Preparation and Absolute Configuration of (−)-(*E*)-α-*trans*-Bergamotenone

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The synthesis, absolute configuration, and olfactive evaluation of (−)-(*E*)-α-*trans*-bergamotenone (= (−)-(1′*S*,6′*R*,*E*)-5-(2′,6′-dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)pent-3-en-2-one; (−)-**1**), as well as its homologue (−)-**19** are reported. The previously arbitrarily attributed absolute configuration of **1** and of (−)-α-*trans*-bergamotene (= (−)-(1*S*,6*R*)-2,6-dimethyl-6-(4-methylpent-3-enyl)bicyclo[3.1.1]hept-2-ene; (−)-**2**), together with those of the structurally related aldehydes (−)-**3a**,**b** and alcohols (−)-**4a**,**b**, have been rigorously assigned.

Introduction. – Recently, *Brunke* and *Schmaus* presented the results of their analyses of sandalwood essential oil [1], and reported therein the discovery of a new constituent **1**, present at the level of 0.01%. This compound was identified by MS, IR, and ^{1}H- and ^{13}C-NMR analyses as a pent-3-en-2-one derived from the substructure of α-*trans*-bergamotene ((−)-**2**; *trans* refers to the relation of Me–C(6) and CH_2(7) with respect to the main ring of the bicycle structure)[1]). Due to the trace quantities isolated, the chiroptical data were not measured, and the olfactive properties, evaluated by GC sniffing, were found to be strongly milky, fatty, walnut, reminiscent of the top note of sandalwood essential oil[2]). *Dragoco*'s chemists also effected a partial synthesis, starting from a distillation fraction of sandalwood essential oil enriched in (−)-(*Z*)-α-*trans*-bergamotenol ((−)-(*Z*)-**4b**; 32% pure). Thus, MnO_2 oxidation afforded a mixture containing (−)-(*Z*)-**3b**[3]) [1a][6], whose autooxidation, in the presence of a catalytic amount of base (0.01 mol-equiv. of ^{t}BuOK in ^{t}BuOH [7]), afforded, apart from C=C isomerization to the (*E*)-diastereoisomer and degradation to norsesquiterpenoids, already described by *Demole* (nor-α- and nor-β-santalenone [8]) and *Mookherjee* (nor-epi-β-santalenone [9]), many other uncharacterized compounds, amongst which **1** (12 mg, 4.2%) was isolated.

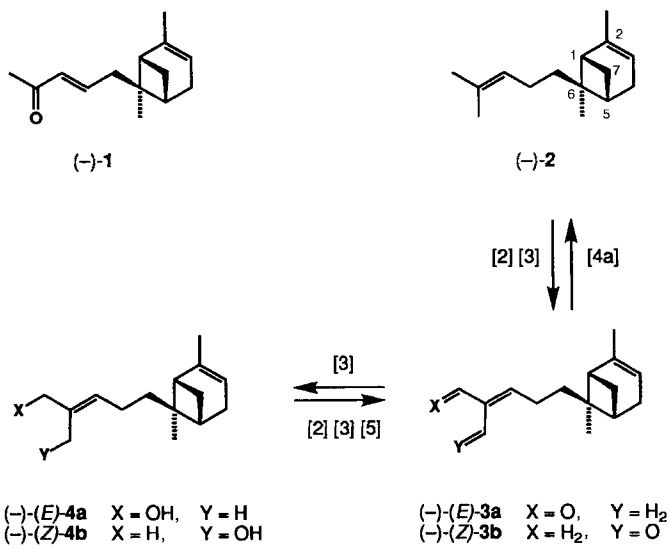
[1]) The aldehyde (−)-(*E*)-**3a** (SeO_2, ^{t}BuOOH, EtOH, 78°; 26% from (−)-**2**; perspiration, woody [2]) was found in *Saussurea lappa* CLARKE [3]. The alcohol (−)-(*E*)-**4a** ($LiAlH_4$, Et_2O; 95% from (−)-(*E*)-**3a** [3]) exhibits animal top notes and woody, sandalwood notes. For earlier analyses of *Santalum* essential oils, with identification of (−)-(*Z*)-**4b** (bright, somewhat woody, waxy, reminiscent of citrus afternote, highly diffusive), see [4].

