

Analogues of α -Campholenal (= (1*R*)-2,2,3-Trimethylcyclopent-3-ene-1-acetaldehyde) as Building Blocks for (+)- β -Necrodol (= (1*S*,3*S*)-2,2,3-Trimethyl-4-methylenecyclopentanemethanol) and Sandalwood-like Alcohols¹⁾

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To complete our panorama in structure–activity relationships (SARs) of sandalwood-like alcohols derived from analogues of α -campholenal (= (1*R*)-2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde), we isomerized the epoxy-isopropyl-apopinene (–)-**2d** to the corresponding unreported α -campholenal analogue (+)-**4d** (Scheme 1). Derived from the known 3-demethyl- α -campholenal (+)-**4a**, we prepared the saturated analogue (+)-**5a** by hydrogenation, while the heterocyclic aldehyde (+)-**5b** was obtained *via* a *Bayer-Villiger* reaction from the known methyl ketone (+)-**6**. Oxidative hydroboration of the known α -campholenal acetal (–)-**8b** allowed, after subsequent oxidation of alcohol (+)-**9b** to ketone (+)-**10**, and appropriate alkyl *Grignard* reaction, access to the 3,4-disubstituted analogues (+)-**4f,g** following dehydration and deprotection. (Scheme 2). Epoxidation of either (+)-**4b** or its methyl ketone (+)-**4h**, afforded stereoselectively the *trans*-epoxy derivatives **11a,b**, while the minor *cis*-stereoisomer (+)-**12a** was isolated by chromatography (*trans/cis* of the epoxy moiety relative to the C₂ or C₃ side chain). Alternatively, the corresponding *trans*-epoxy alcohol or acetate **13a,b** was obtained either by reduction/esterification from *trans*-epoxy aldehyde (+)-**11a** or by stereoselective epoxidation of the α -campholenal (+)-**15a** or of its acetate (–)-**15b**, respectively. Their *cis*-analogues were prepared starting from (+)-**12a**. Either (+)-**4h** or (–)-**11b**, was submitted to a *Bayer-Villiger* oxidation to afford acetate (–)-**16a**. Since isomerizations of (–)-**16** lead preferentially to β -campholene isomers, we followed a known procedure for the isomerization of (–)-epoxyverbenone (–)-**2e** to the norcampholenal analogue (+)-**19a**. Reduction and subsequent protection afforded the silyl ether (–)-**19c**, which was stereoselectively hydroborated under oxidative condition to afford the secondary alcohol (+)-**20c**. Further oxidation and epimerization furnished the *trans*-ketone (–)-**17a**, a known intermediate of either (+)- β -necrodol (= (+)-(1*S*,3*S*)-2,2,3-trimethyl-4-methylenecyclopentanemethanol; **17c**) or (+)-(*Z*)-lancifolol (= (1*S*,3*R*,4*Z*)-2,2,3-trimethyl-4-(4-methylpent-3-enylidene)cyclopentanemethanol). Finally, hydrogenation of (+)-**4b** gave the saturated *cis*-aldehyde (+)-**21**, readily reduced to its corresponding alcohol (+)-**22a**. Similarly, hydrogenation of β -campholenol (= 2,3,3-trimethylcyclopent-1-ene-1-ethanol) gave access *via* the *cis*-alcohol *rac*-**23a**, to the *cis*-aldehyde *rac*-**24**.

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Introduction. – We have already described the synthesis of α -campholenal analogues [1], necessary for both the building of a large database of new sandalwood-like alcohols, and the validation of a structure–activity relationship (SAR) model based on an olfactive comparison of their enantiomers. To pursue with the second chapter of this study, which shall compare, complete, and refine models (see **Bc,d** in [2]³⁾) resulting from superimposition (see **A** in [3]), we now wish to present the preparation of some new key starting materials.

Results and Discussion. – Epoxidation of α -pinene analogues (–)-**1** [1] [4] allows, by two independent pathways, the transformation of the corresponding epoxy derivatives (–)-**2**, either to the fencholenal analogues (+)-**3b,c** [5] [6] or to the α -campholenal analogues (+)-**4a–c** [1] [6] [7] (*Scheme 1*). We thus completed our structure collection by oxidation of the known isopropyl apopinene (–)-**1d**⁴⁾ [8] (AcO₂H, toluene; 70%) to the unreported epoxy derivative (–)-**2d**. Further isomerization (ZnCl₂, toluene; 26%) afforded, after an efficient distillation, aldehyde (+)-**4d**, an analogue of α -campholenal (= (1*R*)-2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde). Interested in investigating the electronic or H-bond acceptor influence on receptor(s) interactions⁵⁾ when the unsaturation is situated in the lipophilic cyclic part of the molecule, we chose to hydrogenate aldehyde (+)-**4a** to the corresponding saturated aldehyde (+)-**5a** (H₂, 5% Pd/C, EtOH; 88%), to avoid stereochemical complications resulting from a supplementary substituent.

Also curious with respect to the role played by the lipophilicity, we prepared the oxaaanalogue (+)-**5b** via a *Bayer-Villiger* oxidation (MCPBA, CH₂Cl₂; 98%) of the known ketone (+)-**6**⁶⁾ [10] (*Scheme 1*). The resulting acetate (+)-**7a** was saponified (KOH, H₂O, EtOH; 63%), and the corresponding alcohol (+)-**7b** was oxidized (PCC, CH₂Cl₂; 55%) to (+)-**5b**.

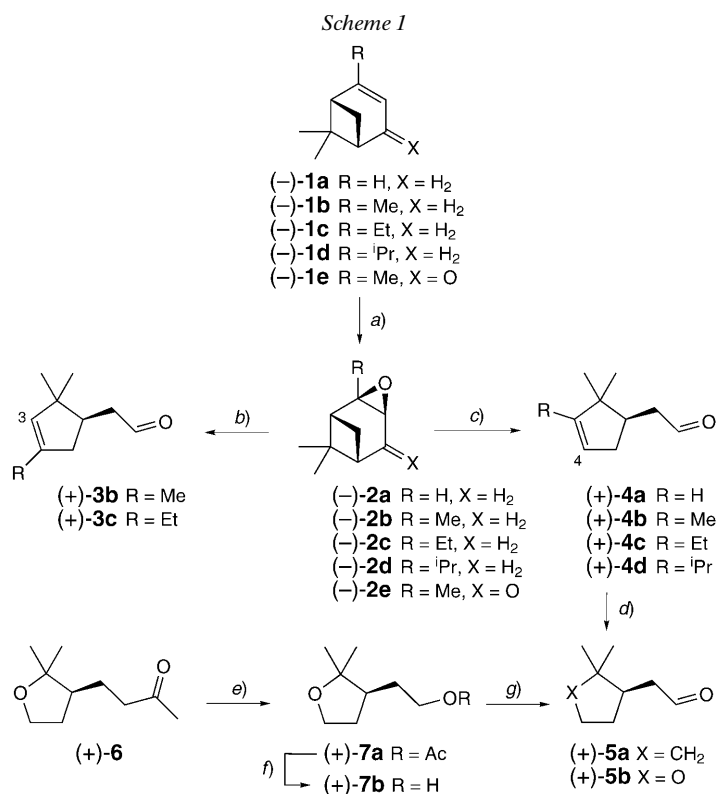
Although we had already reached some conclusions about the steric influence of the substitutions in either position C(3) or C(4) of (+)-**4a** and analogues, we were also interested in preparing analogues with substitution in both positions. Accordingly, the known acetal (–)-**8b** [11a] was submitted to a stereoselective hydroboration (BH₃·Me₂S, THF, NaOH, H₂O₂; 98%) (*Scheme 2*). The resulting secondary alcohol (+)-**9b** was then oxidized (PCC, CH₂Cl₂; 77%) to ketone (+)-**10**, prior to either a Me (98%) or Et (96%) *Grignard* addition affording stereoselectively the tertiary alcohols (+)-**9f,g**. Further dehydration (P₂O₅, toluene; 98%) furnished the unsaturated ace-

³⁾ See the conclusion in [3].

⁴⁾ $[\alpha]_D^{20} = -29.6$ ($c = 1.0$, EtOH).

⁵⁾ At *Givaudan AG*, *Bieri* and co-workers identified endogenous olfactory receptors present in rat primary olfactory receptor neurons, for which activation was dependent on the presence of a rigidifying C=C bond (or a cyclopropane ring of similar electronic density) in the side chain of a same class of olfactively active α -campholenal-derived hydroxy-substituted agonists. Neither the typical sandalwood-like (3*α*, 5*α*)-androst-16-en-3-ol nor the octanal, as negative control, activated these receptors [9]. Their conclusions are unfortunately based on racemic material. We are indebted to the main author for this confirmation.

⁶⁾ $\alpha_D^{20} = +10.4$. ¹³C-NMR: 21.9 (*q*); 24.3 (*t*); 27.5 (*q*); 29.9 (*q*); 31.8 (*t*); 43.0 (*t*); 48.1 (*d*); 64.8 (*t*); 81.6 (*s*); 208.4 (*s*); herbaceous. (–)-(*R*)-**6**: $\alpha_D^{20} = -10.7$; phenolic, urine, aromatic, artemisia.



a) AcO₂H, AcOH, NaHCO₃, toluene; or 30% H₂O₂ soln., NaOH, MeOH. b) HBr, Et₂O, then AgNO₃, ^tBuOH. c) ZnBr₂, toluene, 110°. d) H₂, 5% Pd/C, EtOH. e) MCPBA (3-chloroperbenzoic acid), CH₂Cl₂, 40°. f) KOH, H₂O, EtOH, 85°. g) PCC (pyridinium chlorochromate), CH₂Cl₂.

tals $(+)\text{-8f,g}$, which were readily hydrolyzed to the corresponding aldehydes $(+)\text{-4f'}$, $\mathbf{g}$ (10% aqueous HCl solution, THF; 81–40%). By epoxidizing the commercially available sandalwood-like odorant *Brahmanol*^{®8)}, Schulze and co-workers earlier showed that the diastereoisomers possessing the O-atom *cis* with respect to the side chain were stronger in odor than those with a corresponding *trans*-epoxy moiety [13a]. Since this synthetic approach is restricted to mono-unsaturated skeletons as starting materials, often as mixtures of diastereoisomers in their branched saturated side chain, we were only interested in preparing α -campholenal analogues $(+)\text{-11a}^9)$ [11b] [14] and $(+)\text{-12a}$, already possessing the appropriate epoxy configuration, for fur-

7) Independently, Schulze and co-workers followed another approach for the preparation of $\mathbf{4f}$, which, like $\mathbf{4a}$, is of undefined absolute configuration in [12].

8) 2-Methyl-4-(2,2,3-trimethylcyclopent-3-en-1-yl)butan-1-ol (= β ,2,2,3-tetramethylcyclopent-3-ene-1-butanol), chiroptical properties not reported.

9) $[\alpha]_D^{20} = +6.8$ ($c = 1.1$, EtOH). ¹³C-NMR: 13.2 (*q*); 19.0 (*q*); 20.6 (*q*); 32.0 (*t*); 37.3 (*d*); 41.3 (*s*); 44.2 (*t*); 62.1 (*d*); 68.3 (*s*); 202.0 (*s*); odorless.

ther aldol condensations. Epoxidation of α -campholenal (+)-**4b** (AcO₂H, AcONa, CH₂Cl₂; 78% [11b]) afforded a 95:5 mixture of (+)-**11a**/(+)-**12a**, separated by column chromatography (CC) on SiO₂. Their independent reductions (NaBH₄, MeOH) gave the corresponding unreported alcohols (+)-**13a** (80%) and (+)-**14a** (83%), while further esterification (Ac₂O, py) afforded the epoxy acetates (+)-**13b**¹⁰ [13] (86%) and (+)-**14b** (74%), respectively. Since we could not directly and satisfactorily reverse the stereoselectivity of the epoxidation, starting from either (+)-**4b**, (+)-**15a** or (–)-**15b** [1][15][16]¹¹), we also unsuccessfully attempted an intramolecular epoxidation (30% H₂O₂ solution, THF or ^tBuOOH, (PhCH₂)Me₃NOH, THF, 20°) *via* the trimellityl anhydride monoester (–)-**15c**, obtained from the corresponding commercially available acyl chloride and (+)-**15a** (AgCN, toluene 110°; 29%).

The known secondary alcohol (+)-**15d**¹²) [18] was oxidized to the corresponding known ketone (+)-**4h** [18a][19], prior to further stereoselective epoxidation to (–)-**11b** (MCPBA, CH₂Cl₂; 83%; 91% *trans*) [13a]. Alternatively, either of the methyl ketones (+)-**4h** and (–)-**11b** was treated with an excess of MCPBA in refluxing CH₂Cl₂ to afford the corresponding epoxyacetate (–)-**16a** (33%), which was saponified (LiOH·H₂O, THF/H₂O 5:2, 82%) to the corresponding primary alcohol (–)-**16b**, prior to be protected as its ^tBuMe₂Si ether (–)-**16c** (^tBuMe₂SiCl, 1*H*-imidazole, DMF; 71%)¹³). This approach, towards a potential intermediate of (+)- β -necrodol (= (1*S*,3*S*)-2,2,3-trimethyl-4-methylenecyclopentanemethanol; (+)-**17c**) [16b][20]¹⁴) *via* diastereoselective isomerization of epoxides **16** was nevertheless not realized, due to the concurrent *Nametkin* rearrangement, leading efficiently to β -campholenic derivatives [5d].

