1.20 (*m*, H_{ax}−C(7)); 1.47 (*m*, H_{eq}−C(7)); 1.55 (*m*, H_{ax}−C(5)); 1.58 (*m*, H_{ax}−C(8)); 1.72 (*m*, H_{eq}−C(8)); 1.73 (*m*, H_{eq}−C(5)); 1.95 (*dd*, $J = 19.0$, 2.0, H_β−C(3)); 2.25 (*m*, H_{eq}−C(4)); 2.55 (*dd*, $J =$ 19.0, 7.0, H_α−C(3)); 2.92 (*m*, H_α−C(3a)); 5.69 (*m*, H−C(1)). NOE-DIFF: H_α−C(3)/H_β−C(3); H_β−C(3)/

H_α–C(3), H–C(3a); H–C(3a)/H_α–C(3), H_α–C(4), Me–C(9a); H_β–C(4)/H–C(3a), H_α–C(4). ^{13}C-NMR ($CDCl_3$): 18.4 (*t*, C(8)); 19.3 (*q*, *Me*$_{ax}$–C(6)); 21.3 (*t*, C(5)); 21.7 (*q*, *Me*–C(9a)); 33.3 (*q*, *Me*$_{eq}$–C(6)); 33.9 (*s*, C(6)); 35.8 (*t*, C(4)); 37.0 (*t*, C(9)); 38.3 (*d*, C(3a)); 39.9 (*s*, C(9a)); 41.8 (*t*, C(7)); 42.4 (*t*, C(3)); 53.7 (*d*, C(5a)); 121.9 (*d*, C(1)); 194.5 (*s*, C(2)). MS (70 eV): 232 (57, M^+), 217 (12, $[M-Me]^+$), 190 (30, $[M-C_2H_2O]^+$), 175 (30, $C_{13}H_{19}^+$), 161 (12, $C_{12}H_{17}^+$), 147 (19, $C_{11}H_{15}^+$), 135 (19, $C_{10}H_{15}^+$), 122 (38, $C_9H_{14}^+$), 109 (100, $C_8H_{13}^+$), 91 (40, $C_7H_7^+$), 79 (26, $C_6H_7^+$), 69 (27, $C_5H_9^+$), 55 (46, $C_4H_7^+$), 41 (77, $C_3H_5^+$). Odor: weak, woody, camphoraceous.

(–)-(1S,6R,9S,10S)-5,5,9,10-Tetramethyltricyclo[4.3.3.0^{1,6}]dodecan-7-one ((–)-**17**) and *(–)-(1S,6R,10S)-9-Methylidene-5,5,10-trimethyltricyclo[4.3.3.0^{1,6}]dodec-7-ene* ((–)-**18**). Under N_2 atmosphere at r.t., $LiAlH_4$ (150 mg, 3.95 mmol) was added to a stirred soln. of (–)-**13**/(–)-**14** (3:1; 1.00 g, 4.30 mmol) in Et_2O (10 ml). Stirring was continued at r.t. for 20 h prior to quenching with little AcOEt. H_2O and 2N aq. HCl were added, and the product was extracted with Et_2O (3×). The combined org. extracts were dried (Na_2SO_4), and the solvent was evaporated. The resulting residue was separated by repeated FC (silica gel; 10% $AgNO_3$, hexane/Et_2O, 9:1 and 4:1) to furnish (–)-**17** (150 mg, 20%) and (–)-**18** (70 mg, 10%).

*Data of (–)-***17**. $[\alpha]_D^{20} = -27.6$ ($c = 1.1$, $CHCl_3$). CD (dioxane): λ_{max} 296 ($\Delta\varepsilon = -0.64$), 305 ($\Delta\varepsilon = -0.57$). IR (neat): 1730*s* (C=O, sat.). ^{1}H-NMR ($CDCl_3$): 0.85 (*s*, Me$_{ax}$–C(5)); 0.92 (*d*, $J = 6.5$, Me$_{eq}$–C(10)); 0.95 (*s*, Me$_{eq}$–C(5)); 1.06 (*d*, $J = 7.0$, Me–C(9)); 1.15 (*m*, H$_{ax}$–C(2)); 1.18 (2*m*, H$_{ax}$–C(4), H$_{ax}$–C(11)); 1.33 (*m*, H$_{eq}$–C(4)); 1.51 (*m*, H$_{ax}$–C(3)); 1.64 (*m*, H$_{eq}$–C(2)); 1.65 (*m*, H$_{eq}$–C(3)); 1.67 (*m*, H$_{eq}$–C(11)); 1.69 (*m*, H$_{ax}$–C(12)); 1.70 (*m*, H–C(10)); 1.94 (*m*, H$_{eq}$–C(12)); 2.04 (*dd*, $J = 20.0$, 9.5, H–C(8) *syn* to Me–C(9)); 2.43 (*dd*, $J = 20.0$, 9.5, H–C(8) *anti* to Me–C(9)); 2.56 (*m*, H–C(9)). NOE-DIFF: Me$_{ax}$–C(5)/H$_{ax}$–C(2), H$_{eq}$–C(4), H–C(8), H–C(9); Me$_{eq}$–C(5)/CH$_2$(4), CH$_2$(12); Me–C(9)/H–C(8), H–C(9). ^{13}C-NMR ($CDCl_3$): 15.4 (*q*, *Me*–C(9)); 15.7 (*q*, *Me*–C(10)); 17.2 (*t*, C(3)); 22.9 (*t*, C(2)); 24.5 (*q*, *Me*$_{ax}$–C(5)); 27.3 (*q*, *Me*$_{eq}$–C(5)); 27.5 (*t*, C(12)); 30.1 (*t*, C(11)); 31.7 (*d*, C(9)); 32.8 (*s*, C(5)); 36.2 (*t*, C(4)); 38.3 (*d*, C(10)); 43.9 (*t*, C(8)); 52.1 (*s*, C(1)); 66.6 (*s*, C(6)); 221.3 (*s*, C(7)). MS (70 eV): 234 (42, M^+), 191 (8, $[M-C_3H_7]^+$), 179 (100, $C_{13}H_{23}^+$), 163 (35, $C_{12}H_{19}^+$), 149 (88, $C_{11}H_{17}^+$), 133 (51, $C_{10}H_{13}^+$), 121 (35, $C_9H_{13}^+$), 109 (49, $C_8H_{13}^+$), 93 (56, $C_7H_9^+$), 81 (63, $C_6H_9^+$), 69 (69, $C_5H_9^+$), 43 (56, $C_3H_7^+$). Odor: Close to *Ambrox*® (**2**), very natural, reminiscent of ambergris tincture.