[2]) Compound **1** was patented as a flavour (0.005 ppm) in a walnut aroma, as well as in perfumery compositions containing synthetic or natural sandalwood-like alcohols, to reinforce the fatty top notes [1a]; its factor of dilution *FD* is 256. For comparison, the *FD* of (+)-(*Z*)-α-santalol and (−)-(*Z*)-β-santalol are 512 and 1024, respectively [1b].

[3]) For a selective synthesis of (−)-(*Z*)-**3b** from (−)-(*Z*)-**4b**, followed by chemical correlation with (−)-**2** (aldehydic, orange, slightly conifer), see [4a] [5].

Particularly interested in the absolute configuration of sandalwood-like alcohols [10], we realized that the absolute configuration indicated for (−)-**2**, and consequently for (−)-(*Z*)-**3b**, (−)-(*Z*)-**4b**, and **1**[3]) [6], although correct according to the 'Dictionary of Terpenoids and Sesquiterpenoids' [11], was in disagreement with previous reports [3][4a][5]. Significantly, concerning the determination of the absolute configuration of α-*trans*-bergamotene ((−)-**2**), all authors, without exception, referred to the same publication of *Kováts* [12]. We were thus particularly surprised to find in this original paper that the absolute configuration of (−)-**2** was arbitrarily assigned as being that of the also naturally co-occurring (−)-α-pinene[4]). In addition, *Kováts* had unluckily confused (−)-α-pinene with its enantiomer, (+)-α-pinene![5]) (see also below). This situation prompted us to re-investigate this subject.

Scheme 1



Results and Discussion. – We decided to start the synthesis of the target compound (−)-**1** from (−)-α-*trans*-bergamotene ((−)-**2**), a sesquiterpene initially isolated by *Ruzicka* and coworkers in 1950 [16] and occurring in more than twenty-five different plants [17]. Although the extracts of *Lausium anamalayanum* BEDD are the richest in