Starting from the known α -campholenic enamines (+)-**18a,b**¹⁵) [3][22], we also prepared the α -norcampholenal (+)-**19a**¹⁶) by photo-oxygenation (Rose Bengal, MeOH, H₂O, AcONa, O₂, *h* ν ; 35%)¹⁷). However, since this method gave partially racemized

¹⁰) [α]_D²⁰ = +6.1, (*c* = 1.3, EtOH). ¹³C-NMR: 13.2 (*q*); 18.7 (*q*); 20.8 (*q*); 21.0 (*q*); 28.6 (*t*); 32.0 (*t*); 39.6 (*d*); 41.3 (*s*); 62.3 (*d*); 63.8 (*t*); 68.7 (*s*); 171.1 (*s*); fruity, ester. (–)-**13b**: [α]_D²⁰ = –6.2, (*c* = 1.5, EtOH); cedar, camphor.

¹¹) (+)-**15a** (MCPBA, CH₂Cl₂, 20°; 84%) afforded a 73:27 mixture of (+)-**13a**/(+)-**14a**. Starting from either (–)-**8b** or (–)-**15b**, Schulze and co-workers obtained up to 11–19% of *cis*-epoxy derivatives using AcO₂H/Na₂CO₃ in toluene at 110° [13a]. For X-ray analyses of *trans*-epoxides, see [11a][17a]. For *cis*-epoxides of fencholenic derivatives, see [5b][17b].

¹²) α _D²⁰ = +9.7. ¹³C-NMR: 12.6 (*q*); 19.7 (*q*); 23.2 (*q*); 25.6 (*q*); 35.8 (*t*); 39.9 (*t*); 47.0 (*s*); 47.6 (*d*); 67.9 (*d*); 121.8 (*d*); 148.5 (*s*); spicy, slightly perillc.

¹³) Direct oxidation of α -campholenal (+)-**4b** (2.2 equiv. of MCPBA, CH₂Cl₂, 40°; 60%) afforded epoxy acid (+)-**11c**, alternatively also obtained in 39% yield by AgNO₃/NaOH oxidation of (+)-**11a**.

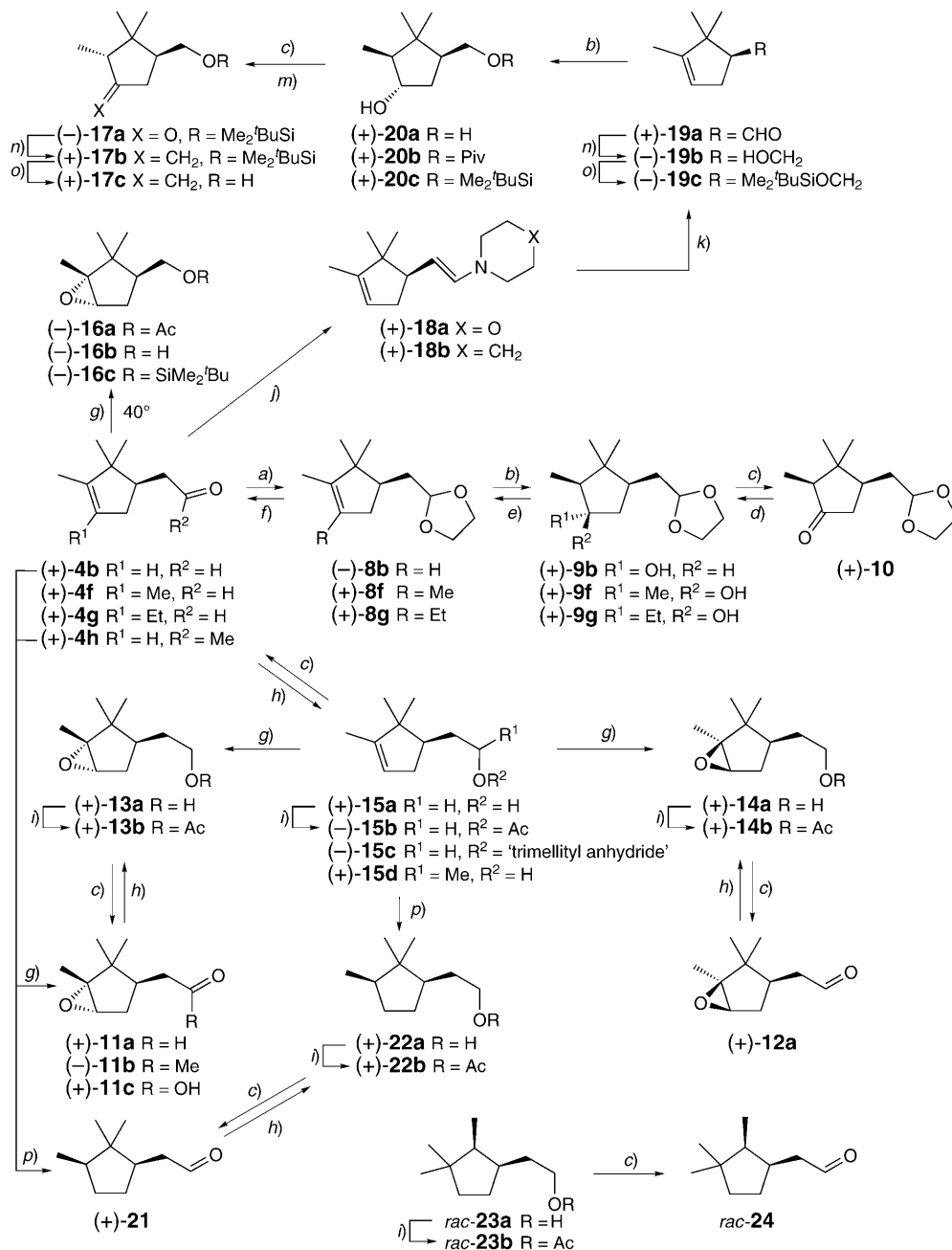
¹⁴) For the synthesis of (–)- α -necrodol and epimers, see [16a], then [21].

¹⁵) (+)-(*R,E*)-**18b**: α _D²⁰ = +13.6. ¹³C-NMR: 13.0 (*q*); 20.3 (*t*); 24.5 (*t*); 25.1 (*t*); 25.4 (2*t*); 37.2 (*t*); 47.7 (*s*); 50.3 (2*t*); 53.1 (*d*); 101.8 (*d*); 121.8 (*d*); 140.6 (*d*); 148.4 (*s*). (–)-(*S,E*)-**18b**: α _D²⁰ = –18.8.

¹⁶) Our initial interest in both enantiomers of this aldehyde was motivated by the opening (AlCl₃/LiAlH₄, Et₂O; 95–98%) of their acetals derived from optically pure butane-2,3-diol, to afford oxa-sandalwood-like alcohols of well established configuration in the side chain. These twenty years old results shall be published in due course.

¹⁷) We are indebted to Drs. M. Bortolussi and J. Vaillant from *De Laire Cie* for kindly providing us (13th October 1987) with the detailed *Exper. Part* of their unpublished photo-oxygenation of (+)-**18a** to (+)-**19a**.

Scheme 2



a) Ethylene glycol, TsOH. b) $\text{BH}_3 \cdot \text{Me}_2\text{S}$, THF, then NaOH, 30% H_2O_2 soln. c) PCC, CH_2Cl_2 . d) R^1MgX , Et_2O . e) P_2O_5 , toluene. f) 10% aq. HCl soln., THF, 50° . g) MCPBA, CH_2Cl_2 . h) NaBH_4 , MeOH. i) Ac_2O , pyridine. j) Morpholine or piperidine, TsOH, cyclohexane. k) MeOH, H_2O , Rose Bengal, AcONa , $h\nu$, O_2 . l) $\text{Me}_2^t\text{BuSiCl}$, 1*H*-imidazole, DMF or CH_2Cl_2 . m) MeONa , MeOH, 65° . n) $\text{TiCl}_4\text{ZnCH}_2\text{Br}_2$, THF, CH_2Cl_2 . o) Bu_4NF , THF. p) H_2 , 10% Pd/C, AcOEt .

material, we preferred the known rearrangement of epoxy-verbenone (–)-**2e** [23], using the protocol of *Thomas-Bessière-Chrétien* and co-workers (ZnBr_2 , toluene; 47%) [24]¹⁸). This aldehyde was either immediately reduced (LiAlH_4 , Et_2O , 94%) to the corresponding primary alcohol (–)-**19b** [25]¹⁹) or submitted to a hydroboration ($\text{BH}_3\cdot\text{Me}_2\text{S}$, THF; 72%) [15b][26] to stereoselectively afford diol (+)-**20a**²⁰). For an alternative approach to (+)- β -necrodol, we initially protected the primary OH function with pivalic acid to afford (+)-**20b** (tBuCO_2H , dicyclohexylcarbodiimide (DCC), *N,N*-dimethylpyridin-4-amine (DMAP), CH_2Cl_2 ; 74%), but finally, preferred a tBuMe_2Si protection ($\text{tBuMe}_2\text{SiCl}$, 1*H*-imidazole, DMF, -30° to 20° ; 95%) to give (+)-**20c**²¹). An alternative and more logical access to (+)-**20c** was *via* protection ($\text{tBuMe}_2\text{SiCl}$, 1*H*-imidazole, DMF, -30° to 20° ; 40%) of (–)-**19b** to (–)-**19c**, followed by hydroboration and oxidation ($\text{BH}_3\cdot\text{SMe}_2$, CH_2Cl_2 , then H_2O_2 ; 22%). Further oxidation (PCC, CH_2Cl_2 ; 80%) gave access to the known intermediate (–)-**17a** [27], after epimerization at the Me-substituted α -position (MeONa , MeOH ; 87%) [20d]. The remaining steps consisted in a methylenation reaction ($\text{TiCl}_4/\text{CH}_2\text{Br}_2/\text{Zn}$, THF, CH_2Cl_2 ; 51%) [20b], followed by desilylation of (+)-**17b** (Bu_4NF , THF; 93%) to the nonnatural (+)- β -necrodol (+)-**17c**²²). We completed our work by hydrogenating (+)- α -campholenal (+)-**4b** (H_2 , 10% Pd/C, AcOEt ; 78%) to the known but uncharacterized saturated *cis*-aldehyde (+)-**21** [29]. Its reduction (LiAlH_4 , Et_2O ; 95%) afforded the known but also uncharacterized *cis*-alcohol (+)-**22a** [16c][30]. Alternatively, this latter was also obtained by a stereoselective hydrogenation of alcohol (+)-**15a** (H_2 , 10% Pd/C, AcOEt ; 90%; >94% *cis*)²³), prior to further re-oxidation (PCC, CH_2Cl_2 ; 98%) to aldehyde (+)-**21**²⁴). Similarly, hydrogenation (10% *Raney*-Ni, 90 bar, EtOH ; 53%)²⁵) of β -campholenol (=2,3,3-trimethylcyclopent-1-ene-1-ethanol) [31] gave the unreported saturated *cis*-analogue *rac*-**23a**, which was oxidized (PCC, CH_2Cl_2 ; 98%) to the corresponding *cis*-aldehyde *rac*-**24**.

¹⁸) The absolute configuration of (–)-**2e** is erroneously depicted in the French paper.

¹⁹) Its epoxidation (MCPBA, CH_2Cl_2 , 20° ; 72%) afforded a 1:1 mixture of (–)-**16b** and 4,4,5-trimethyl-6-oxabicyclo[3.1.0]hexane-1-methanol. Similarly, (–)-**19c** was epoxidized (MCPBA, CH_2Cl_2 , 20° ; 77%) to (–)-**16c**. For *rac*-**19b**, see [26].

²⁰) For the corresponding stereoisomer, see [27].

²¹) Although being a multi-step procedure, (+)-**20c** may alternatively be obtained *via* a bis-protection/regio-monodeprotection process ($\text{tBuMe}_2\text{SiCl}$, 1*H*-imidazole, CH_2Cl_2 ; then Bu_4NF , THF; 97%).

²²) Isolated from the defensive spray of the red-lined carrion beetle *Necrodes surinamensis* [28], natural (–)- β -necrodol may be similarly obtained from the antipodal (+)-epoxy-verbenone (+)-**2e** ($\alpha_D^{20} = +119.2$) *via* (–)-**20a** ($[\alpha]_D^{20} = -30.6$, ($c = 1.0$, EtOH)). The report [16b] prompted us to stop our efforts in that direction, as well as in chemical-yields optimization.