*Data of (–)-***18**. $[\alpha]_D^{20} = -102.5$ ($c = 1.0$, $CHCl_3$). IR (neat): 1635*m* (C=C, diene); 870*s*, 810*m* (C–H, methylene). ^{1}H-NMR ($CDCl_3$): 0.71 (*s*, Me$_{ax}$–C(5)); 0.81 (*d*, $J = 6.5$, Me–C(10)); 0.94 (*s*, Me$_{eq}$–C(5)); 1.16–1.98 (*m*, 11 H); 4.61, 4.84 (2*s*, CH$_2$=C(9)); 5.92 (*d*, $J = 5.5$, H–C(7)); 5.98 (*d*, $J = 5.5$, H–C(8)). ^{13}C-NMR ($CDCl_3$): 13.1 (*q*, *Me*–C(10)); 17.7 (*t*, C(3)); 22.5 (*t*, C(11)); 26.9, 27.9 (2*q*, 2 *Me*–C(5)); 31.0 (*t*, C(2)); 33.4, 34.1 (2*t*, C(4), C(12)); 35.2 (*s*, C(5)); 45.8 (*d*, C(10)); 56.3 (*s*, C(1)); 65.6 (*s*, C(6)); 101.0 (*t*, CH$_2$=C(9)); 130.2 (*d*, C(8)); 145.6 (*d*, C(7)); 160.4 (*s*, C(9)). MS (70 eV): 216 (23, M^+), 201 (13, $[M-Me]^+$), 173 (26, $[M-C_3H_7]^+$), 159 (14, $[M-C_4H_9]^+$), 145 (23, $[M-C_5H_{11}]^+$), 134 (100, $C_{10}H_{14}^+$), 119 (64, $C_9H_{11}^+$), 105 (35, $C_8H_9^+$), 91 (39, $C_7H_7^+$), 41 (30, $C_3H_5^+$), 28 (64, $C_2H_4^+$).

*Compound (–)-***17** *and (1S,6R,10S)-9-Methylidene-5,5,10-trimethyltricyclo[4.3.3.0^{1,6}]dodecan-7-one* (**19**). A 3.5M soln. of sodium bis(2-methoxyethoxy)aluminum hydride in toluene (SDMA; 8.6 ml, 30.1 mmol) was diluted with toluene (4.0 ml) and then added dropwise at r.t. under N_2 into a stirred soln. of (–)-**13** (2.30 g, 9.90 mmol) in toluene (5.0 ml). Stirring was continued at r.t. for 68 h, and the mixture was poured onto ice/2N aq. NaOH 1:1 and extracted with Et_2O (3×). The combined org. extracts were washed with 2N aq. HCl and brine, dried (Na_2SO_4), and evaporated on the rotary evaporator. The resulting residue was purified by FC (silica gel; hexane/Et_2O 97:3 and 95:5) to provide (–)-**17** (1.08 g, 47%) and **19** (62 mg, 3%).

Data of **19**. ^{1}H-NMR ($CDCl_3$): 0.78 (*d*, $J = 6.5$, Me–C(10)); 0.84 (*s*, Me$_{ax}$–C(5)); 0.91 (*s*, Me$_{eq}$–C(5)); 1.08 (*m*, H$_{ax}$–C(2)); 1.10–1.40 (*m*, CH$_2$(4)); 1.32 (*m*, H$_{ax}$–C(11)); 1.38–1.60 (*m*, CH$_2$(3)); 1.46 (*m*, H–C(10)); 1.72 (*m*, H$_{eq}$–C(11)); 1.78 (*m*, H$_{ax}$–C(12)); 1.84 (*m*, H$_{eq}$–C(2)); 2.08 (*m*, H$_{eq}$–C(12)); 2.93 (*ddd*, $J = 22.0$, 2.0, 2.0, H$_b$–C(8)), 3.14 (*ddd*, $J = 22.0$, 2.0, 2.0, H$_a$–C(8)), 4.99 (*ddd*, $J = 7.0$, 2.0, 2.0, CH$_2$=C(9)). ^{13}C-NMR ($CDCl_3$): 12.3 (*q*, *Me*–C(10)); 17.8 (*t*, C(3)); 21.5 (*t*, C(2)); 24.6 (*q*, *Me*$_{ax}$–C(5)); 26.7 (*q*, *Me*$_{eq}$–C(5)); 27.9 (*t*, C(12)); 29.8 (*t*, C(11)); 33.7 (*s*, C(5)); 37.3 (*t*, C(4)); 43.3 (*t*, C(8)); 44.7 (*d*, C(10)); 56.2 (*s*, C(1)); 68.1 (*s*, C(6)); 105.2 (*t*, C(15)); 147.6 (*s*, C(9)); 220.6 (*s*, C(7)). MS (70 eV): 232 (48, M^+), 217 (14, $[M-Me]^+$), 204 (27, $[M-CO]^+$), 190 (25, $[M-C_2H_2O]^+$), 189 (26, $[M-C_3H_7]^+$), 176 (46, $C_{13}H_{20}^+$), 161 (64, $C_{12}H_{17}^+$), 147 (72, $C_{11}H_{15}^+$), 133 (45, $C_{10}H_{13}^+$), 105 (62, $C_8H_9^+$), 91 (80, $C_7H_7^+$), 82 (65, $C_6H_{10}^+$), 77 (47, $C_5H_9^+$), 69 (43, $C_4H_7^+$), 55 (47, $C_4H_7^+$), 41 (100, $C_3H_5^+$).

*Compound (–)-***17**. At r.t. under N_2, a 3.5M soln. of SDMA in toluene (72.0 ml, 252 mmol) was added dropwise with stirring to a soln. of (–)-**13**/(–)-**14** (3:1; 16.6 g, 71.4 mmol) in toluene (140 ml), and the mixture was heated to 78° for 23 h. The mixture was then cooled to 6° and poured into ice/H_2O 1:1. Subsequently, 2N aq. NaOH and Et_2O were added, and the biphasic soln. was vigorously stirred for 1 h. The org. layer was separated,

washed with 2N aq. HCl and brine, dried (Na_2SO_4), and concentrated on the rotary evaporator. Distillation of the crude material (17.0 g) provided at 92–96°/0.07 mbar a mixture (8.65 g, 52%) consisting of (−)-**17** (65%), (−)-**14** (20%), and (−)-**13** (7%).