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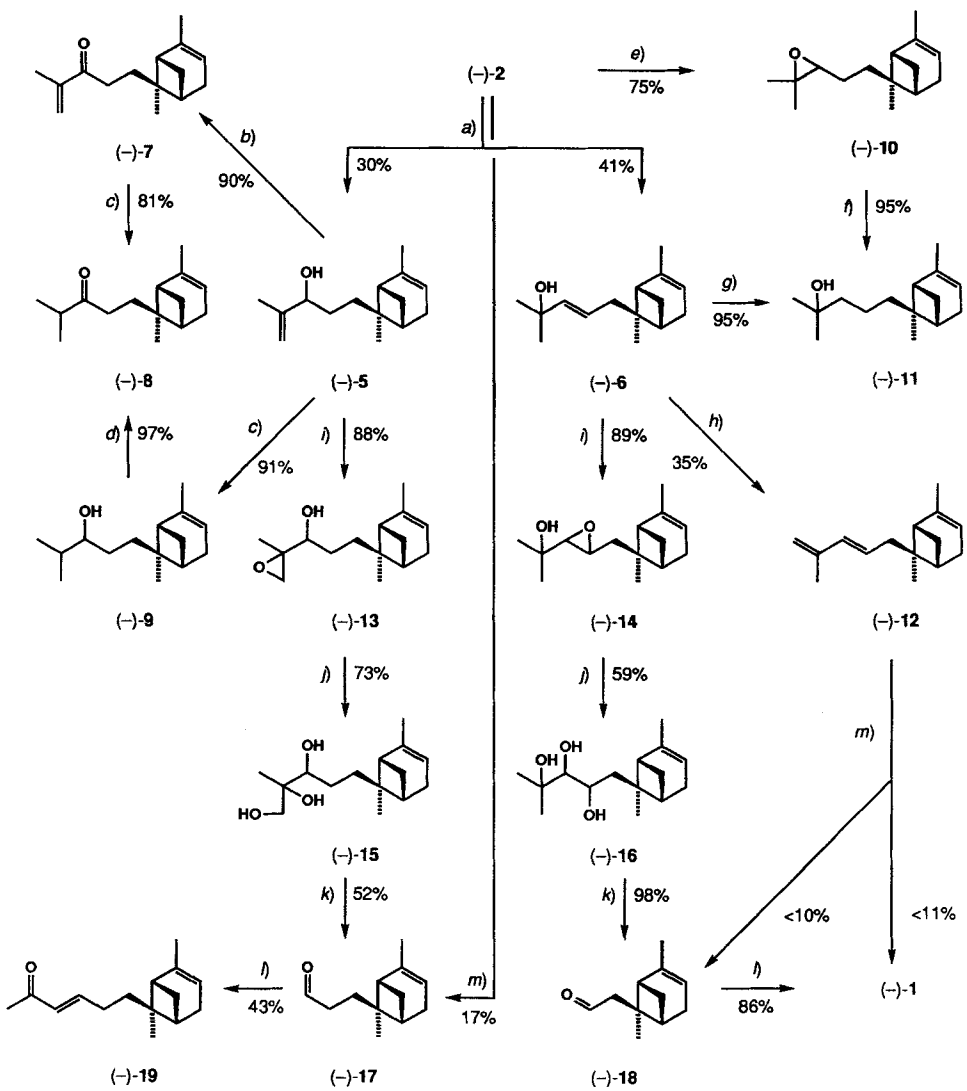
[4]) See Footnote 11 in [12]; 'Demnach käme der nativen Verbindung die in der Formel dargestellte Struktur des *trans*-α-Bergamotens zu. Die in der Formel willkürlich gewählte absolute Konfiguration ist das Analogon des im Öl ebenfalls vorkommenden (−)-α-Pinens'. It is now known that a plant or a tree may produce, by two independent pathways, the two antipodal forms of α- and β-pinene, and that the optical purity of α-pinene may depend on its location (roots, trunk, branches, needles) [13].

[5]) The absolute configurations of (−)-α-*cis*- and (+)-β-*cis*-bergamotene are known by chemical correlations with (−)-β-pinene [14]. For a total synthesis of (−)-α-*cis*- and (+)-β-*cis*-bergamotenoic acid, see [15]. It is noteworthy that the chiroptical properties of (+)-(1*S*)-β-*cis*- and (+)-(1*S*)-β-*trans*-bergamotene [11] are of inverted sign with respect to those of (−)-(1*S*)-β-pinene.

(–)-**2** (26%), we used the spinning band distillation head fractions of begamot essential oil (*Citrus bergamia*; (–)-**2** of 93% purity, $[\alpha]_D^{20} = -31.0$ ($CHCl_3$); [16]: $[\alpha]_D^{20} = -44.1$ ($c = 3.86$, $CHCl_3$)) that we earlier photooxygenated (1. Rose Begal, *hv*, O_2, EtOH; 2. $NaBH_4$ [2]) to obtain in 73% yield a 42:58 mixture of alcohols (–)-**5** (by GC and NMR analytically indistinguishable mixture of diastereoisomers) and (–)-**6**, easily separated

Scheme 2



a) 1. O_2, *hv*, MeOH, Rose Bengal; 2. $NaBH_4$. *b*) MnO_2, petroleum ether. *c*) H_2, *Raney*-Ni, EtOH. *d*) PCC, CH_2Cl_2. *e*) AcOOH, AcONa, CH_2Cl_2. *f*) $LiAlH_4$, Et_2O. *g*) H_2, 5% Pd/C, EtOH. *h*) $KHSO_4$, 130°. *i*) [VO(acac)$_2$], ^{t}BuOOH, toluene. *j*) KOH, H_2O, DMSO, 100°. *k*) $Pd(OAc)_4$, K_2CO_3, toluene. *l*) $Ph_3PCHC(O)Me$, toluene, 110°. *m*) O_3, –78°, CH_2Cl_2/MeOH 1:1, then Me_2S.

by chromatography on SiO_2. For each of these alcohols, we chose to effect the same degradation scheme[6]).