²³) An identical stereoselectivity was observed by hydrogenation of alcohol (+)-**15a** under various conditions such as: *Crabtree*'s, $[\text{Ir}(\text{cod})(\text{py})(\text{PCy}_3)]^+(\text{PF}_6)^-$ in CH_2Cl_2 (88% *cis*); 10% $\text{Rh}/\text{Al}_2\text{O}_3$ in cyclohexane (93% *cis*); *Pearlman*'s, 20% $\text{Pd}(\text{OH})_2/\text{C}$ in cyclohexane (93% *cis*); *Raney*-Ni in cyclohexane (94% *cis*) or PtO_2 in cyclohexane (94% *cis*).

²⁴) Acylation of (+)-**22a** (Ac_2O , pyridine, 95%) afforded the known but uncharacterized acetate (+)-**22b** [30].

²⁵) With 10% Pd/C in AcOH under 90 bar H_2 , a 5:3 *cis/trans* mixture of *rac*-**23a** was obtained *via* double-bond migration, contaminated by 20% of isomerized alcohol *rac*-**22a**. Acetylation of *rac*-**23a** (Ac_2O , pyridine; 56%) afforded *rac*-**23b**.

Conclusions. – In connection with SAR studies of sandalwood-like alcohols derived from α -campholenal (+)-**4b**, we prepared the sterically demanding unreported analogue (+)-**4d**, starting from the known isopropyl- α -apopinene derivative (–)-**1d**. The new analogues (+)-**5a,b** should help us in comparing both the lipophilicity and H-bond influence, in the absence of steric effects, between their appropriate derivatives, with those derived from the dimethyl aldehyde (+)-**4a**. Oxidative hydroboration of the protected α -campholenal acetal (–)-**8b** allowed, after oxidation to ketone (+)-**10**, the introduction of a supplementary alkyl substituent onto the C=C bond of the α -campholenal analogue (+)-**4f,g**, via a *Grignard* reaction, dehydration, and deprotection sequence. The stereoselective epoxidation of either α -campholenal (+)-**4b** or its corresponding alcohol (+)-**15a**, permitted the synthesis of the main *trans*-epoxy-aldehyde (+)-**11a**, as well as the isolation of the minor *cis*-stereoisomers (+)-**12a** and (+)-**14a**. Over-oxidation of methyl ketones (+)-**4h** or (–)-**11b**, with MCPBA afforded the *trans*-epoxy ester (–)-**16a**. The known ZnBr_2 isomerization of epoxyverbenone (–)-**1e** delivered the norcampholenal analogue (+)-**19a**. Its corresponding alcohol (–)-**19b** was protected as its silyl ether (–)-**19c**, prior to an oxidative hydroboration. The resulting secondary alcohol (+)-**20c** was oxidized, thus allowing isolation of epimerized ketone (–)-**17a**. This latter was then transformed to (+)- β -necrodol (+)-**17c** after appropriate methylation and deprotection. Finally, hydrogenation of β -campholenol furnished the *cis*-alcohol *rac*-**23a**, prior to oxidation to the corresponding *cis*-aldehyde *rac*-**24**. These new derivatives, available in both enantiomeric series, shall help us to investigate the influence of the lipophilic part in sandalwood-like alcohols derived from campholenal analogues.

Experimental Part

General. For optical purity of the starting materials and generalities, see [1].

(–)-(1*R*,2*R*,3*S*,5*R*)-2,3-Epoxy-2-isopropyl-6,6-dimethylbicyclo[3.1.1]heptane (= (1*R*,2*R*,4*S*,6*R*)-7,7-Dimethyl-2-(1-methylethyl)-3-oxatricyclo[4.1.1.0^{2,4}]octane; (–)-**2d**). As described in the *General Procedure A* of [1]: (–)-**2d** (70%). B.p. 80°/0.31 mbar. $[\alpha]_{\text{D}}^{20} = -49.3$ ($c=1.0$, EtOH). IR: 2967, 2919, 2873, 1470, 1384, 1367, 1240, 1055, 1039, 919, 874. ¹H-NMR: 0.81 (*d*, $J=7$, 3 H); 0.90 (*s*, 3 H); 0.95 (*d*, $J=7$, 3 H); 1.30 (*s*, 3 H); 1.64 (*d*, $J=9$, 1 H); 1.72 (*m*, 1 H); 1.79 (*sept.*, $J=7$, 1 H); 1.87 (*m*, 1 H); 2.0 (*m*, 2 H); 2.11 (*t*, $J=6$, 1 H); 3.23 (*d*, $J=5$, 1 H). ¹³C-NMR: 16.8 (*q*); 17.2 (*q*); 20.4 (*q*); 25.7 (*t*); 26.9 (*q*); 27.8 (*t*); 30.8 (*d*); 40.1 (*d*); 40.6 (*s*); 42.8 (*d*); 55.1 (*d*); 66.3 (*s*). MS: 180 (8, M^{+}), 165 (32), 137 (35), 121 (40), 111 (52), 95 (90), 83 (56), 69 (84), 67 (78), 55 (70), 43 (83), 41 (100). Minty, terpenes.

(+)-(1*R*)-3-Isopropyl-2,2-dimethylcyclopent-3-ene-1-acetaldehyde ((+)-**4d**). As described in the *General Procedure B* of [1], (–)-**2d** afforded, after 30 min, quantitatively a 56:44 mixture of (+)-**4d**/ (–)-(1*S*,2*R*)-2-isopropyl-6,6-dimethylbicyclo[3.1.1]heptan-3-one. Purification by distillation through a 10 cm Vigreux column: pure (+)-**4d** (26%), the bicycloheptanone (32%).

Data of (+)-4d: B.p. 100°/3.8 Torr. $[\alpha]_{\text{D}}^{20} = +10.4$ ($c=0.95$, CCl_4). IR: 2959, 1727, 1466, 1364. ¹H-NMR: 0.82 (*s*, 3 H); 1.04 (*d*, $J=7$, 3 H); 1.05 (*s*, 3 H); 1.07 (*d*, $J=7$, 3 H); 1.91 (*m*, 1 H); 2.23 (*m*, 2 H); 2.38 (*m*, 1 H); 2.5 (*m*, 2 H); 5.32 (*br. t*, 1 H); 9.80 (*t*, $J=4$, 1 H). ¹³C-NMR: 20.9 (*q*); 24.1 (*q*); 24.4 (*q*); 26.0 (*q*); 26.3 (*d*); 35.5 (*t*); 44.6 (*d*); 45.0 (*t*); 47.9 (*s*); 119.1 (*d*); 159.1 (*s*); 203.1 (*d*). MS: 180 (1, M^{+}), 136 (45), 121 (100), 105 (11), 95 (20), 91 (11), 67 (12), 41 (17).

(–)-(1*S*,2*R*)-2-Isopropyl-6,6-dimethylbicyclo[3.1.1]heptan-3-one: B.p. 60°/2.7 Torr. $[\alpha]_{\text{D}}^{20} = -58.3$, ($c=1.2$, CHCl_3). IR: 2957, 1712, 1467, 1411, 1386, 1369, 1324, 1150, 1040. ¹H-NMR: 0.82 (*d*, $J=7$, 3 H); 0.88 (*s*, 3 H); 1.00 (*d*, $J=7$, 3 H); 1.27 (*d*, $J=12$, 1 H); 1.34 (*s*, 3 H); 2.06 (*m*, 1 H); 2.14 (*dt*, $J=2$,

7, 1 H); 2.30 (*m*, 1 H); 2.34 (*m*, 1 H); 2.42 (*dd*, $J=2, 16$, 1 H); 2.48 (*m*, 1 H); 2.62 (*dt*, $J=2, 16$, 1 H). ^{13}C -NMR: 20.1 (*2q*); 21.6 (*q*); 26.5 (*q*); 28.4 (*d*); 30.3 (*t*); 38.0 (*d*); 39.6 (*d*); 39.8 (*s*); 45.1 (*t*); 57.4 (*t*); 214.0 (*s*). MS: 180 (13, M^+), 137 (8), 111 (68), 95 (21), 83 (78), 69 (100), 55 (69), 41 (78).

(+)-(1*R*)-2,2,3,4-Tetramethylcyclopent-3-ene-1-acetaldehyde ((+)-**4f**). A mixture of acetal (+)-**8f** (32.6g, 155 mmol) in THF (325 ml) and 10% aq. HCl soln. (239 ml) was heated at 50° for 2.5 h. The cold soln. was extracted with Et₂O. The org. phase was washed with sat. aq. NaHCO₃ soln. and H₂O, dried (Na₂SO₄), concentrated, and purified by distillation through a 15 cm Vigreux column: pure (+)-**4f** (81%). B.p. 41°/0.8 mbar. $[\alpha]_{\text{D}}^{20} = +25.3$. IR: 2957, 1727, 1470. ^1H -NMR: 0.76 (*s*, 3 H); 0.98 (*s*, 3 H); 1.51 (*br. s*, 3 H); 1.59 (*br. s*, 3 H); 1.94 (*m*, 1 H); 2.20 (*m*, 1 H); 2.35 (*m*, 1 H); 2.38 (*dd*, $J=4, 10$, 1 H); 2.52 (*ddd*, $J=4, 7, 10$, 1 H); 9.80 (*t*, $J=4$, 1 H). ^{13}C -NMR: 9.5 (*q*); 14.1 (*q*); 20.1 (*q*); 26.1 (*q*); 41.4 (*t*); 42.8 (*d*); 45.1 (*t*); 48.1 (*s*); 128.8 (*s*); 138.5 (*s*); 203.3 (*d*). MS: 166 (7, M^+), 151 (11), 122 (100), 109 (67), 107 (81), 105 (12), 91 (28), 81 (22), 41 (27). Green, fatty, floral, herbal, cocoa, camphoraceous, pungent.

(+)-(1*R*)-4-Ethyl-2,2,3-trimethylcyclopent-3-ene-1-acetaldehyde ((+)-**4g**). As described for (+)-**4f**. (+)-**4g** (40%). B.p. 65°/0.7 mbar. $[\alpha]_{\text{D}}^{20} = +22.2$ ($c=1.0$, CHCl₃). IR: 2961, 2714, 1727, 1462, 1361. ^1H -NMR: 0.76 (*s*, 3 H); 0.97 (*t*, $J=7$, 3 H); 0.98 (*s*, 3 H); 1.50 (*br. s*, 3 H); 1.93 (*m*, 1 H); 2.01 (*q*, $J=7$, 2 H); 2.18 (*m*, 1 H); 2.37 (*m*, 2 H); 2.52 (*ddd*, $J=4, 7, 16$, 1 H); 9.81 (*t*, $J=4$, 1 H). ^{13}C -NMR: 9.4 (*q*); 12.6 (*q*); 20.1 (*q*); 21.6 (*t*); 26.0 (*q*); 38.4 (*t*); 42.8 (*d*); 45.1 (*t*); 48.1 (*s*); 134.3 (*s*); 137.7 (*s*); 203.3 (*d*). MS: 180 (10, M^+), 165 (8), 136 (70), 121 (100), 105 (14), 91 (18), 41 (20).

(+)-(1*R*)-2,2-Dimethylcyclopentane-1-acetaldehyde ((+)-**5a**). A soln. of (+)-**4a** (1380 mg, 10 mmol) in EtOH (10 ml) was hydrogenated at 1 atm H₂ over 5% Pd/C (70 mg). Filtration, concentration, and bulb-to-bulb distillation afforded pure (+)-**5a** (88%). B.p. 61°/10 mbar. $\alpha_{\text{D}}^{20} = +8.9$. IR: 2955, 2716, 1727, 1466, 1367. ^1H -NMR: 0.77 (*s*, 3 H); 1.00 (*s*, 3 H); 1.32 (*m*, 1 H); 1.46 (*m*, 2 H); 1.60 (*m*, 1 H); 1.64 (*m*, 1 H); 1.90 (*m*, 1 H); 1.97 (*m*, 1 H); 2.18 (*ddd*, $J=4, 10, 16$, 1 H); 2.48 (*ddd*, $J=2, 4, 16$, 1 H); 9.78 (*t*, $J=4$, 1 H). ^{13}C -NMR: 21.4 (*t*); 21.9 (*q*); 27.7 (*q*); 30.5 (*t*); 40.7 (*s*); 41.2 (*t*); 43.7 (*d*); 45.2 (*t*); 203.2 (*d*). MS: 140 (5, M^+), 125 (20), 107 (32), 97 (49), 96 (47), 81 (80), 69 (54), 55 (77), 41 (100), 39 (64), 29 (50). Green, aldehydic, camphoraceous.

(-)-**5a**: $[\alpha]_{\text{D}}^{20} = -8.2$ ($c=1.0$, CHCl₃).