Reaction of (−)-Episclareolide (**20**) *with PPA.* At 100°, **20** (3.00 g, 12.0 mmol) was added with stirring into PPA (11.3 g). Stirring was continued at this temp. for 15 min, and the mixture was then poured into H_2O. The product was extracted with CH_2Cl_2, and the org. extract was washed to neutrality and concentrated on the rotary evaporator. The resulting residue was purified by FC (silica gel; hexane/Et_2O 8:2 and 5:5) to provide (−)-**13**/(−)-**14** (1:1; 359 mg, 13%) and (−)-**12**/(−)-**15** (87:13; 180 mg, 6%).

Reaction of (−)-Isosclareolide with PPA. At 100°, isosclareolide [19][20] (4.00 g, 16.0 mmol) was added with stirring into PPA (15.0 g). Stirring was continued for 15 min, and the mixture was poured into H_2O. The product was extracted with CH_2Cl_2, and the extract was washed to neutrality and concentrated on the rotary evaporator. FC (silica gel; hexane/Et_2O 8:2 and 5:5) of the resulting residue furnished (−)-**13**/(−)-**14** (6:1; 740 mg, 20%) and (−)-**12**/(−)-**15** (92:8; 384 mg, 10%).

*(2a*R,*3*R,*5a*R*)-2a,3,4,5,5a,6,7,8-Octahydro-2a,3,6,6-tetramethyl-1(2*H*)-acenaphthylen-1-one* (**24**). (+)-Sclareolide (**1**; 50.0 g, 200 mmol) was added to a stirred soln. of P_2O_5 (24.0 g, 169 mmol) in MsOH (240 g, 2.50 mol), and the resulting mixture was heated for 50 min at 105°. The mixture was cooled with an ice bath and quenched with ice/H_2O 1:1. The product was extracted with Et_2O (3×), and the combined org. extracts were washed with 2N aq. NaOH and brine. Evaporation of the solvent on the rotary evaporator and distillation of the resulting residue (31.5 g) furnished at 115–119°/0.6 mbar a fraction (9.50 g, 20%) containing (−)-**12** (50%), (−)-**13** (3%), (−)-**14** (13%), (−)-**15** (19%), and **24** (8%), and at 119–126°/0.6 mbar a fraction (11.5 g, 25%) containing (−)-**12** (70%) and (−)-**15** (26%). A sample (6.50 g) of the lower-boiling fraction was separated by FC (575 g silica gel; hexane/Et_2O 6l95:5, 6l9:1, 4l8:2) to afford pure **24** (241 mg), besides pure (−)-**12** (1.03 g), (−)-**13** (63 mg), (−)-**14** (259 mg), and (−)-**15** (199 mg).

Data of **24**. IR (neat): 1695*s* (C=O, unsat.), 1640*m* (C=C). ^{1}H-NMR ($CDCl_3$): 0.78 (*d*, *J* = 7.0, Me−C(3)); 0.87 (*s*, Me_{ax}−C(6)); 0.95 (*s*, Me_{eq}−C(6)); 1.31 (*m*, H_b−C(7)); 1.32 (*s*, Me−C(2a)); 1.36 (*dd*, *J* = 13.0, 4.0, H_{ax}−C(5)); 1.43 (*m*, H_a−C(7)); 1.51 (*m*, H_b−C(4)); 1.74 (*m*, H_{eq}−C(5)); 1.99 (*d*, *J* = 18.5, H_α−C(2)); 2.00 (*m*, H−C(3)); 2.00–2.25 (*m*, CH_2(8)); 2.06 (*m*, H_a−C(4)); 2.16 (*m*, H−C(5a)); 2.51 (*d*, *J* = 18.5, H_β−C(2)). NOE-DIFF: Me−C(2a)/H_α−C(2), H−C(3), H−C(5a); Me−C(3)/H_β−C(2), H−C(3), H_{eq}−C(4), H_{ax}−C(5). ^{13}C-NMR ($CDCl_3$): 14.5 (*q*, *Me*−C(3)); 16.7 (*t*, C(8)); 22.0 (*t*, C(5)); 23.9 (*q*, Me_{ax}−C(6)); 26.5 (*q*, *Me*−C(2a)); 27.7 (*q*, Me_{eq}−C(6)); 28.1 (*t*, C(4)); 31.6 (*s*, C(6)); 33.8 (*t*, C(7)); 37.4 (*d*, C(3)); 42.9 (*d*, C(5a)); 44.3 (*s*, C(2a)); 47.4 (*t*, C(2)); 134.8 (*s*, C(8a)); 179.4 (*s*, C(8b)); 206.7 (*s*, C(1)). MS (eV): 232 (100, M^+), 217 (28, $[M-Me]^+$), 203 (4, $[M-CHO]^+$), 176 (55, $C_{13}H_{20}^+$), 161 (45, $C_{12}H_{17}^+$), 148 (43, $C_{11}H_{16}^+$), 134 (47, $C_{10}H_{14}^+$), 119 (31, $C_9H_{11}^+$), 105 (38, $C_8H_9^+$), 91 (50, $C_7H_7^+$), 77 (22, $C_6H_5^+$), 55 (20, $C_4H_7^+$), 41 (37, $C_3H_5^+$).