Firstly, however, we oxidized (−)-**5** (MnO_2, petroleum ether) to enone (−)-**7** (90%), a precursor of ketone (−)-**8** (H_2, *Raney*-Ni, EtOH; 81%), naturally occurring in Brazilian *Phoebe* oil [18], and otherwise obtained either from (−)-**7** (Bu_3SnH, toluene, 100°; 21% [19]) or by oxidation (pyridinium chlorochromate (PCC), CH_2Cl_2; 97%) of the semihydrogenated secondary alcohol (−)-**9** (H_2, *Raney*-Ni, EtOH; 91% from (−)-**5**; 2:1 diastereoisomer mixture, distinguishable by the ^{1}H-NMR signal, of H_{anti}-C(7')). Peracid oxidation of (−)-α-*trans*-bergamotene ((−)-**2**) (AcOOH, AcONa, CH_2Cl_2) furnished a 9:1 mixture of mono- and diepoxides from which (−)-**10** (75%), a natural constituent of lavender essential oil (*Lavandula augustifolia* MILLER [20]), was separated by chromatography as a 1:1 diastereoisomer mixture. The oxirane moiety was reduced ($LiAlH_4$, Et_2O) to afford the sandalwood-like tertiary alcohol (−)-**11** (95%), alternatively isolated in 95% yield by selective hydrogenation of (−)-**6** (H_2, 5% Pd/C, EtOH).

Dehydration of (−)-**6** ($KHSO_4$, 130°) furnished triene (−)-**12** (35%), whose partial ozonolysis (0.25 mol-equiv. of O_3, $MeOH/CH_2Cl_2$ 1:1, −78°, then Me_2S) allowed us to identify the desired pent-3-en-2-one (−)-**1** as a minor component (11%) of the crude product mixture. Similarly, selective oxidative cleavage of the C=C bond in the side chain of (−)-**2** was also unsuccessful, due to the reactivity of the endocyclic unsaturation (O_3, AcOEt, −78°, then Me_2S [21]; or $OsO_4/NaIO_4$ [22]).

We then decided to take advantage of the allylic hydroxy function and thus regioselectively epoxidized (−)-**5** and (−)-**6** ([VO(acac)$_2$], ^{t}BuOOH, toluene [23]) to obtain diastereoisomer mixtures of epoxy alcohols (−)-**13** (88%; 1:1 mixture, distinguishable) and (−)-**14** (89%; 1:1 mixture), respectively. After several unsuccessful attempts to oxidatively degrade these epoxy alcohols directly to the desired aldehydes[7]), we decided to proceed stepwise. Hydrolysis of the epoxy moieties (KOH, DMSO, H_2O, 100°) gave diastereoisomer mixtures of the triols (−)-**15** (73%; 1:1 mixture, distinguishable) and (−)-**16** (59%; 1:1 mixture), respectively, which were independently submitted to various oxidative conditions[7]); we eventually found that $Pb(OAc)_4$ gave the best results, affording the desired aldehydes (−)-**17**[8]) (52%) and (−)-**18** (98%). Finally, standard *Wittig* condensation ($Ph_3PCHC(O)Me$, toluene, 110° [31]), afforded hex-3-en-2-one (−)-**19** (43%) and (−)-(*E*)-α-*trans*-bergamotenone ((−)-**1**; 86%), respectively. The latter was analytically identical to the naturally occurring compound[9]).

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[6]) Theoretically, the photooxygenation of (−)-(*Z*)-**4b**, present in the essential oil of *Santalum album* L. [4b], could give rise to a homoallylic alcohol with a hydroperoxy group at a tertiary C-atom, degradable into (−)-**1**.