(+)-(3*R*)-Tetrahydro-2,2-dimethylfuran-3-acetaldehyde ((+)-**5b**). As described in the *General Procedure K* of [3]: (+)-**5b** (55%). B.p. 70°/1.3 mbar. $\alpha_{\text{D}}^{20} = +6.5$. IR: 2972, 1725, 1368, 1153, 1050, 840. ^1H -NMR: 1.03 (*s*, 3 H); 1.26 (*s*, 3 H); 1.63 (*m*, 1 H); 2.28 (*m*, 2 H); 2.41 (*dd*, $J=4, 10$, 1 H); 2.54 (*ddd*, $J=4, 7, 16$, 1 H); 3.83 (*m*, 2 H); 9.81 (*t*, $J=4$, 1 H). ^{13}C -NMR: 22.4 (*q*); 27.3 (*q*); 31.9 (*t*); 42.1 (*d*); 45.2 (*t*); 64.9 (*t*); 81.3 (*s*); 201.2 (*d*). MS: 142 (0, M^+), 127 (52), 99 (11), 83 (21), 59 (72), 55 (63), 43 (100).

(-)-**5b**: $\alpha_{\text{D}}^{20} = -7.0$.

(+)-(3*R*)-Tetrahydro-2,2-dimethylfuran-3-ethanol Acetate ((+)-**7a**). MCPBA (48.3 g, 0.15 mol) was added to a soln. of ketone (+)-**6** (17.45 g, 0.103 mol) in CH₂Cl₂ (175 ml). The mixture was refluxed for 92 h, while three successive portions of MCPBA (6.44g, 20 mmol) were added after 28, 52, and 68 h. The cold mixture was washed with H₂O, 15% aq. NaOH soln., and H₂O to neutrality, dried (MgSO₄), concentrated, and purified by CC (SiO₂, 80 g toluene/AcOEt 95 : 5): pure (+)-**7a** (98%). B.p. 100°/0.14 mbar. $\alpha_{\text{D}}^{20} = +5.2$. IR: 2996, 1734, 1520, 1430. ^1H -NMR: 1.02 (*s*, 3 H); 1.25 (*s*, 3 H); 1.50 (*m*, 1 H); 1.66 (*m*, 1 H); 1.79 (*m*, 2 H); 2.06 (*s*, 3 H); 2.12 (*m*, 1 H); 3.78 (*q*, $J=7, 1$ H); 3.86 (*dt*, $J=4, 7, 1$ H); 4.11 (*m*, 2 H). ^{13}C -NMR: 21.0 (*q*); 22.0 (*q*); 27.4 (*q*); 29.4 (*t*); 31.8 (*t*); 45.4 (*d*); 63.8 (*t*); 64.9 (*t*); 81.6 (*s*); 171.1 (*s*). MS: 186 (1, M^+), 171 (10), 129 (12), 111(19), 86 (9), 68 (24), 43 (100). Tyres.

(-)-**7a**: $\alpha_{\text{D}}^{20} = -2.1$. Spicy, sulfury.

(+)-(3*S*)-Tetrahydro-2,2-dimethylfuran-3-ethanol ((+)-**7b**). A soln. of (+)-**7a** (14.95g, 80.4 mmol) and KOH (16.0 g, 285.3 mmol) in H₂O (16 ml) and EtOH (64.3 ml) was heated under reflux for 30 min. The cold soln. was concentrated, then saturated with NaCl, and extracted with toluene. The org. phase was washed to neutral with brine, dried (Na₂SO₄), concentrated, and purified by CC (cyclohexane/AcOEt 6 : 4 → 1 : 1): pure (+)-**7b** (63%). B.p. 90°/0.34 mbar. $[\alpha]_{\text{D}}^{20} = +5.6$ ($c=0.35$, CHCl₃). IR: 3396, 2931, 1654, 1457, 1368, 1050. ^1H -NMR: 1.02 (*s*, 3 H); 1.24 (*s*, 3 H); 1.42 (*m*, 1 H); 1.63 (*m*, 1 H); 1.69 (*m*, 1 H); 1.87 (*m*, 1 H); 2.12 (*m*, 1 H); 2.20 (*br. s*, 1 OH); 3.62 (*m*, 1 H); 3.75 (*m*, 2 H); 3.85 (*dt*, $J=4, 7, 1$ H). ^{13}C -NMR: 22.0 (*q*); 27.4 (*q*); 31.8(*t*); 33.4 (*t*); 45.0 (*d*); 61.8 (*t*); 65.0 (*t*); 81.8 (*s*). MS: 144 (0, M^+), 129 (85), 111 (18), 86 (23), 68 (55), 59 (95), 55 (44), 43 (100).

(–)-**7b**: $\alpha_D^{20} = -3.1$. Saffron, sulfury, phenolic.

(+)-2-[(1*R*)-2,2,3,4-Tetramethylcyclopent-3-en-1-yl]methyl]-1,3-dioxolane ((+)-**8f**). A soln. of alcohol (+)-**9f** (28.9 g, 127 mmol) in toluene (25 ml) was added dropwise at 0° to a suspension of P₂O₅ (27 g, 190 mmol) in toluene (38 ml). After 3 h, the temp. was raised to 20°, and after a supplementary 1.5 h, the mixture was poured onto ice and extracted with Et₂O. The org. phase was washed to neutral with H₂O, dried (Na₂SO₄), concentrated, and purified by bulb-to-bulb distillation; pure (+)-**8f** (98%). B.p. 60°/0.09 mbar. $\alpha_D^{20} = +20.5$. IR: 2954, 1442, 1360, 1147, 1044, 943. ¹H-NMR: 0.72 (s, 3 H); 0.97 (s, 3 H); 1.48 (br. s, 3 H); 1.58 (br. s, 3 H); 1.62 (m, 1 H); 1.75 (m, 1 H); 1.86 (m, 1 H); 1.98 (m, 1 H); 2.28 (br. dd, *J* = 7, 12, 1 H); 3.83 (m, 2 H); 3.97 (m, 2 H); 4.88 (dd, *J* = 6, 7, 1 H). ¹³C-NMR: 9.5 (q); 14.1 (q); 19.7 (q); 25.9 (q); 34.3 (t); 41.7 (t); 44.4 (d); 48.1 (s); 64.6 (t); 64.9 (t); 104.8 (d); 128.6 (s); 138.6 (s). MS: 210 (12, *M*⁺), 139 (16), 133 (26), 122 (100), 109 (67), 107 (42), 73 (88). Perspiration, menthol.

(+)-[(1*R*)-4-Ethyl-2,2,3-trimethylcyclopent-3-en-1-yl]methyl]-1,3-dioxolane ((+)-**8g**). As described for (+)-**8f**: (+)-**8g** (98%). B.p. 90°/0.26 mbar. $[\alpha]_D^{20} = +16.0$ (*c* = 1.0, CHCl₃). IR: 2958, 2876, 1463, 1410, 1360, 1146, 1089, 1034, 982, 943. ¹H-NMR: 0.72 (s, 3 H); 0.94 (t, *J* = 7, 3 H); 0.97 (s, 3 H); 1.50 (br. s, 3 H); 1.65 (m, 1 H); 1.77 (m, 1 H); 1.86 (m, 1 H); 1.95 (m, 1 H); 2.02 (q, *J* = 7, 2 H); 2.32 (dd, *J* = 7, 14, 1 H); 3.87 (m, 2 H); 3.99 (m, 2 H); 4.90 (dd, *J* = 4, 6, 1 H). ¹³C-NMR: 9.4 (q); 12.8 (q); 19.7 (q); 21.6 (t); 25.8 (q); 34.3 (t); 38.6 (t); 44.4 (d); 48.1 (s); 64.6 (t); 64.9 (t); 104.8 (d); 134.5 (s); 137.9 (s). MS: 224 (21, *M*⁺), 153 (19), 147 (19), 136 (100), 123 (78), 121 (61), 107 (18), 73 (82), 45 (33).

(+)-(1*S*,2*S*,4*R*)-4-[(1,3-Dioxolan-2-yl)methyl]-2,3,3-trimethylcyclopentanol ((+)-**9b**). A soln. of BH₃·Me₂S (68 ml, 725 mmol) was added dropwise at 0° to a soln. of acetal (–)-**8b** (143 g, 723 mmol) in THF (1.4 l). After an additional hour at 0°, 10% aq. NaOH soln. (360 ml), then 30% H₂O₂ soln. (108 ml) were added dropwise at –10°. The mixture was extracted with Et₂O and the org. phase washed with H₂O to neutrality, dried (Na₂SO₄), concentrated, and distilled: (+)-**9b** (98%). B.p. 120°/0.12 mbar. $\alpha_D^{20} = +47.5$. IR: 3422, 2957, 1411, 1367, 1145, 1062, 955, 858. ¹H-NMR: 0.54 (s, 3 H); 0.91 (s, 3 H); 0.96 (d, *J* = 7, 3 H); 1.42 (m, 2 H); 1.62 (br. s, 1 OH); 1.72 (m, 2 H); 1.81 (m, 2 H); 1.89 (m, 1 H); 3.83 (m, 2 H); 3.98 (m, 2 H); 4.83 (dd, *J* = 4, 6, 1 H). ¹³C-NMR: 11.6 (q); 15.7 (q); 25.7 (q); 34.5 (t); 39.4 (t); 43.0 (s); 43.8 (d); 54.0 (d); 64.6 (t); 64.9 (t); 78.3 (d); 104.4 (d). MS: 214 (0.5, *M*⁺), 73 (100), 45 (8). Without character.

(+)-(1*R*,2*S*,4*R*)-4-[(1,3-Dioxolan-2-yl)methyl]-1,2,3,3-tetramethylcyclopentanol ((+)-**9f**). A soln. of MeI (45.3 g, 320 mmol) in Et₂O (61 ml) was added dropwise to a suspension of Mg (7.75 g, 320 mmol) in Et₂O (61 ml) then, a soln. of ketone (+)-**10** (52 g, 245 mmol) in Et₂O (61 ml) was added dropwise. After 1 h at 20°, the mixture was poured onto ice/NH₄Cl. The mixture was extracted with Et₂O, the org. phase was washed with H₂O to neutrality, dried (Na₂SO₄), concentrated, and purified by bulb-to-bulb distillation: pure (+)-**9f** (98%). B.p. 100°/0.14 mbar. $\alpha_D^{20} = +31.1$. IR: 3508, 2954, 1451, 1369, 1287, 1145, 1022, 912. ¹H-NMR: 0.72 (s, 3 H); 0.86 (d, *J* = 7, 3 H); 0.89 (s, 3 H); 1.14 (br. s, 1 OH); 1.26 (s, 3 H); 1.29 (q, *J* = 7, 1 H); 1.56 (m, 3 H); 1.77 (dd, *J* = 8, 12, 1 H); 2.17 (m, 1 H); 3.85 (m, 2 H); 3.97 (m, 2 H); 4.85 (dd, *J* = 4, 6, 1 H). ¹³C-NMR: 7.0 (q); 15.6 (q); 26.8 (q); 30.6 (q); 34.3 (t); 43.6 (s); 44.3 (d); 47.2 (t); 54.5 (d); 64.7 (t); 64.8 (t); 78.0 (s); 104.5 (d). MS: 228 (0.5, *M*⁺), 157 (16), 73 (100), 43 (23). Dusty, gasoline.

(+)-(1*R*,2*S*,4*R*)-4-[(1,3-Dioxolan-2-yl)methyl]-1-ethyl-2,3,3-trimethylcyclopentanol ((+)-**9g**). As described for (+)-**9f**, with EtBr: (+)-**9b** (96%). B.p. 100°/0.11 mbar. $\alpha_D^{20} = +34.8$. IR: 3510, 2954, 1464, 1367, 1144, 1031, 945, 882. ¹H-NMR: 0.72 (s, 3 H); 0.85 (d, *J* = 7, 3 H); 0.89 (s, 3 H); 0.93 (t, *J* = 7, 3 H); 1.11 (br. s, 1 OH); 1.32 (q, *J* = 7, 2 H); 1.41 (m, 2 H); 1.52 (m, 2 H); 1.78 (dd, *J* = 6, 10, 1 H); 2.19 (dd, *J* = 7, 10, 1 H); 3.85 (m, 2 H); 3.97 (m, 2 H); 4.85 (dd, *J* = 4, 6, 1 H). ¹³C-NMR: 7.5 (q); 8.6 (q); 15.9 (q); 26.7 (q); 34.4 (t); 35.2 (t); 43.4 (s); 44.2 (t); 44.3 (d); 52.7 (d); 64.7 (t); 64.8 (t); 80.4 (s); 104.4 (d). MS: 242 (0, *M*⁺), 213 (10), 171 (18), 125 (9), 73 (100), 57 (13), 45 (12). Floral, watery.

(+)-(2*S*,4*S*)-4-[(1,3-Dioxolan-2-yl)methyl]-2,3,3-trimethylcyclopentanone ((+)-**10**). As described in the General Procedure K of [3]: (+)-**10** (77%). B.p. 110°/0.22 mbar. $\alpha_D^{20} = +138.0$. IR: 2962, 1740, 1371, 1144, 1050. ¹H-NMR: 0.63 (s, 3 H); 0.95 (d, *J* = 7, 3 H); 1.12 (s, 3 H); 1.58 (ddd, *J* = 4, 12, 14, 1 H); 1.88 (dd, *J* = 12, 20, 1 H); 1.96 (m, 2 H); 2.03 (m, 1 H); 2.55 (dd, *J* = 10, 20, 1 H); 3.86 (m, 2 H); 3.98 (m, 2 H); 4.88 (dd, *J* = 4, 5, 1 H). ¹³C-NMR: 7.4 (q); 15.6 (q); 25.7 (q); 33.8 (t); 40.9 (d); 41.6 (s); 41.8 (t); 56.6 (d); 64.7 (t); 65.0 (t); 104.0 (d); 219.2 (s). MS: 212 (2, *M*⁺), 73 (100), 55 (7), 45 (10), 41 (9). Without character.