*(−)-(3a*R,*3aβ,5aβ,9aα,9bβ)-2,3,3a,4,5,5a,6,7,8,9,9a,9b-Dodecahydro-6,6,9a-trimethyl-1*H*-benz[*e*]inden-2-one* ((−)-**11**) *and (−)-(3a*S,*3aα,5aβ,9aα,9bα)-2,3,3a,4,5,5a,6,7,8,9,9a,9b-Dodecahydro-6,6,9a-trimethyl-1*H*-benz[*e*]inden-2-one* ((−)-**32**). At amb. pressure, a soln. of (−)-**12**/(−)-**15** (3:1; 11.5 g, 49.5 mmol) in EtOH (150 ml) was hydrogenated for 42 h in the presence of Pd/C (5%; 600 mg, 0.6 mol-%). Filtration, evaporation of the solvent on the rotary evaporator, and recrystallization (hexane/Et_2O 7:3) of the crude material (10.2 g) furnished (−)-**11** (4.00 g, 35%). FC (silica gel (500 g); hexane/Et_2O 1l97:3, 2l95:4, 2l90:10) of the mother liquor provided after recrystallization (pentane) at −80° (−)-**32** (1.55 g, 13%), besides a further amount of (−)-**11** (1.70 g, 15%).

Data of (−)-**11**. M.p. 123–125° (hexane/Et_2O 7:3). $[\alpha]_D^{20} = -138.6$ (*c* = 0.96, $CHCl_3$). IR (neat): 1730*s* (C=O, sat.). ^{1}H-NMR ($CDCl_3$): 0.79 (*s*, Me_{ax}−C(9a)); 0.84 (*s*, Me_{ax}−C(6)); 0.89 (*m*, H_{ax}−C(9)); 0.90 (*s*, Me_{eq}−C(6)); 0.93 (*dd*, *J* = 8.0, 7.0, H−C(5a)); 1.19 (*m*, H_{ax}−C(7)); 1.32–1.60 (*m*, CH_2(5), CH_2(8)); 1.42 (*m*, H_{eq}−C(7)); 1.60 (*m*, H_{eq}−C(9)); 1.73 (*m*, H_{ax}−C(4)); 1.88 (*m*, H_{eq}−C(4)); 1.95 (*m*, H−C(9b)); 2.12 (2*m*, CH_2(3)); 2.15 (*dd*, *J* = 18.0, 8.5, H_{ax}−C(1)); 2.30 (*d*, *J* = 18.0, H_{eq}−C(1)); 2.48 (*m*, C(3a)). NOE-DIFF: H−C(3a)/H−C(3), H−C(4), H−C(9b); Me_{ax}−C(6)/Me_{eq}−C(6), Me−C(9a); Me−C(9a)/H−C(1), Me_{ax}−C(6); H−C(9b)/H−C(1), H−C(3a). ^{13}C-NMR ($CDCl_3$): 15.5 (*q*, Me_{ax}−(9a)); 17.2, 17.9 (2*t*, C(5), C(8)); 21.7 (*q*, Me_{ax}−C(6)); 27.7 (*t*, C(4)); 32.8 (*s*, C(6)); 33.4 (*q*, Me_{eq}−C(6)); 35.7 (*d*, C(3a)); 36.7 (*s*, C(9a)); 40.2 (*t*, C(9)); 41.8, 41.9 (2*t*, C(3), C(7)); 43.0 (*t*, C(1)); 50.1 (*d*, C(9b)); 53.5 (*d*, C(5a)); 220.6 (*s*, C(2)). MS (70 eV): 234 (41, M^+), 219 (60, $[M-Me]^+$), 201 (16, $[M-Me-H_2O]^+$), 149 (20, $C_{11}H_{17}^+$), 123 (99, $C_9H_{15}^+$), 109 (100, $C_8H_{13}^+$), 96 (67, $C_7H_{12}^+$), 81 (58, $C_6H_9^+$), 69 (79, $C_5H_9^+$), 55 (65, $C_4H_7^+$), 41 (97, $C_3H_7^+$). Odor: weak, slightly woody, sandalwood, more powerful on dry down.

Data of (−)-**32**. M.p. 47–49° (pentane, −80°). $[\alpha]_D^{20} = -137.1$ (*c* = 0.89, $CHCl_3$). IR (neat): 1735*s* (C=O, sat.). ^{1}H-NMR ($CDCl_3$): 0.85 (*s*, Me_{ax}−C(6)); 0.88 (*s*, Me_{eq}−C(6)); 1.04 (*m*, H_{ax}−C(4)); 1.10–1.30 (*m*, CH_2(3)); 1.11 (*m*, H−C(9b)); 1.13 (*s*, Me_{ax}−C(9a)); 1.15 (*m*, H_{ax}−C(7)); 1.35 (*m*, H_{ax}−C(5)); 1.40

(m, H_{ax}–C(8)); 1.43 (m, H_{eq}–C(7)); 1.54 (m, H_{eq}–C(5)); 1.63 (m, H_{eq}–C(8)); 1.72 (m, H_{eq}–C(4)); 1.91 (dd, J = 8.0, 7.0, H–C(5a)); 1.97 (dd, J = 18.0, 8.0, H_{α}–C(1)); 2.05–2.28 (m, CH_2(9)); 2.28 (dd, J = 18.0, 8.0, H_{β}–C(1)); 2.46 (2m, H–C(3a), H–C(9b)). NOE-DIFF: H–C(3a)/H–C(1), H–C(9b), Me–C(9a); H–C(9b)/H–C(1), H–C(3a), H_{eq}–C(4), Me–C(9a). ^{13}C-NMR ($CDCl_3$): 18.4 (t, C(8)); 20.9 (t, C(5)); 21.6 (q, Me_{ax}–C(9a)); 21.8 (q, Me_{ax}–C(6)); 29.5 (t, C(4)); 32.6 (s, C(6)); 32.8 (d, C(3a)); 33.3 (q, Me_{eq}–C(6)); 35.4 (s, C(9a)); 36.89 (t, C(9)); 38.5 (t, C(3)); 42.1 (t, C(7)); 45.3 (d, C(9b)); 47.4 (t, C(1)); 51.2 (d, C(5a)); 219.4 (s, C(2)). MS (70 eV): 234 (23, M^+), 219 (35, $[M-Me]^+$), 201 (12, $[M-Me-H_2O]^+$), 149 (25, $C_{11}H_{17}^+$), 123 (55, $C_9H_{15}^+$), 109 (65, $C_8H_{13}^+$), 96 (50, $C_7H_{12}^+$), 81 (41, $C_6H_9^+$), 69 (60, $C_5H_9^+$), 55 (65, $C_4H_7^+$), 41 (100, $C_3H_7^+$). Odor: weak, ambery, woody.