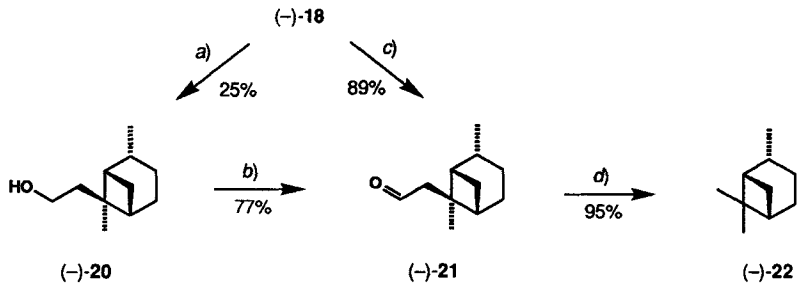
[7]) HIO_4, H_2O, neat, or THF, or acetone [24]; $Ce(NH_4)_2(NO_3)_6$, MeCN, H_2O [25]; LiBr, 1-methylpyrolidin-2-one, toluene, 110° [26]; $(Et_4N)IO_4$, CH_2Cl_2 or MeOH [27]; $Pb(OAc)_4$, K_2CO_3, toluene [28].

[8]) This aldehyde, also obtained by partial ozonolysis of (−)-**2** (25% mol-equiv. of O_3, $MeOH/CH_2Cl_2$ 1:1, −78°, then Me_2S; 17%), is naturally occurring in costus root oil (*Saussurea lappa* CLARKE) [29]. The *Wittig* condensation (2-(triphenylphosphoranylidene)propanal [30], toluene, 110°, 20 h; 43%) furnished (−)-(*E*)-**3a** [29]. Aldehyde (−)-**18** (< 10%) was also detected by GC analysis in the mixture obtained after partial ozonolysis of (−)-**12**.

[9]) With the exception of the chiroptical properties which could not be compared. We are indebted to Dr. *Schmaus* for informing us that the NMR analyses reported in [1] were measured in C_6D_6; the enone olefinic and methyl signals are remarkably different in $CDCl_3$ (0.1–0.4 ppm shift, see *Exper. Part*). For the NMR analyses of *cis*- and *trans*-α- and β-bergamotene, see [32].

An initial attempt to determine the absolute configuration of (−)-**1** by deformylation of (−)-**18** ([RhCl(PPh$_3$)$_3$], toluene, 110° [33]) gave (−)-α-pinene in less than 10% yield. In addition, contamination by diverse unidentified parasite compounds rendered the chiroptical and chiral GC analyses difficult and inconclusive. In the hope that the saturated aldehyde would be more stable under these conditions, we hydrogenated (−)-**18** in acetic acid in the presence of PtO_2 and obtained the primary alcohol (−)-**20** (25%) as a 95:5 *cis*/*trans* diastereoisomer mixture (*Scheme 3*). Subsequent oxidation (pyridinium chlorochromate (PCC), CH_2Cl_2; 77%) gave the saturated aldehyde (−)-**21** in the same diastereoisomer ratio. Alternatively, an identical mixture was directly obtained, in 89% yield, by hydrogenation (5% Pd/C, EtOH) followed by acidic treatment (15% HCl/H_2O, THF) to hydrolyse the partially formed corresponding diethyl acetal. Deformylation of (−)-**21** under the previously mentioned *Wilkinson* conditions, cleanly and quantitatively afforded a 95:5 (−)-*cis*/(−)-*trans*-pinane mixture, easily separable and identifiable by chiral GC analysis[10]).

Scheme 3



a) PtO_2, AcOH, H_2. *b*) PCC, CH_2Cl_2. *c*) 5% Pd/C, EtOH, H_2, then THF, H_3O^+. *d*) [RhCl(PPh$_3$)$_3$], toluene, 110°.