(-)-1-[(1*R*,3*R*,5*S*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hex-3-yl]propan-2-one ((-)-**11b**). MCPBA (2.0 g, 12 mmol) was added to a soln. of ketone (+)-**4h** (1.96 g, 12 mmol) in CH₂Cl₂ (40 ml). After 2 h, the mixture was extracted with brine to neutral, dried (Na₂SO₄), concentrated, and bulb-to-bulb distilled: pure (-)-**11b** (83%). B.p. 165°/0.2 mbar. [α]_D²⁰ = -1.9, (*c* = 2.2, CHCl₃). IR: 2963, 2936, 2873, 1713, 1467, 1444, 1421, 1365, 1241, 1166, 1145, 1046, 919, 845, 732. ¹H-NMR: 0.77 (s, 3 H); 1.00 (s, 3 H); 1.25 (dd, *J* = 7, 10, 1 H); 1.33 (s, 3 H); 1.92 (*m*, 1 H); 2.14 (s, 3 H); 2.15 (*m*, 2 H); 2.39 (dd, *J* = 2, 10, 1 H). ¹³C-NMR: 13.2 (*q*); 18.9 (*q*); 20.6 (*q*); 29.9 (*q*); 32.0 (*t*); 38.6 (*d*); 41.2 (*s*); 44.1 (*t*); 62.2 (*d*); 68.4 (*s*); 208.6 (*s*). MS: 182 (1, *M*⁺), 141 (11), 123 (15), 109 (46), 97 (42), 95 (29), 81 (27), 69 (21), 55 (18), 43 (100).

(+)-(1*R*,3*S*,5*S*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-acetic Acid ((+)-**11c**). MCPBA (5.1 g, 29 mmol) was added in portions at 0° to a soln. of campholenal (+)-**4b** (4.9 g, 29 mmol) in CH₂Cl₂ (100 ml). After 4 h at 20°, MCPBA (5.1 g, 29 mmol) was added, and the mixture was refluxed for 1 h. The cold mixture was washed with H₂O, 15% aq. NaHSO₃ soln., 15% aq. NaOH soln., and H₂O to neutrality, dried (MgSO₄), concentrated, and purified by CC (SiO₂, CH₂Cl₂/Et₂O 98:2) and bulb-to-bulb distillation: pure (+)-**11c** (60%).

Alternatively, a few drops of 10% aq. NaOH soln. were added to adjust to pH 9.5 a mixture of (+)-**11a** (340 mg, 2.0 mmol) and 30% aq. AgNO₃ soln. (4.4 ml) in EtOH (16 ml). The mixture was stirred for 3 h at 20° and then filtered. The precipitate was rinsed with 50% hot EtOH/H₂O, and the filtrate was concentrated and then extracted with CH₂Cl₂. The aq. phase was acidified with 10% HCl soln. and extracted with CH₂Cl₂ (3 × 50 ml). The org. phase was washed with brine to neutral, dried (Na₂SO₄), concentrated, and bulb-to-bulb distilled: pure (+)-**11c**. B.p. 124°/0.4 mbar. [α]_D²⁰ = +5.8 (*c* = 1.6, CHCl₃). IR: 3200, 2964, 2934, 2873, 1706, 1466, 1444, 1419, 1376, 1366, 1303, 1281, 1211, 1144, 1083, 1060, 1046, 926, 842, 785, 759. ¹H-NMR: 0.77 (s, 3 H); 1.02 (s, 3 H); 1.34 (s, 3 H); 1.35 (*m*, 1 H); 1.93 (*m*, 1 H); 2.07 (dd, *J* = 11.3, 14.3, 1 H); 2.21 (dd, *J* = 7.2, 13.8, 1 H); 2.32 (dd, *J* = 4.1, 14.3, 1 H); 3.27 (s, 1 H); 9.7 (br. s, 1 H). ¹³C-NMR: 13.2 (*q*); 18.8 (*q*); 20.5 (*q*); 32.0 (*t*); 34.4 (*t*); 39.3 (*d*); 41.0 (*s*); 62.2 (*d*); 68.7 (*s*); 179.3 (*s*). MS: 184 (0, *M*⁺), 169 (22), 140 (21), 124 (88), 109 (92), 95 (55), 86 (47), 70 (90), 55 (51), 43 (100).

(+)-(1*S*,3*R*,5*R*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-acetaldehyde ((+)-**12a**). This less polar stereoisomer was isolated in 3% yield during the chromatographic purification of (+)-**11a** [11b] [14] (SiO₂, heptane/AcOEt 10:1). [α]_D²⁰ = +20.4 (*c* = 1.5, MeOH). IR: 3021, 2971, 1741, 1467, 1377, 1272, 1144, 848. ¹H-NMR: 0.99 (s, 3 H); 1.02 (s, 3 H); 1.29 (s, 3 H); 1.65 (*d*, *J* = 10, 1 H); 2.09 (*m*, 1 H); 2.15 (*m*, 1 H); 2.62 (*m*, 2 H); 3.29 (s, 1 H); 9.72 (*t*, *J* = 2, 1 H). ¹³C-NMR: 13.1 (*q*); 18.5 (*q*); 26.9 (*q*); 32.1 (*t*); 38.9 (*d*); 42.4 (*s*); 50.1 (*t*); 63.8 (*d*); 70.2 (*s*); 203.0 (*d*). MS: 168 (2, *M*⁺), 153 (13), 109 (54), 83 (100), 69 (50), 55 (81), 43 (78), 41 (81). Cumin, mastic.

(+)-(1*R*,3*S*,5*S*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-ethanol ((+)-**13a**). NaBH₄ (112.4 mg, 2.97 mmol) was added portionwise to a soln. of (+)-**11a** (500 mg, 2.97 mmol) in MeOH (5 ml) at 0°. After 15 min, the mixture was equilibrated at 20°, and after 30 additional min., the mixture was poured onto ice. The aq. phase was saturated with NaCl and extracted with Et₂O (3 × 10 ml). The org. phase was dried (Na₂SO₄), concentrated, and bulb-to-bulb distilled: pure (+)-**13a** (80%). B.p. 150°/0.2 mbar. [α]_D²⁰ = +11.4 (*c* = 1.1, EtOH). IR: 3412, 2934, 2871, 1467, 1442, 1375, 1364, 1144, 1077, 1052, 1028, 1004, 911, 843. ¹H-NMR: 0.73 (s, 3 H); 1.00 (s, 3 H); 1.3 (*m*, 2 H); 1.33 (s, 3 H); 1.5 (*m*, 1 H); 1.6 (*m*, 1 H); 1.72 (br. s, 1 OH); 2.08 (dd, *J* = 5, 8, 1 H); 3.25 (s, 1 H); 3.65 (*m*, 2 H). ¹³C-NMR: 13.2 (*q*); 18.7 (*q*); 20.8 (*q*); 32.1 (*t*); 32.7 (*t*); 39.4 (*d*); 41.3 (*s*); 61.7 (*t*); 62.7 (*d*); 69.1 (*s*). MS: 170 (17, *M*⁺), 155 (20), 137 (21), 125 (28), 111 (100), 109 (38), 83 (50), 69 (59), 55 (83), 43 (79), 41 (77).

(-)-**13a**: [α]_D²⁰ = -11.5 (*c* = 1.1, EtOH). Camphor.

(+)-(1*S*,3*S*,5*R*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-ethanol ((+)-**14a**). NaBH₄ (11.2 mg, 0.296 mmol) was added to a soln. of (+)-**12a** (50 mg, 0.297 mmol) in MeOH (2 ml) at 0°. After 1 h at 20°, the mixture was poured onto ice. The aq. phase was saturated with NaCl and extracted with Et₂O (3 × 20 ml). The org. phase was dried (Na₂SO₄), concentrated, and bulb-to-bulb distilled: pure (+)-**14a** (83%). [α]_D²⁰ = +36.6 (*c* = 1.1, EtOH). IR: 3406, 2957, 2871, 1469, 1442, 1423, 1375, 1364, 1137, 1053, 1006, 935, 853, 835, 732. ¹H-NMR: 0.97 (s, 3 H); 1.03 (s, 3 H); 1.29 (s, 3 H); 1.52 (*m*, 2 H); 1.63 (*m*, 1 H); 1.73 (*m*, 1 H); 1.77 (*d*, *J* = 12, 1 H); 1.92 (dd, *J* = 7, 12, 1 H); 3.28 (s, 1 H); 3.50 (*m*, 1 H); 3.66 (*m*, 1 H). ¹³C-NMR: 13.2 (*q*); 18.5 (*q*); 27.5 (*q*); 30.2 (*t*); 36.8 (*t*); 42.1 (*d*); 42.9 (*s*); 61.9 (*t*); 64.2 (*d*); 70.4 (*s*). MS: 170 (10, *M*⁺), 155 (16), 137 (21), 125 (20), 111 (90), 109 (41), 83 (41); 69 (52), 55 (78), 43 (93), 41 (100).

(+)-(1*S*,3*S*,5*R*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-ethanol Acetate ((+)-**14b**). A soln. of (+)-**14a** (20 mg, 0.117 mmol) and Ac₂O (52.8 mg, 0.517 mmol) in pyridine (40.9 mg, 0.517 mmol) was heated at 60° for 1 h. H₂O (0.1 ml) was then added to the cold soln. Extraction with CH₂Cl₂ and washing with H₂O to neutral furnished, after concentration and bulb-to-bulb distillation, pure (+)-**14b** (74%). B.p. 160°/0.2 mbar. $[\alpha]_D^{20} = +27.5$ (*c* = 1.1, EtOH). IR: 2960, 2872, 1736, 1469, 1442, 1386, 1365, 1232, 1138, 1034, 852. ¹H-NMR: 0.99 (s, 3 H); 1.02 (s, 3 H); 1.31 (s, 3 H); 1.55 (*m*, 2 H); 1.78 (*d*, *J* = 12, 1 H); 1.82 (*m*, 1 H); 1.92 (*dd*, *J* = 7, 12, 1 H); 2.04 (s, 3 H); 3.29 (s, 1 H); 3.95 (*m*, 1 H); 4.04 (*m*, 1 H). ¹³C-NMR: 13.2 (*q*); 18.5 (*q*); 21.0 (*q*); 27.4 (*q*); 30.2 (*t*); 32.7 (*t*); 42.4 (*d*); 42.9 (*s*); 63.8 (*t*); 64.0 (*d*); 70.3 (*s*); 171.3 (*s*). MS: 212 (1, *M*⁺), 170 (12), 152 (20), 137 (36), 124 (20), 109 (46), 81 (19), 67 (34), 55 (26), 43 (100).

2-[(1*R*)-2,2,3-Trimethylcyclopent-3-en-1-yl]ethyl 1,3-Dihydro-1,3-dioxo-isobenzofuran-5-carboxylate ((-)-**15c**). A mixture of trimellitic anhydride acid chloride (= 1,3-dihydro-1,3-dioxoisobenzofuran-5-caronyl chloride) (2.19 g, 10 mmol), alcohol (+)-**15a** (1.54 g, 10 mmol), and AgCN (1.47 g, 11 mmol) in toluene (20 ml) was heated under reflux for 5 h. The cold mixture was filtered, concentrated, and purified by CC (SiO₂, toluene/AcOEt 9:1 → 1:1, then Et₂O): pure (-)-**15c** (29%). $[\alpha]_D^{20} = -0.5$ (*c* = 2.2, CHCl₃). IR: 2922, 2852, 1859, 1774, 1702, 1488, 1419, 1349, 1294, 1229, 1171, 1124, 1103, 1071, 919, 885. ¹H-NMR: 0.81 (s, 3 H); 1.02 (s, 3 H); 1.38–1.58 (*m*, 1 H); 1.62 (s, 3 H); 1.75 (*m*, 1 H); 1.92 (*m*, 2 H); 2.36 (*m*, 1 H); 4.43 (*m*, 2 H); 5.25 (br. s, 1 H); 8.12 (*dd*, *J* = 4, 10, 1 H); 8.6 (*dd*, *J* = 4, 10, 1 H); 8.72 (s, 1 H). ¹³C-NMR: 12.6 (*q*); 19.7 (*q*); 25.7 (*q*); 29.1 (*t*); 35.5 (*t*); 47.0 (*s*); 47.0 (*d*); 66.4 (*t*); 121.5 (*d*); 125.8 (*d*); 127.5 (*d*); 131.8 (*s*); 136.6 (*s*); 137.2 (*d*); 137.6 (*s*); 148.6 (*s*); 161.5 (*s*); 164.0 (*s*); 168.1 (*s*). MS: 328 (2, *M*⁺), 175 (11), 136 (17), 121 (100), 108 (29), 103 (14), 93 (32), 75 (13).