*(–)-(2*S*,2α,3aβ,5aβ,9aα,9bβ)-2,3,3a,4,5,5a,6,7,8,9,9a,9b-Dodecahydro-2,6,6,9a-tetramethyl-1*H*-benz[*e*]inden-2-ol* ((–)-**10**). During 5 min, with occasional heating by means of a heat gun, a soln. of MeI (910 mg, 6.41 mmol) in Et_2O (4.0 ml) was added to a stirred suspension of Mg turnings (160 mg, 6.58 mmol) in Et_2O (4.0 ml) under N_2. After heating the *Grignard* reagent to reflux for 30 min, a soln. of (–)-**11** (1.00 g, 4.27 mmol) in Et_2O (12 ml) was added dropwise with stirring. The mixture was refluxed for 22 h prior to pouring into ice/sat. aq. NH_4Cl. The product was extracted with Et_2O, the Et_2O extract was washed with 2% aq. HCl, sat. aq. $NaHCO_3$, and brine, and dried ($MgSO_4$). The solvent was evaporated on the rotary evaporator, and bulb-to-bulb distillation of the resulting residue provided 1.00 g (94%) of (–)-**10**. $[\alpha]_D^{20} = -36.6$ (c = 1.1, $CHCl_3$). IR (neat): 3300 (br., O–H). ^{1}H-NMR ($CDCl_3$): 0.85 (s, Me_{eq}–C(6)); 0.89 (s, Me_{ax}–C(6)); 0.90 (m, H_b–C(1)); 0.96 (m, H–C(5a)); 1.13 (m, H_{ax}–C(7)); 1.32 (s, Me–C(2)); 1.33 (m, H_{ax}–C(8)); 1.40 (m, H_{eq}–C(7)); 1.43 (m, H_{ax}–C(5)); 1.49 (m, H_b–C(3)); 1.51 (m, H_{eq}–C(8)); 1.52 (m, H_{ax}–C(4)); 1.53 (m, H_{eq}–C(5)); 1.55 (m, H_a–C(1)); 1.62 (m, H_{ax}–C(9)); 1.63 (m, H_{eq}–C(4)); 1.65 (m, H–C(9b)); 1.72 (m, H_{eq}–C(9)); 1.73 (m, H_a–C(3)); 2.02 (m, H–C(3a)). NOE-DIFF: Me–C(2)/H–C(3a); Me_{eq}–C(6)/H–C(5a). ^{13}C-NMR ($CDCl_3$): 17.6 (q, Me–C(9a)); 18.4 (t, C(8)); 19.3 (t, C(5)); 21.6 (q, Me_{ax}–C(6)); 27.0 (t, C(4)); 29.6 (q, Me–C(2)); 33.0 (q, Me_{eq}–C(6)); 33.2 (s, C(6)); 35.5 (d, C(3a)); 35.7 (s, C(9a)); 41.5 (t, C(9)); 42.4 (t, C(7)); 42.7 (t, C(1)); 48.5 (t, C(3)); 50.5 (d, C(5a)); 52.7 (d, C(9b)); 78.2 (s, C(2)). MS (70 eV): 250 (1, M^+), 232 (14, $[M-H_2O]^+$), 217 (16, $[M-H_2O-Me]^+$), 123 (40, $C_9H_{15}^+$), 107 (43, $C_8H_{11}^+$), 94 (100, $C_7H_{10}^+$), 81 (41, $C_6H_9^+$), 69 (38, $C_5H_9^+$), 55 (34, $C_4H_7^+$), 43 (63, $C_3H_7^+$). Odor: Weak, woody, ambery, *Ambrox*® (**2**).

*(–)-(2*S*,2α,3aβ,5aβ,9aα,9bβ)-2,3,3a,4,5,5a,6,7,8,9,9a,9b-Dodecahydro-6,6,9a-trimethyl-1*H*-benz[*e*]inden-2-ol* ((–)-**33**). Under N_2, a soln. of (–)-**11** (1.20 g, 5.12 mmol) in Et_2O (20 ml) was added dropwise during 6 min to a stirred suspension of $LiAlH_4$ (50 mg, 1.32 mmol) in Et_2O (14 ml). After stirring at r.t. for 150 min, AcOEt (2 ml), H_2O (2 ml), and 2N aq. H_2SO_4 (4 ml) were added to the mixture. The aq. layer was extracted with Et_2O (3×), the combined org. extracts were washed to neutrality with H_2O and brine, and concentrated to dryness. Crystallization of the crude material (pentane, –80°) furnished (–)-**33** (1.02 g, 84%). M.p. 82–85° (pentane). $[\alpha]_D^{20} = -33.6$ (c = 0.93, $CHCl_3$). IR (KBr): 3300 (br., O–H). ^{1}H-NMR ($CDCl_3$): 0.85 (s, Me_{ax}–C(6)); 0.88 (s, Me_{eq}–C(6)); 0.89 (m, H_b–C(1)); 0.95 (s, Me–C(9a)); 0.96 (m, H–C(5a)); 1.13 (ddd, J = 12.0, 12.0, 4.0, H_b–C(7)); 1.24 (ddd, J = 11.0, 11.0, 9.0, H_b–C(9)); 1.33 (m, H_b–C(8)); 1.38–1.58 (m, CH_2(5)); 1.40 (m, H_a–C(7)); 1.46 (m, H_b–C(3)); 1.53 (m, H_a–C(8)); 1.54–1.62 (m, CH_2(4)); 1.57 (m, H_a–C(1)); 1.60 (m, H–C(9b)); 1.92 (m, H_a–C(3)); 1.96 (m, H–C(3a)); 2.02 (m, H_a–C(9)). ^{13}C-NMR ($CDCl_3$): 17.7 (q, Me–C(9a)); 18.4 (t, C(8)); 19.3 (t, C(5)); 21.7 (q, Me_{eq}–C(6)); 27.1 (t, C(4)); 33.1 (q, Me_{ax}–C(6)); 33.2 (s, C(6)); 35.1 (d, C(3a)); 35.4 (t, C(3)); 35.6 (s, C(9a)); 42.0 (t, C(9)); 42.4 (t, C(7)); 42.7 (t, C(1)); 50.5 (d, C(5a)); 52.0 (d, C(9b)); 72.9 (d, C(2)). MS: 236 (17, M^+), 221 (29, $[M-Me]^+$), 203 (28, $[M-Me-H_2O]^+$), 177 (4, $[M-C_3H_7O]^+$), 162 (5, $[M-C_3H_7O-Me]^+$), 147 (12, $[M-C_3H_7O-Me-Me]^+$), 133 (11, $C_{10}H_{13}^+$), 123 (100, $C_9H_{15}^+$), 109 (24, $C_8H_{13}^+$), 95 (32, $C_7H_{11}^+$), 81 (34, $C_6H_9^+$), 69 (39, $C_5H_9^+$), 55 (45, $C_4H_7^+$), 41 (63, $C_3H_5^+$). Odor: Very weak to almost odorless.