Conclusion. – Starting from (−)-α-*trans*-bergamotene ((−)-**2**), we synthesized and unambiguously determined the absolute configuration of (−)-**1** and, therefore, for the first time, of the structurally related naturally occurring derivatives (−)-**2**, (−)-**3a**, (−)-**4b**, (−)-**8**, (−)-**10**, and (−)-**17**, by chemical correlation with (−)-(1*S*,2*R*)-*cis*-pinane ((−)-**22**)[11]). The wrong absolute configuration of (−)-**2**, reported in several previous reports [1][2][6][11][12], stems from an error in depicting the absolute-configuration structure of (−)-α-pinene by *Kováts* [38][12]). However, others [3][4a][5], using his arbitrary hypothesis[4]), were able to assign the correct configuration.

The fatty, oily organoleptic properties of (−)-**1**, strong compared to nor-α-, nor-β-, and nor-epi-β-santalenone [6], allow its possible application for the reconstitution of sandalwood essential oil top notes, despite the fact that (−)-**1** itself does not possess any woody, sandalwood-like character.

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[10]) Permethylated-β-cyclodextrin column (length 9 m); t_R of pinane in min; (+)-*trans*, 9.44; (−)-*trans*, 9.77; (−)-*cis*, 10.85; (+)-*cis*, 11.87 [34].

[11]) For an unfounded *corrigendum*, see [35]. For the determination of the absolute configuration of (−)-α-pinene and for its hydrogenation to (−)-*cis*-pinane ((−)-**22**), see [36] and [37], respectively.

[12]) This is a common error, even nowadays [39].

We are indebted to Dr. *F. Näf* for motivating the revival of this project, as well as to Mr. *R. Brauchli* and *W. Thommen* for ^{13}C-NMR analyses and attributions.

Experimental Part

General. See [10a].

(−)-(1'S,6R',E)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpent-2-en-1-al ((−)-(*E*)-**3a**). For synthesis and analyses, see [2][3]. B.p. 70–75°/0.01 Torr. $[\alpha]_D^{20} = -46.7$. $n_D = 1.5099$, $d^{20} = 0.9596$. ^{13}C-NMR: 9.1 (*Me*–C(2)); 17.4 (*Me*–C(6')); 23.0 (*Me*–C(2')); 25.1 (C(4)); 31.2 (C(4')); 31.6 (C(7')); 37.1 (C(5)); 39.0 (C(5')); 41.3 (C(6')); 45.4 (C(1')); 116.7 (C(3')); 139.1 (C(2)); 144.1 (C(2')); 155.6 (C(3)); 195.4 (C(1)).

(−)-(1'S,6R',E)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpent-2-en-1-ol ((−)-(*E*)-**4a**). For synthesis and analyses, see [3]. B.p. 120–130°/0.37 Torr. $[\alpha]_D^{20} = -46.1$. $n_D = 1.5078$, $d^{20} = 0.9620$. ^{13}C-NMR: 13.6 (*Me*–C(2)); 17.5 (*Me*–C(6')); 23.0 (*Me*–C(2')); 23.4 (C(4)); 31.2 (C(4')); 31.6 (C(7')); 38.3 (C(5)); 39.0 (C(5')); 41.2 (C(6')); 45.4 (C(1')); 68.9 (C(1)); 116.5 (C(3')); 127.0 (C(3)); 134.4 (C(2)); 144.4 (C(2')).

(−)-(1'S,6'R,3R)/(1'S,6'R,3S)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'en-6'-yl)-2-methylpent-1-en-3-ol ((−)-**5**), *and (−)-(1'S,6'R,E)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpent-3-en-2-ol* ((−)-**6**). (−)-α-*trans*-Bergamotene ((−)-**2**; 93% pure; 20.4 g, 0.1 mol) in EtOH (200 ml) and i-PrOH (25 ml) was photooxygenated in the presence of Rose Bengal (300 mg) with a 125-W *Philips-HPK* lamp at 15–18°. Absorption of O_2 (2.24 l, 0.1 mol), with a flow of 40 ml/min, was accomplished in 3 h. The irradiation was then interrupted, and $NaBH_4$ (3.5 g, 0.092 mol) was added portionwise to the cold well-stirred soln. After 12 h and final addition of H_2O (500 ml), the mixture was extracted with Et_2O (6 × 100 ml), the org. phase evaporated, and the residue bulb-to-bulb distilled to afford a 42:58 mixture of (−)-**5**/(−)-**6** (73%). Purification by CC (SiO_2 (1.2 kg), toluene/AcOEt 95:5) gave first (−)-**5** (30%) and then (−)-**6** (41%).