(-)-(1*R*,3*S*,5*S*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-methanol Acetate ((-)-**16a**). MCPBA (5.86 g, 34 mmol) was added in portions at 0° to a soln. of ketone (+)-**4h** (5.65 g, 34 mmol) in CH₂Cl₂ (100 ml). After 2 h at 20°, MCPBA (5.86 g, 34 mmol) was added, and the mixture was refluxed for 24 h, while three successive portions of MCPBA (5.86 g, 34 mmol) were added after 24, 48, and 72 h. The cold mixture was washed with H₂O, 15% aq. NaOH soln., and H₂O to neutrality, dried (MgSO₄), concentrated, and purified by CC (SiO₂, CH₂Cl₂): pure (-)-**16a** (33%). B.p. 100°/0.14 mbar. $\alpha_D^{20} = -4.0$. IR: 2963, 1738, 1467, 1443, 1387, 1365, 1231, 1146, 1031, 971, 844. ¹H-NMR: 0.82 (s, 3 H); 1.08 (s, 3 H); 1.12 (s, 3 H); 1.39 (*dd*, *J* = 10, 12, 1 H); 1.85 (*dd*, *J* = 7, 12, 1 H); 2.03 (s, 3 H); 2.09 (*t*, *J* = 7, 1 H); 3.27 (s, 1 H); 3.99 (*d*, *J* = 7, 2 H). ¹³C-NMR: 12.8 (*q*); 18.7 (*q*); 20.9 (*q*); 21.6 (*q*); 30.0 (*t*); 40.9 (*s*); 41.7 (*d*); 62.2 (*d*); 64.8 (*t*); 68.9 (*s*); 171.0 (*s*). MS: 198 (0, *M*⁺), 183 (1), 155 (9), 138 (38), 123 (65), 95 (41), 69 (36), 55 (26), 43 (100), 41 (32). Fruity, estery.

(+)-**16a**: $\alpha_D^{20} = +4.1$. Cedar, camphor.

(-)-(1*R*,3*S*,5*S*)-1,2,2-Trimethyl-6-oxabicyclo[3.1.0]hexane-3-methanol ((-)-**16b**). A soln. of (-)-**16a** (200 mg, 1.0 mmol) and LiOH·H₂O (200 mg, 4.8 mmol) in THF (5 ml) and H₂O (2 ml) was stirred for 24 h at 20°. The mixture was saturated with NaCl and extracted with Et₂O. The org. phase was washed to neutral with brine, dried (Na₂SO₄), concentrated, and purified by CC (cyclohexane/AcOEt 9:1): pure (-)-**16b** (82%). B.p. 62°/0.4 mbar. $[\alpha]_D^{20} = -4.2$ (*c* = 1.0, CHCl₃). IR: 3411, 2959, 2932, 2872, 1466, 1442, 1375, 1364, 1144, 1075, 1024, 998, 926, 841, 806. ¹H-NMR: 0.82 (s, 3 H); 1.08 (s, 3 H); 1.31 (s, 3 H); 1.39 (*m*, 1 H); 1.54 (br. s, 1 OH); 1.73 (*dd*, *J* = 7.5, 10.2, 1 H); 2.11 (*dd*, *J* = 6.6, 13.3, 1 H); 3.27 (s, 1 H); 3.53 (*dd*, *J* = 7.5, 10.2, 1 H); 3.64 (*dd*, *J* = 6.6, 10.2, 1 H). ¹³C-NMR: 12.85 (*q*); 18.6 (*q*); 21.9 (*q*); 30.1 (*t*); 40.9 (*s*); 45.3 (*d*); 62.4 (*d*); 63.5 (*t*); 69.3 (*s*). MS: 156 (1, *M*⁺), 141 (56), 125 (66), 113 (43), 95 (39), 85 (32), 71 (60), 55 (83), 43 (100).

Alternatively, MCPBA (123 mg, 0.7 mmol) was added at 20° to a soln. of alcohol (-)-**19b** (100 mg, 0.7 mmol). After 1 h, the mixture was washed to neutral with H₂O, dried (Na₂SO₄), and concentrated to afford in 72% yield a 1:1 mixture of **16b** and 4,4,5-trimethyl-6-oxabicyclo[3.1.0]hexane-1-methanol. Purification by CC (SiO₂, heptane/AcOEt 3:1) afforded 4,4,5-trimethyl-6-oxabicyclo[3.1.0]hexane-1-methanol (27%). IR: 3419, 2958, 2869, 1575, 1467, 1441, 1377, 1363, 1281, 1259, 1124, 1081, 1016, 901, 824. ¹H-NMR: 0.92 (s, 3 H); 1.07 (s, 3 H); 1.27 (*m*, 2 H); 1.29 (s, 3 H); 1.32 (br. s, 1 OH); 1.78 (*m*, 1 H); 2.02 (*dd*, *J* = 7, 12, 1 H); 3.78 (*d*, *J* = 12, 1 H); 3.86 (*d*, *J* = 12, 1 H). ¹³C-NMR: 10.6 (*q*); 22.1 (*q*); 24.2 (*q*); 26.7 (*t*); 34.2 (*t*); 41.3 (*s*); 62.4 (*t*); 71.3 (*s*); 73.2 (*s*). MS: 156 (3, *M*⁺), 141 (11), 125 (33), 107 (23), 95 (51), 83 (100), 69 (28), 55 (69), 43 (78).

(-)-(1*R*,3*S*,5*S*)-3-[[[(*tert*-Butyl)dimethylsilyl]oxy]methyl]-1,2,2-trimethyl-6-oxabicyclo[3.1.0]hexane (= (-)-(*tert*-Butyl)dimethyl[[[(1*R*,3*S*,5*S*)-1,2,2-trimethyl-6-oxabicyclo[3.1.0]hex-3-yl]methoxy]silane; ((-)-**16c**). Me₂BuSiCl (41.7 mg, 0.28 mmol) was added to a soln. of (-)-**16b** (36 mg, 0.23 mmol) in DMF (3 ml) at -30°, followed by 1*H*-imidazole (19 mg, 0.28 mmol). After 2 h at 20°, the reaction mixture was diluted with Et₂O and extracted with brine to neutral. The org. phase was dried (Na₂SO₄), concentrated, and purified by CC (SiO₂, cyclohexane/AcOEt 95:5): pure (-)-**16c** (71%). [α]_D²⁰ = -8.0 (*c* = 0.6, CCl₄). IR: 2956, 2929, 2856, 1471, 1442, 1387, 1361, 1252, 1145, 1114, 1085, 1059, 1004, 833, 772. ¹H-NMR: 0.0 (*s*, 3 H); 0.023 (*s*, 3 H); 0.82 (*s*, 3 H); 0.88 (*s*, 9 H); 1.08 (*s*, 3 H); 1.3 (*s*, 3 H); 1.33 (*m*, 1 H); 1.71 (*m*, 1 H); 2.0 (*dd*, *J* = 7, 14, 1 H); 3.23 (*s*, 1 H); 3.53 (*m*, 2 H). ¹³C-NMR: -5.5 (*q*); -5.4 (*q*); 12.9 (*q*); 18.2 (*s*); 18.6 (*q*); 22.0 (*q*); 25.9 (*3q*); 29.8 (*t*); 40.9 (*s*); 44.9 (*d*); 62.5 (*d*); 63.2 (*t*); 69.4 (*s*). MS: 270 (1, *M*⁺), 213 (95); 183 (13); 171 (8); 157 (13), 143 (33), 125 (21), 121 (34), 75 (100), 73 (30).

(-)-(2*R*,4*S*)-4-[[[(*tert*-Butyl)dimethylsilyl]oxy]methyl]-2,3,3-trimethylcyclopentanone [27] ((-)-**17a**). A soln. of alcohol (+)-**20c** (700 mg, 2.57 mmol) in CH₂Cl₂ (5 ml) was added to a suspension of PCC (858 mg, 3.98 mmol) and Celite® (850 mg) in CH₂Cl₂ (20 ml). After 2.5 h, Et₂O was added, and the mixture was filtered through a short SiO₂ column to afford (+)-(2*S*,4*S*)-4-[[[(*tert*-butyl)dimethylsilyl]oxy]methyl]-2,3,3-trimethylcyclopentanone (*cis*-**17a**, 80%). [α]_D²⁰ = +42.0 (*c* = 1.0, EtOH). IR: 2955, 2927, 2856, 1740, 1463, 1388, 1362, 1251, 1088, 833, 773. ¹H-NMR: 0.04 (*s*, 6 H); 0.66 (*s*, 3 H); 0.89 (*s*, 9 H); 0.92 (*d*, *J* = 7, 3 H); 1.20 (*s*, 3 H); 1.9 (*dd*, *J* = 9, 14, 1 H); 2.02 (*q*, *J* = 7, 1 H); 2.12 (*m*, 1 H); 2.43 (*dd*, *J* = 7, 14, 1 H); 3.63 (*dd*, *J* = 7, 12, 1 H); 3.78 (*dd*, *J* = 7, 12, 1 H). ¹³C-NMR: -5.4 (2*q*); 7.0 (*q*); 16.0 (*q*); 18.3 (*s*); 26.0 (3*q*); 27.2 (*q*); 39.3 (*t*); 40.9 (*s*); 47.3 (*d*); 57.5 (*d*); 63.1 (*t*); 219.1 (*s*). MS: 270 (0, *M*⁺), 213 (30), 183 (17), 157 (15), 121 (48), 93 (22), 75 (100), 69 (30), 41 (30).

A soln. of pure *cis*-**17a** (90 mg, 0.333 mmol) in MeOH (2 ml) was treated at 65° for 2 h with a 30% MeONa/MeOH soln. (66 mg, 0.366 mmol) to afford in 87% yield *trans/cis*-**17a** 3:7. Purification by CC (SiO₂, CH₂Cl₂) gave a *trans/cis*-**17a** 65:35 (22%). Analyses for *trans*-**17a** (= (-)-**17a**) were deduced from the mixture: ¹H-NMR: 0.04 (*s*, 6 H); 0.66 (*s*, 3 H); 0.87 (*s*, 9 H); 0.89 (*d*, *J* = 7, 3 H); 1.10 (*s*, 3 H); 1.9 (*dd*, *J* = 9, 14, 1 H); 2.02 (*q*, *J* = 7, 1 H); 2.12 (*m*, 1 H); 2.38 (*dd*, *J* = 7, 14, 1 H); 3.68 (*dd*, *J* = 7, 12, 1 H); 3.73 (*dd*, *J* = 7, 12, 1 H). ¹³C-NMR: -5.4 (2*q*); 8.6 (*q*); 15.9 (*q*); 18.2 (*s*); 24.6 (3*q*); 29.8 (*q*); 39.2 (*t*); 40.9 (*s*); 45.5 (*d*); 53.5 (*d*); 63.9 (*t*); 221.3 (*s*). MS: 270 (0, *M*⁺), 213 (32), 183 (17), 157 (16), 121 (48), 93 (20), 75 (100), 69 (23), 41 (25).

(+)-(tert-Butyl)dimethyl[[[(1*S*,3*S*)-2,2,3-trimethyl-4-methylenecyclopentyl]methoxy]silane ((+)-**17b**). TiCl₄ (1.13 ml, 10.3 mmol) was added at -40° to a suspension of Zn dust (2.87 g, 44 mmol) and CH₂Br₂ (1.01 ml, 14.4 mmol) in THF (25 ml). After 3 days at 5°, the resulting slurry (7.5 ml, *ca.* 2.58 mmol) was added at 5° to a soln. of ketone (-)-**17a** (350 mg, 1.3 mmol; *ca.* 65:35 *trans/cis*) in CH₂Cl₂ (6 ml), and after 2 h at 5°, the mixture was diluted with CH₂Cl₂, poured into a cold sat. aq. NaHCO₃ soln. and extracted with Et₂O. The combined extracts were washed with brine, dried (Na₂SO₄) concentrated, and purified by CC (SiO₂, cyclohexane/Et₂O 95:5): pure *trans*-isomer(+)-**17b** (51%). [α]_D²⁰ = +11.8 (*c* = 0.7, CCl₄). IR: 2957, 2928, 2857, 1656, 1471, 1463, 1388, 1362, 1253, 1101, 1087, 1065, 1006, 939, 873, 833, 773. ¹H-NMR: 0.04 (*s*, 3 H); 0.05 (*s*, 3 H); 0.80 (*s*, 3 H); 0.89 (*s*, 9 H); 0.92 (*d*, *J* = 7, 3 H); 0.93 (*s*, 3 H); 1.81 (*m*, 1 H); 2.18 (*m*, 1 H); 2.27 (*m*, 1 H); 2.52 (*ddq*, *J* = 2, 7, 14, 1 H); 3.46 (*dd*, *J* = 7, 10, 1 H); 3.67 (*dd*, *J* = 5, 10, 1 H); 4.76 (*br. s*, 1 H); 4.82 (*br. s*, 1 H). ¹³C-NMR: -5.4 (2*q*); 13.5 (*q*); 18.3 (*s*); 23.0 (*q*); 23.9 (*q*); 25.9 (3*q*); 33.9 (*t*); 42.1 (*s*); 48.5 (*d*); 48.6 (*d*); 64.2 (*t*); 104.4 (*t*); 156.8 (*s*). MS: 268 (0, *M*⁺), 211 (62), 135 (51), 121 (38), 75 (100), 73 (28).