*(–)-(2*R*,2β,3aβ,5aβ,9aα,9bβ)-2,3,3a,4,5,5a,6,7,8,9,9a,9b-Dodecahydro-6,6,9a-trimethyl-1*H*-benz[*e*]inden-2-ol* ((–)-**34**). At –45°, a soln. of (–)-**11** (1.00 g, 4.27 mmol) in Et_2O (25 ml) was added to liq. NH_3 (250 ml), followed by EtOH (29 ml, 497 mmol). Between –45 and –38°, Li metal (2.43 g, 350 mmol) was added in small chips during 75 min. Stirring was continued at –35° for 15 min, prior to removal of the cooling bath. With evaporation of NH_3, the mixture was allowed to warm to r.t. prior to the careful addition of H_2O (250 ml). The resulting soln. was acidified with 2N HCl (180 ml) and extracted with Et_2O (3 × 80 ml). The combined Et_2O extracts were washed with H_2O and brine, dried ($MgSO_4$), and evaporated. FC (silica gel; hexane/Et_2O 9:1) and recrystallization (pentane/Et_2O, –80°) of the residue provided (–)-**34** (200 mg, 20%). M.p. 76–78° (pentane/Et_2O). $[\alpha]_D^{20} = -7.63$ (c = 1.1, $CHCl_3$). IR (KBr): 3300 (br., O–H). ^{1}H-NMR ($CDCl_3$): 0.83 (m, Me_{ax}–C(6)); 0.76 (s, Me–C(9a)); 0.86 (m, Me_{eq}–C(6)); 0.87 (m, H_b–C(9)); 0.90 (m, H–C(5a)); 1.15 (m, H_b–C(1)); 1.39 (m, H_a–C(1)); 1.52 (m, H_b–C(3)); 1.57 (m, H_a–C(9)); 1.59 (m, H_b–C(7)); 1.62 (m, H_2–C(4)); 1.68 (m, H_a–C(7)); 1.81 (ddd, J = 6.5, 6.5, 5.0, H–C(9b)); 1.98 (ddd, J = 14.5, 7.5, 4.0, H_a–C(3)); 2.29

(*m*, H–C(3a)). ^{13}C-NMR ($CDCl_3$): 16.9 (*q*, *Me*–C(9a)); 18.3 (*t*, C(8)); 21.7 (*q*, Me_{ax}–C(6)); 27.1 (*t*, C(4)); 33.1 (*s*, C(6)); 33.3 (*q*, Me_{eq}–C(6)); 35.7 (*d*, C(3a)); 35.9 (*s*, C(9a)); 37.8 (*t*, C(3)); 41.7 (*t*, C(9)); 42.1 (*t*, C(7)); 42.3 (*t*, C(1)); 52.2 (*d*, C(5a)); 53.8 (*d*, C(9b)); 73.4 (*d*, C(2)). MS (70 eV): 236 (10, M^+), 221 (20, $[M-Me]^+$), 218 (23, $[M-H_2O]^+$), 203 (41, $[M-Me-H_2O]^+$), 177 (4, $[M-C_3H_7O]^+$), 162 (4, $[M-C_3H_7O-Me]^+$), 133 (19, $C_{10}H_{13}^+$), 123 (97, $C_9H_{15}^+$), 109 (42, $C_8H_{13}^+$), 95 (58, $C_7H_{11}^+$), 83 (67, $C_6H_{11}^+$), 69 (53, $C_5H_9^+$), 55 (68, $C_4H_7^+$), 41 (100, $C_3H_5^+$). Odor: Very weak to almost odorless.

(±)-rac-cis-*1,2,3,4,4a,5,8,8a-Octahydro-8a-methylnaphthalen-1-one* (**37**). At –10 to 0° under Ar, a soln. of *2-methylcyclohex-2-enone* (**36**; 30.0 g, 272 mmol) in toluene (300 ml) was added dropwise with stirring into a suspension of $AlCl_3$ (32.8 g, 246 mmol) in toluene (300 ml). The cooling bath was removed, and the mixture was stirred at r.t. for 30 min. Additional toluene (770 ml) was added, and *buta-1,3-diene* (**35**, 46.0 g, 850 mmol) was slowly introduced into the mixture. After heating to 70° and stirring at this temp. for 19 h, the mixture was poured into H_2O (700 ml), and the product was extracted with Et_2O (3 ×). The combined Et_2O extracts were washed with 10% aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated. Distillation of the resulting residue afforded at 109–110°/6 mbar **37** (29.1 g, 65%). IR (neat): 1705*s* (C=O). ^{1}H-NMR ($CDCl_3$): 1.12 (*s*, Me–C(8a)); 1.51–2.70 (*m*, H–C(4a), CH_2(2), CH_2(8)); 5.61 (*m*, H–C(6), H–C(7)). MS (70 eV): 164 (27, M^+), 149 (26, $[M-Me]^+$), 131 (32, $[M-Me-H_2O]^+$), 121 (100, $[M-C_3H_7]^+$), 105 (59, $C_8H_9^+$), 93 (68, $C_7H_9^+$), 79 (62, $C_6H_7^+$).