The pure *cis*-isomer (+)-*cis*-**17b** was also obtained (23%) after CC for anal. purposes. [α]_D²⁰ = +39.2 (*c* = 1.1, CCl₄). IR: 2956, 2928, 2899, 2857, 1657, 1471, 1388, 1366, 1253, 1098, 1074, 1025, 1006, 874, 834, 814, 773, 663. ¹H-NMR: 0.05 (*s*, 6 H); 0.52 (*s*, 3 H); 0.90 (*s*, 9 H); 0.91 (*d*, *J* = 7, 3 H); 1.05 (*s*, 3 H); 1.81 (*m*, 1 H); 1.98 (*m*, 1 H); 2.07 (*m*, 1 H); 2.58 (*ddq*, *J* = 1, 7, 14, 1 H); 3.51 (*dd*, *J* = 7, 10, 1 H); 3.69 (*dd*, *J* = 5, 10, 1 H); 4.72 (*br. s*, 1 H); 4.82 (*br. s*, 1 H). ¹³C-NMR: -5.4 (2*q*); 10.4 (*q*); 14.8 (*q*); 18.3 (*s*); 26.0 (3*q*); 26.6 (*q*); 34.3 (*t*); 42.1 (*s*); 50.0 (*d*); 50.8 (*d*); 64.1 (*t*); 103.9 (*t*); 155.5 (*s*). MS: 268 (0, *M*⁺), 211 (88), 181 (82), 135 (28), 121 (30), 89 (70), 75 (100), 73 (58).

(+)- β -Necrodol (= (+)-(1*S*,3*S*)-2,2,3-Trimethyl-4-methylenecyclopentanemethanol; (+)-**17c**). A mixture of (+)-**17b** (100 mg, 0.373 mmol), 1*M* Bu₄NF in THF/H₂O 95:5 (0.37 ml, 0.37 mmol), and THF (2 ml) was stirred for 24 h at 20°. The mixture was diluted with brine and extracted with Et₂O, and the org. phase

was washed to neutral with brine, dried (Na_2SO_4), concentrated, and purified by bulb-to bulb distillation: pure (+)-**17c** (93%). B.p. $120^\circ/0.1$ mbar. $[\alpha]_{\text{D}}^{20} = +15.9$ ($c = 1.0$, CHCl_3). For analyses and olfactive properties, see [16].

(+)-(1*S*)-2,2,3-Trimethylcyclopent-3-ene-1-carboxaldehyde ((+)-**19a**). A soln. of (–)-epoxyverbenone (–)-**2e** (10.0 g, 65 mmol; $\alpha_{\text{D}}^{20} = -112.5$) in toluene (40 ml) was added dropwise to a refluxing soln. of dry ZnBr_2 (1.82 g, 8 mmol) in toluene (10 ml). After 1.5 h. a second quantity of ZnBr_2 (1.82 g, 8 mmol) was added. After 2.25 h, the temp. was equilibrated to 20° , and H_2O (20 ml) and then AcOH (2 ml) were added. The mixture was extracted with Et_2O , the org. phase was washed with NaHCO_3 and H_2O to neutrality, dried (Na_2SO_4), and concentrated to remove Et_2O , then the soln. in remaining toluene was purified by CC (SiO_2 , toluene/ AcOEt 97:3): (+)-**19a** (47%).

In a 5-l Pyrex reactor, a mixture of enamine (+)-**18a** (300 g, 1.35 mol), MeOH (4275 ml), H_2O (225 ml), Rose Bengal (4.5 g) and AcONa (4.5 g, 54.9 mmol) were irradiated at 18° with a Philips-Hoki lamp (1200 W) for 6 h under O_2 . After absorption of O_2 (31 l, 1.24 mol), DMS (300 ml, 4.09 mol) was added, and after 18 h at 20° , the mixture was concentrated and then distilled to afford a yellow oil (160 g, b.p. $29-61^\circ/2.5$ Torr), which was fractionated with a 1.0-m spinning band apparatus: pure **19a** (35%). B.p. $65^\circ/13$ Torr. $[\alpha]_{\text{D}}^{20} = +7.5$ ($c = 1.8$, CHCl_3). IR: 2956, 2850, 2700, 1717, 1450, 1355, 1125, 1008, 795. $^1\text{H-NMR}$: 1.00 (s, 3 H); 1.22 (s, 3 H); 1.62 (br. s, 3 H); 2.36 (ddt, $J = 3, 7, 16$, 1 H); 2.58 (m, 1 H); 2.70 (dt, $J = 3, 7$, 1 H); 5.26 (br. s, 1 H); 9.76 (d, $J = 2.5$, 1 H). $^{13}\text{C-NMR}$: 11.8 (q); 21.5 (q); 27.1 (q); 29.4 (t); 49.0 (s); 61.6 (d); 121.1 (d); 146.9 (s); 204.6 (d). MS: 138 (18, M^+), 123 (56), 95 (100), 67 (65), 55 (27), 41 (32). Vaguely mint, green.

(–)-**19a**: Obtained from (+)-epoxyverbenone ($\alpha_{\text{D}}^{20} = +119.2$). $\alpha_{\text{D}}^{20} = -6.8$. Almond, pharmacy.

(–)-(1*S*)-2,2,3-Trimethylcyclopent-3-ene-1-methanol ((–)-**19b**). As described in the General Procedure I of [3]: (–)-**19b** (94%). B.p. $100^\circ/8.5$ mbar. $\alpha_{\text{D}}^{20} = -18.4$. IR: 3427, 2957, 1716, 1464, 1360, 1270. $^1\text{H-NMR}$: 0.88 (s, 3 H); 1.08 (s, 3 H); 1.60 (br. s, 3 H); 1.85 (br. s, 1 OH); 1.96 (m, 1 H); 2.07 (m, 1 H); 2.37 (m, 1 H); 3.65 (dd, $J = 7, 9$, 1 H); 3.80 (dd, $J = 7, 9$, 1 H); 5.22 (br. s, 1 H). $^{13}\text{C-NMR}$: 12.2 (q); 19.9 (q); 26.9 (q); 33.4 (t); 46.5 (s); 51.9 (d); 64.3 (t); 121.3 (d); 148.3 (s). MS: 140 (19, M^+), 125 (37), 107 (100), 95 (28), 91 (36), 79 (33), 67 (23), 55 (21), 41 (27). Camphor, celluloid.

(–)-(4*S*)-{[(tert-Butyl)dimethylsilyl]oxy}methyl-1,5,5-trimethylcyclopent-1-ene (= (–)-(tert-Butyl)dimethyl{[(1*S*)-2,2,3-trimethylcyclopent-3-en-1-yl]methoxy}silane; (–)-**19c**). As described for (–)-**16c**: (–)-**19c** (40%). B.p. $75^\circ/1.0$ mbar. $[\alpha]_{\text{D}}^{20} = -4.1$ ($c = 1.9$, CHCl_3). IR: 2954, 2928, 2857, 1471, 1463, 1387, 1360, 1252, 1102, 1068, 1006, 824, 772. $^1\text{H-NMR}$: 0.05 (s, 6 H); 0.85 (s, 3 H); 0.9 (s, 9 H); 1.08 (s, 3 H); 1.58 (s, 3 H); 1.88 (m, 1 H); 2.05 (quint., $J = 7$, 1 H); 2.25 (m, 1 H); 3.60 (dd, $J = 7, 10$, 1 H); 3.74 (dd, $J = 7, 10$, 1 H); 5.20 (br. s, 1 H). $^{13}\text{C-NMR}$: -5.3 (2q); 12.3 (q); 18.4 (s); 19.8 (q); 26.0 (3q); 27.0 (q); 33.3 (t); 46.5 (s); 51.8 (d); 64.2 (t); 121.4 (d); 148.5 (s). MS: 254 (0, M^+), 197 (100), 121 (74), 107 (57), 89 (74), 75 (70), 73 (28).

(+)-(1*S*,3*S*,4*S*)-4-Hydroxy-2,2,3-trimethylcyclopentanemethanol ((+)-**20a**). As described for (+)-**9b**, from (+)-**19a** with 2.0 mol-equiv. of $\text{BH}_3\cdot\text{Me}_2\text{S}$ complex: (+)-**20a** (72%). B.p. $150^\circ/0.2$ mbar. $[\alpha]_{\text{D}}^{20} = +31.0$ ($c = 1.0$, EtOH). IR: 3333, 2958, 1456, 1367, 1064. $^1\text{H-NMR}$: 0.61 (s, 3 H); 0.94 (d, $J = 7, 3$ H); 1.02 (s, 3 H); 1.49 (quint., $J = 7$, 1 H); 1.72 (br. s, 2 OH); 1.82 (m, 2 H); 2.01 (m, 1 H); 3.49 (dd, $J = 7, 9$, 1 H); 3.72 (dd, $J = 4, 7$, 1 H); 3.85 (dt, $J = 4, 7$, 1 H). $^{13}\text{C-NMR}$: 11.0 (q); 16.1 (q); 27.0 (q); 36.9 (t); 42.1 (s); 50.3 (d); 54.5 (d); 64.1 (t); 77.9 (d). MS: 158 (1, M^+), 140 (5), 125 (13), 109 (44), 71 (51), 70 (100), 67 (32), 55 (55), 43 (53), 41 (57).

(–)-**20a**: $[\alpha]_{\text{D}}^{20} = -30.6$ ($c = 1.0$, EtOH), obtained analogously in 78% yield from (–)-**19a**.

(+)-[(1*S*,3*S*,4*S*)-4-Hydroxy-2,2,3-trimethylcyclopentyl]methyl 2,2-Dimethylpropanoate ((+)-**20b**). A mixture of (+)-**20a** (490 mg, 3.1 mmol), pivalic acid (=2,2-dimethylpropanoic acid; 400 mg, 3.92 mmol), DCC (800 mg, 3.88 mmol), and DMAP (5 mg) in CH_2Cl_2 (10 ml) was stirred at 20° for 3.5 h. After filtration, the mixture was extracted with pentane/ H_2O . The org. phase was washed with sat. aq. NaHCO_3 soln. and H_2O to neutrality, dried (Na_2SO_4), concentrated, and purified by CC (SiO_2 , toluene/ AcOEt 8:2 $\rightarrow$ 7:3): pure (+)-**20b** (74%). B.p. $180^\circ/0.27$ mbar. $[\alpha]_{\text{D}}^{20} = +7.5$ ($c = 0.3$, EtOH). IR: 3404, 2960, 1729, 1481, 1368, 1286, 1163, 1033. $^1\text{H-NMR}$: 0.63 (s, 3 H); 0.96 (d, $J = 7$, 3 H); 1.03 (s, 3 H); 1.19 (s, 9 H); 1.51 (quint., $J = 7$, 1 H); 1.72 (br. s, 1 OH); 1.77 (m, 1 H); 1.85 (m, 1 H); 2.17 (m, 1

H); 3.84 (*dt*, $J=4, 7, 1$ H); 3.96 (*dd*, $J=7, 9, 1$ H); 4.08 (*dd*, $J=7, 10, 1$ H). $^{13}\text{C-NMR}$: 11.1 (*q*); 16.2 (*q*); 26.9 (*q*); 27.2 (*3q*); 36.5 (*t*); 38.8 (*s*); 42.2 (*s*); 46.6 (*d*); 54.3 (*d*); 65.4 (*t*); 77.7 (*d*); 178.8 (*s*). MS: 242 (0, M^{+}), 224 (2), 140 (10), 122 (22), 107 (40), 103 (25), 85 (27), 70 (54), 57 (100), 41 (60).

Data of By-product (10%) 4-(2,2-Dimethyl-1-oxopropoxy)-2,2,3-trimethylcyclopentyl 2,2-Dimethylpropanoate. IR: 2960, 1730, 1480, 1370, 1285, 1165, 1035. $^1\text{H-NMR}$: 0.69 (*s*, 3 H); 0.90 (*d*, $J=7, 3$ H); 1.06 (*s*, 3 H); 1.20 (*s*, 18 H); 1.59–1.80 (*m*, 2 H); 1.90–2.18 (*m*, 2 H); 3.95 (*dd*, $J=8, 10, 1$ H); 4.10 (*dd*, $J=8, 10, 1$ H); 4.71 (*dt*, $J=4, 8, 1$ H). $^{13}\text{C-NMR}$: 11.1 (*q*); 16.0 (*q*); 26.7 (*q*); 27.1 (*3q*); 27.2 (*3q*); 33.9 (*t*); 38.6 (*s*); 38.8 (*s*); 41.7 (*s*); 46.8 (*d*); 50.8 (*d*); 65.2 (*t*); 79.6 (*d*); 178.7 (*s*); 178.8 (*s*). MS: 326 (0, M^{+}), 241 (1), 225 (8), 123 (58), 107 (27), 57 (100).