(±)-rac-cis-*1,2,3,4,4a,5,6,7,8,8a-Decahydro-8a-methylnaphthalen-1-one* (**38**). A 300-ml autoclave was charged with a soln. of **37** (23.0 g, 140 mmol) in EtOH (280 ml), and 5 wt.-% Pd/C (1.15 g, 0.54 mmol) was added. Following two times of two cycles of evacuation and flushing with first N_2 and then H_2, the mixture was hydrogenated at 10 bar H_2 for 2 h. The catalyst was removed by filtration over a pad of silica gel, and the filtrate was concentrated in a rotary evaporator. The resulting residue was purified by FC (silica gel; hexane/Et_2O 98:2) to provide **38** (22.0 g, 95%). IR (neat): 1705*s* (C=O). ^{1}H-NMR ($CDCl_3$): 0.84–0.98, 1.26–2.58 (*m*, H–C(4a), CH_2(2), CH_2(8)); 1.21 (*s*, Me–C(8a)). MS (70 eV): 166 (30, M^+), 151 (17, $[M-Me]^+$), 124 (58, $[M-C_3H_6]^+$), 111 (100, $C_8H_{15}^+$), 95 (46, $C_7H_{11}^+$), 81 (58, $C_6H_9^+$), 67 (44, $C_5H_7^+$), 28 (55, CO^+).

tert-*Butyl (±)*-rac-*(4aα)-1,2,3,4,4a,5,6,7,8,8a-Decahydro-1α-hydroxy-8aα-methylnaphthalene-1-acetate* (**39**). At –78° under of N_2, a 1.6M BuLi soln. in hexane (12.5 ml, 20.0 mmol) was added dropwise within 10 min to a soln. of ^{i}Pr$_2$NH (2.85 ml, 20.2 mmol) in toluene (50 ml). The mixture was stirred at 0° for 30 min, and, at –78°, a soln. of ^{t}BuOAc (2.70 ml, 20 mmol) in toluene (10 ml) was added dropwise within 10 min. After stirring at this temp. for 30 min, a soln. of **38** (1.70 g, 10.2 mmol) in toluene (10 ml) was added at 0° within 15 min. Stirring was continued at 0° for 16 h, prior to the careful addition of H_2O (100 ml). The product was extracted with Et_2O (3 ×), and the combined extracts were washed with 10% aq. $NaHCO_3$ and brine, dried ($MgSO_4$), and evaporated on the rotary evaporator. FC (silica gel (100 g); hexane/Et_2O 97:3) of the resulting residue afforded **39** (2.42 g, 84%). IR (neat): 1720*s* (OC=O), 3510*s* (O–H), 1145*m* (O–CO). ^{1}H-NMR ($CDCl_3$): 1.01 (*s*, Me–C(8a)); 1.23–1.82 (*m*, H–C(4a), CH_2(2)–CH_2(8)); 1.47 (*s*, Me_3C); 2.50 (*dd*, *J* = 14.5, 2.0, H_{ax} of CH_2CO); 2.62 (*d*, *J* = 14.5, H_{eq} of CH_2CO); 3.70 (*s*, OH). NOE-DIFF: Me–C(8a)/H_{ax} of CH_2CO. ^{13}C-NMR (C_6D_6): 14.3 (*q*, Me–C(8a)); 22.3, 22.9, 23.0 (3*t*, C(3), C(6), C(7)); 27.0, 27.7 (2*t*, C(5), C(8)); 28.0 (*q*, *Me*$_3$C); 31.9 (*t*, C(4)); 33.5 (*t*, C(2)); 39.3 (*d*, C(4a)); 40.3 (*t*, *C*H_2CO); 40.6 (*s*, C(8a)); 75.6 (*s*, Me_3C); 80.9 (*s*, C(1)); 174.0 (*s*, CO). MS (70 eV): 282 (1, M^+), 226 (70, $[M-C_4H_8]^+$), 208 (60, $[M-C_4H_{10}O]^+$), 167 (10, $[M-C_6H_{11}O_2]^+$), 148 (100, $[M-C_6H_{12}O_2-H_2O]^+$), 122 (26, $C_9H_{14}^+$), 108 (22, $C_8H_{12}^+$), 81 (40, $C_6H_9^+$), 67 (22, $C_5H_7^+$), 57 (53, $C_4H_9^+$), 43 (23, $C_3H_7^+$).

*(±)-(1*RS*,1*RS*)-9-Methyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* (**40**). At 100° under Ar, **39** (10.0 g, 35.4 mmol) was added dropwise with stirring into PPA (37.5 g). After stirring at this temp. for 1 h, the mixture was allowed to cool down, and, at 70°, H_2O (50 ml) was added. The product was extracted with Et_2O (3 ×), and the combined Et_2O extracts were washed with 10% aq. $NaHCO_3$ and brine. After drying ($MgSO_4$) and evaporation of the solvent, the crude material was purified by FC (silica gel; hexane/Et_2O 97:3) to furnish **40** (3.50 g, 52 %). IR (neat): 1700*s* (C=O), 1610*m* (C=C). ^{1}H-NMR ($CDCl_3$): 1.08–1.96 (*m*, CH_2(2)–CH_2(5), CH_2(10)–CH_2(12)); 2.03 (*d*, *J* = 1.5, Me–C(9)); 5.88 (*d*, *J* = 1.5, H–C(8)). ^{13}C-NMR ($CDCl_3$): 14.7 (*q*, *Me*–C(9)); 16.9, 17.0 (2*t*, C(3), C(4)); 22.4 (*t*, C(2)); 28.6, 28.7 (2*t*, C(11), C(12)); 35.0, 36.5 (2*t*, C(5), C(10)); 57.2, 57.7 (2*s*, C(1), C(6)); 131.1 (*d*, C(8)); 182.3 (*s*, C(9)); 214.3 (*s*, C(7)). MS (70 eV): 190 (100, M^+), 175 (88, $[M-Me]^+$), 161 (79, $[M-CHO]^+$), 147 (40, $[M-Me-CO]^+$), 136 (36, $C_{10}H_{16}^+$), 105 (28, $C_8H_9^+$), 91 (26, $C_7H_7^+$), 79 (21, $C_6H_7^+$). Odor: Woody, camphoraceous, resinous, cognac.

*(±)-(1*RS*,2*SR*,6*SR*)-2,9-Dimethyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* (**41**) and *(±)-(1*RS*,2*RS*,6*SR*)-2,9-Dimethyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* (**42**). At 100° under Ar, (±)-*rac*-1,2,3,4,4a,5,6,7,8,8a-decahydro-1-hydroxy-8,8a-dimethylnaphthalen-1-acetate (6.00 g, 20.2 mmol) was added dropwise with stirring into PPA (19.0 g). After stirring at this temp. for 1 h, the mixture was allowed to cool down, and, at 60°, H_2O (50 ml) was

added, and the product was subsequently extracted with Et_2O (3×). The combined extracts were washed with 10% aq. $NaHCO_3$, H_2O, and brine, dried ($MgSO_4$), and evaporated on the rotary evaporator. The resulting residue was purified by FC (silica gel (400 g); hexane/Et_2O 8:1 98:2, 10:1 95:5, 4:1 90:10) to provide pure **41** (254 mg, 6%) and pure **42** (149 mg, 4%).

Data of **41**. IR (neat): 1710*s* (C=O), 1615*m* (C=C). ^{1}H-NMR ($CDCl_3$): 1.08 (*d*, *J* = 7.0, Me–C(2)); 1.11–1.81 (*m*, H–C(2), CH_2(3)–CH_2(5), CH_2(10), CH_2(11)); 1.91–1.98 (*m*, CH_2(12)); 2.12 (*d*, *J* = 1.5, Me–C(9)); 5.88 (*d*, *J* = 1.5, H–C(8)). NOE-DIFF: Me–C(9)/H–C(8). ^{13}C-NMR ($CDCl_3$): 16.9 (*q*, *Me*–C(2)); 19.1 (*q*, *Me*–C(9)); 19.7 (*t*, C(11)); 22.7 (*t*, C(4)); 27.5 (*t*, C(5)); 29.3 (2*t*, C(3), C(12)); 35.2 (*d*, C(2)); 36.7 (*t*, C(10)); 59.0 (*s*, C(1)); 60.8 (*s*, C(6)); 130.1 (*d*, C(8)); 183.2 (*s*, C(9)); 213.1 (*s*, C(7)). MS (70 eV): 204 (97, M^+), 189 (38, $[M-Me]^+$), 176 (16, $[M-CO]^+$), 161 (100, $[M-Me-CO]^+$), 147 (49, $C_{11}H_{15}^+$), 136 (41, $C_{10}H_{16}^+$), 105 (34, $C_8H_9^+$), 91 (31, $C_7H_7^+$), 79 (21, $C_6H_7^+$), 41 (27, $C_3H_5^+$). Odor: Camphoraceous, woody, aromatic.

Data of **42**. IR (neat): 1710*s* (C=O), 1615*m* (C=C). ^{1}H-NMR ($CDCl_3$): 1.08 (*d*, *J* = 7.0, Me–C(2)); 1.13–1.62 (*m*, CH_2(3)–CH_2(5), C(11)); 1.82–2.00 (*m*, H–C(2), CH_2(10), CH_2(12)); 2.17 (*d*, *J* = 1.5 Me–C(9)); 6.02 (*d*, *J* = 1.5, H–C(8)). ^{13}C-NMR ($CDCl_3$): 17.4 (*t*, C(11)); 18.0 (*q*, *Me*–C(2)); 18.6 (*q*, *Me*–C(9)); 22.5 (*t*, C(4)); 26.3 (*t*, C(5)); 29.5 (*t*, C(12)); 35.1 (*t*, C(3)); 36.0 (*d*, C(2)); 37.6 (*t*, C(10)); 60.1 (*s*, C(1)); 61.2 (*s*, C(6)); 134.0 (*d*, C(8)); 181.9 (*s*, C(9)); 214.5 (*s*, C(7)). MS (70 eV): 204 (100, M^+), 189 (57, $[M-Me]^+$), 176 (16, $[M-CO]^+$), 161 (97, $[M-Me-CO]^+$), 147 (64, $C_{11}H_{15}^+$), 136 (73, $C_{10}H_{16}^+$), 121 (85, $C_9H_{13}^+$), 105 (39, $C_8H_9^+$), 91 (39, $C_7H_7^+$), 79 (26, $C_6H_7^+$), 41 (34, $C_3H_5^+$). Odor: Camphoraceous, woody, aromatic.

*(±)-(1*RS*,4*RS*,6*RS*)-4,9-Dimethyltricyclo[4.3.3.0^{1,6}]dodec-8-en-7-one* (**43**). At 100° under Ar, *tert*-butyl (±)-*rac*-(4aα)-1,2,3,4,4a,5,6,7,8,8a-decahydro-1β-hydroxy-6β,8aα-dimethylnaphthalene-1-acetate (14.0 g, 47.2 mmol) was added dropwise with stirring to PPA (44.0 g). After stirring for 1 h at this temp., the mixture was allowed to cool, and H_2O (100 ml) was added. The product was extracted with Et_2O (3×), and the combined extracts washed with sat. aq. $NaHCO_3$, H_2O, and brine, dried ($MgSO_4$), and evaporated on the rotary evaporator. FC (silica gel (420 g); hexane/Et_2O 8:1 98:2, 6:1 95:5, 4:1 90:10, 4:1 80:20) afforded **43** (3.94 g, 41%). IR (neat): 1700*s* (C=O), 1615*m* (C=C). ^{1}H-NMR ($CDCl_3$): 0.88 (*d*, *J* = 6.5, Me–C(4)); 0.92–1.92 (*m*, H–C(4), CH_2(2), CH_2(3), CH_2(5), CH_2(10), CH_2(11), CH_2(12)); 2.02 (*d*, *J* = 1.5, Me–C(9)); 5.86 (*d*, *J* = 1.5, H–C(8)). ^{13}C-NMR ($CDCl_3$): 15.0 (*q*, *Me*–C(9)); 23.0 (*q*, *Me*–C(4)); 23.1 (*t*, C(2)), 24.8 (*d*, C(4)); 27.4, 29.1 (2*t*, C(11), C(12)); 34.5, 34.9, 36.4 (3*t*, C(3), C(5), C(10)); 56.5 (*s*, C(6)); 58.2 (*s*, C(1)); 129.2 (*d*, C(8)); 182.0 (*s*, C(9)); 214.6 (*s*, C(7)). MS (70 eV): 204 (100, M^+), 189 (78, $[M-Me]^+$), 175 (35, $[M-CHO]^+$), 161 (58, $[M-Me-CO]^+$), 147 (36, $C_{11}H_{15}^+$), 133 (31, $C_{10}H_{13}^+$), 105 (31, $C_8H_9^+$), 91 (32, $C_7H_7^+$), 41 (27, $C_3H_5^+$). Odor: Buchu leaf, eucalyptus, woody, aromatic.

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