(+)-(1*S*,2*S*,4*S*)-4-[[[(*tert*-Butyl)dimethylsilyl]oxy]methyl]-2,3,3-trimethylcyclopentanol ((+)-**20c**). The diprotected material (+)-(tert-butyl){[(1*S*,2*S*,4*S*)-4-[[[(*tert*-butyl)dimethylsilyl]oxy]methyl]-2,3,3-trimethylcyclopentyl]oxy}dimethylsilane was obtained in quantitative yield according to [27]. B.p. 90°/0.8 mbar. $[\alpha]_{\text{D}}^{20} = +15.3$ ($c=1.0$, EtOH). IR: 3334, 2955, 2928, 2857, 1462, 1388, 1362, 1252, 1094, 1076, 1030, 1005, 833, 772, 665. $^1\text{H-NMR}$: 0.02 (*s*, 12 H); 0.59 (*s*, 3 H); 0.85 (*d*, $J=7, 3$ H); 0.88 (*s*, 18 H); 0.98 (*s*, 3 H); 1.49 (*dq*, $J=1.5, 7, 1$ H); 1.65 (*m*, 2 H); 2.0 (*m*, 1 H); 3.45 (*dd*, $J=7, 10, 1$ H); 3.61 (*dd*, $J=7, 10, 1$ H); 3.73 (*m*, 1 H). $^{13}\text{C-NMR}$: –4.4 (*q*); –4.6 (*q*); –5.3 (*2q*); 11.1 (*q*); 16.2 (*q*); 18.2 (*s*); 18.3 (*s*); 26.0 (*6q*); 27.5 (*q*); 36.9 (*t*); 41.3 (*s*); 49.8 (*d*); 54.2 (*d*); 64.4 (*t*); 78.4 (*d*). MS: 386 (0, M^{+}), 329 (67), 253 (23), 211 (67), 147 (18), 121 (21), 89 (22), 75 (100), 73 (62).

A soln. of this diprotected material (140 mg, 0.362 mmol) in THF (2 ml) was treated overnight at 20° with $\text{Bu}_4\text{NF}\cdot 3\text{H}_2\text{O}$ (114.2 mg, 0.362 mmol). Then the mixture was partitioned between H_2O (20 ml) and Et_2O (3×10 ml). The org. phase was dried (Na_2SO_4) and concentrated: (+)-**20c** (97%). B.p. 100°/0.4 mbar. $[\alpha]_{\text{D}}^{20} = +15.9$ ($c=0.8$, CHCl_3). IR: 3334, 2955, 2928, 2896, 2857, 1462, 1388, 1362, 1252, 1094, 1076, 1030, 1005, 960, 938, 897, 833, 814, 772, 665. $^1\text{H-NMR}$: 0.7 (*s*, 6 H); 0.83 (*s*, 9 H); 0.88 (*s*, 3 H); 0.90 (*s*, 3 H); 0.98 (*d*, $J=7, 3$ H); 1.46 (*sext.*, $J=7, 1$ H); 1.76 (*m*, 2 H); 1.99 (*m*, 1 H); 2.21 (*br. s*, 1 OH); 3.45 (*m*, 1 H); 3.70 (*m*, 1 H); 3.81 (*m*, 1 H). $^{13}\text{C-NMR}$: –2.6 (*2q*); 11.3 (*q*); 16.4 (*q*); 18.5 (*s*); 26.1 (*3q*); 26.3 (*q*); 37.8 (*t*); 41.6 (*s*); 50.7 (*d*); 54.4 (*d*); 64.8 (*t*); 78.7 (*d*). MS: 272 (0, M^{+}), 189 (24), 147 (100), 133 (6), 117 (5), 73 (14).

Cyclopropanol (+)-**20c** was also obtained in 95% yield from (+)-**20a** as described for (–)-**16c**, or in 22% yield (after CC (SiO_2 , heptane/ AcOEt 9:1)) by oxidative hydroboration of silyl ether (–)-**19c** with 1.0 mol-equiv. of $\text{BH}_3\cdot\text{Me}_2\text{S}$ according to the procedure used for (+)-**9b**.

(+)-(1*R*,3*R*)-2,2,3-Trimethylcyclopentaneacetaldehyde ((+)-**21**). As described in the *General Procedure K* of [3] from (+)-**22a**: (+)-**21** (98%). B.p. 100°/0.2 mbar. $[\alpha]_{\text{D}}^{20} = +6.4$ ($c=3.1$, CHCl_3). IR: 2953, 2870, 2714, 1724, 1467, 1409, 1387, 1367, 1316, 1268, 1227, 1185, 1128, 1076, 1034, 915. $^1\text{H-NMR}$: 0.51 (*s*, 3 H); 0.86 (*d*, $J=7, 3$ H); 0.89 (*s*, 3 H); 1.2 (*m*, 2 H); 1.55 (*m*, 1 H); 1.8 (*m*, 1 H); 1.9 (*m*, 2 H); 2.2 (*m*, 1 H); 2.49 (*m*, 1 H); 9.75 (*d*, $J=4, 1$ H). $^{13}\text{C-NMR}$: 13.9 (*q*); 14.6 (*q*); 25.4 (*q*); 28.2 (*t*); 30.2 (*t*); 42.4 (*s*); 44.6 (*d*); 44.8 (*d*); 45.5 (*t*); 203.2 (*d*). MS: 154 (1, M^{+}), 139 (56), 110 (16), 97 (76), 95 (48), 84 (49), 69 (100), 55 (33), 41 (35). Aldehydic, green, camphoraceous.

(–)-**21**: $\alpha_{\text{D}}^{20} = -4.8$. Disgusting.

(+)-(1*R*,3*R*)-2,2,3-Trimethylcyclopentaneethanol ((+)-**22a**). Alcohol (+)-**15a** (23g, 0.13 mol) in AcOEt (250 ml) was hydrogenated over 10% Pd/C (500 mg). After absorption of H_2 (3.4 l) the soln. was filtered, concentrated, and distilled: pure (+)-**22a** (90%). B.p. 100°/0.15 mbar. $[\alpha]_{\text{D}}^{20} = +26.9$ ($c=3.1$, CHCl_3). IR: 3380, 2910, 1480, 1070. $^1\text{H-NMR}$: 0.52 (*s*, 3 H); 0.83 (*d*, $J=7, 3$ H); 0.88 (*s*, 3 H); 1.19 (*m*, 2 H); 1.33 (*m*, 1 H); 1.48 (*m*, 2 H); 1.78 (*m*, 3 H); 1.9 (*br. s*, 1 OH); 3.59 (*m*, 1 H); 3.69 (*m*, 1 H). $^{13}\text{C-NMR}$: 13.9 (*q*); 14.4 (*q*); 25.5 (*q*); 28.2 (*t*); 30.3 (*t*); 33.9 (*t*); 42.3 (*s*); 45.0 (*d*); 47.2 (*d*); 62.6 (*d*). MS: 156 (8, M^{+}), 123 (23), 113 (25), 109 (19), 100 (19), 95 (41), 84 (62), 81 (37), 69 (100), 55 (45), 41 (45). Very vague.

(+)-(1*R*,3*R*)-2,2,3-Trimethylcyclopentaneethanol Acetate ((+)-**22b**). A mixture of alcohol (+)-**22a** (120 mg, 0.77 mmol) and Ac_2O (0.14 ml, 1.48 mmol) in pyridine (1.4 ml) was stirred at 20° for 1 h. The mixture was concentrated under vacuum and purified by bulb-to-bulb distillation: (+)-**22b** (74%). B.p. 120°/0.1 mbar. $\alpha_{\text{D}}^{20} = +22.9$. IR: 2952, 2869, 1739, 1468, 1387, 1365, 1229, 1064, 1029, 966. $^1\text{H-NMR}$: 0.52 (*s*, 3 H); 0.84 (*d*, $J=7, 3$ H); 0.88 (*s*, 3 H); 1.19 (*m*, 2 H); 1.35 (*m*, 1 H); 1.41 (*m*, 1 H); 1.50 (*m*, 1

H); 1.78 (*m*, 3 H); 2.06 (*s*, 3 H); 4.03 (*m*, 1 H); 4.09 (*m*, 1 H). ^{13}C -NMR: 13.9 (*q*); 14.4 (*q*); 21.1 (*q*); 25.5 (*q*); 28.0 (*t*); 29.7 (*t*); 30.2 (*t*); 42.4 (*s*); 45.0 (*d*); 47.4 (*d*); 64.5 (*t*); 171.2 (*s*). MS: 198 (0, M^{+}), 155 (1), 138 (12), 123 (68), 110 (100), 95 (82), 84 (60), 81 (77), 69 (97), 55 (51), 43 (68).

rac-cis-2,3,3-Trimethylcyclopentaneethanol (*rac*-**23a**). A mixture of β -campholenol [31] (250 mg, 1.6 mmol) and Raney Ni (25 mg) in EtOH (5 ml) was hydrogenated (90 bars) for 18 h at 20°. The mixture was then filtered, concentrated, and purified by bulb-to-bulb distillation: pure *rac*-**23a** (53%). B.p. 100°/0.2 mbar. IR: 3321, 2936, 2866, 1462, 1375, 1178, 1055, 1007, 966, 859. ^1H -NMR: 0.75 (*d*, $J=7$, 3 H); 0.88 (*s*, 3 H); 0.98 (*s*, 3 H); 1.28 (*m*, 2 H); 1.43 (*m*, 2 H); 1.57 (*q*, $J=7$, 1 H); 1.65 (br. *s*, OH); 1.66 (*m*, 1 H); 1.80 (*m*, 1 H); 2.19 (*m*, 1 H); 3.61 (*m*, 2 H). ^{13}C -NMR: 10.6 (*q*); 24.6 (*q*); 29.5 (*t*); 30.2 (*q*); 35.6 (*t*); 37.8 (*d*); 39.0 (*t*); 41.4 (*s*); 45.8 (*d*); 62.6 (*t*). MS: 156 (0.5, M^{+}), 141 (3), 138 (4), 127 (20), 123 (39), 110 (60), 95 (78), 82 (85), 69 (100), 67 (70), 55 (76), 41 (53).

rac-cis-2,3,3-Trimethylcyclopentaneethanol Acetate (*rac*-**23b**). As described for (+)-**22b**: *rac*-**23b** (56%). B.p. 90°/0.2 mbar. IR: 2949, 2868, 1740, 1462, 1386, 1364, 1230, 1033. ^1H -NMR: 0.75 (*d*, $J=7$, 3 H); 0.88 (*s*, 3 H); 0.98 (*s*, 3 H); 1.35 (*m*, 2 H); 1.49 (*m*, 2 H); 1.59 (*quint.*, $J=7$, 1 H); 1.75 (*m*, 1 H); 1.83 (*m*, 1 H); 2.05 (*s*, 3 H); 2.17 (*m*, 1 H); 4.06 (*m*, 2 H). ^{13}C -NMR: 10.5 (*q*); 21.1 (*q*); 24.6 (*q*); 29.4 (*t*); 30.1 (*q*); 31.3 (*t*); 38.2 (*d*); 38.9 (*t*); 41.4 (*s*); 45.8 (*d*); 64.4 (*t*); 171.2 (*s*). MS: 198 (0, M^{+}), 123 (33), 110 (97), 95 (100), 82 (52), 69 (49), 67 (35), 55 (32), 43 (45).

rac-cis-2,3,3-Trimethylcyclopentaneacetaldehyde (*rac*-**24**). As described for (–)-**17a**: *rac*-**24** (quant.). B.p. 90°/0.25 mbar. IR: 2921, 2853, 1729, 1535, 1458, 1377, 1260, 1142, 1074, 721. ^1H -NMR: 0.75 (*d*, $J=7$, 3 H); 0.87 (*s*, 3 H); 0.99 (*s*, 3 H); 1.3 (*m*, 1 H); 1.4 (*m*, 1 H); 1.5 (*m*, 1 H); 1.69 (*quint.*, $J=7$, 1 H); 1.92 (*tq*, $J=4.6$, 8.1, 1 H); 2.31 (*ddd*, $J=2$, 9.2, 15.9, 1 H); 2.52 (*dd*, $J=2$, 15.9, 1 H); 2.66 (*m*, 1 H); 9.75 (*t*, $J=2$, 1 H). ^{13}C -NMR: 10.9 (*q*); 24.4 (*q*); 29.6 (*t*); 30.0 (*q*); 35.8 (*d*); 39.1 (*t*); 41.4 (*s*); 45.5 (*d*); 47.2 (*t*); 203.2 (*d*). MS: 154 (3, M^{+}), 110 (62), 95 (100), 83 (68), 69 (47), 55 (46), 41 (30).

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