(−)-**5**: B.p. 140°/0.31 Torr. $[\alpha]_D^{20} = -44.0$. $n_D = 1.500$, $d_4^{20} = 0.9574$. IR: 3348, 2920, 1652, 1446. ^{1}H-NMR: 0.81 (*s*, 3 H); 1.18 (*d*, *J* = 7, 1 H); 1.53 (*m*, 3 OH); 1.6 (*m*, 1 H); 1.63 (*q*, *J* = 2, 3 H); 1.7 (*m*, 1 H); 1.75 (*s*, 3 H); 1.99 (br. *q*, *J* = 5, 1 H); 2.12 (*m*, 2 H); 2.23 (*m*, 1 H); 2.30 (*m*, 1 H); 4.70 (*q*, *J* = 5, 1 H); 4.85 (*s*, 1 H); 4.96 (*s*, 1 H); 5.21 (br. *s*, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(2)); 17.5 (*Me*–C(6')); 23.0 (*Me*–C(2')); 30.3 (C(4)); 31.2 (C(4')); 31.6 (C(7')); 34.0 (C(5)); 39.0 (C(5')); 40.9 (C(6')); 45.4 (C(1')); 76.6 (C(3)); 111.3 (C(1)); 116.5 (C(3')); 144.4 (C(2')); 147.6 (C(2)). MS: 220 (1, $M^{+\cdot}$), 187 (4), 145 (15), 132 (40), 119 (65), 105 (36), 93 (100), 79 (44), 68 (25), 55 (26), 41 (54). Fatty, floral.

(−)-**6**: B.p. 140°/0.31 Torr. $[\alpha]_D^{20} = -42.7$. $n_D = 1.4982$, $d_4^{20} = 0.9542$. IR: 3362, 2923, 1436, 1474, 1148, 972, 883. ^{1}H-NMR: 0.8 (*s*, 3 H); 1.19 (*d*, *J* = 7, 1 H); 1.32 (*s*, 6 H); 1.43 (br. *s*, OH); 1.65 (*q*, *J* = 2, 3 H); 1.99 (*m*, 1 H); 2.15 (*m*, 2 H); 2.25 (*m*, 1 H); 2.33 (*m*, 3 H); 5.22 (*m*, 1 H); 5.68 (*m*, 2 H). ^{13}C-NMR: 17.7 (*Me*–C(6')); 23.0 (*Me*–C(2')); 29.9 (C(1)); 29.9 (*Me*–C(2)); 31.2 (C(4')); 31.3 (C(7')); 38.7 (C(5')); 41.0 (C(5)); 41.3 (C(6')); 45.3 (C(1')); 70.7 (C(2)); 116.7 (C(3')); 124.4 (C(4)); 139.9 (C(3)); 144.2 (C(2')). MS: 220 (1, $M^{+\cdot}$), 159 (7), 145 (12), 132 (24), 119 (30), 105 (34), 93 (100), 79 (40), 43 (66). Sandalwood, elegant, woody, vetiver, cedar, slightly cumin, tenacious.

(−)-(1'S,6'R)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpent-1-en-3-one ((−)-**7**). A suspension of (−)-**5** (2.5 g, 11.36 mmol) and MnO_2 (50 g, 575 mmol) in petroleum ether (150 ml) was stirred for 24 h under N_2 prior to filtration and evaporation. The crude oil was bulb-to-bulb distilled to give pure (−)-**7** (90%). B.p. 100°/0.01 Torr. $[\alpha]_D^{20} = -37.0$, $n_{20} = 1.5001$, $d^{20} = 0.9644$. IR: 1675, 1630, 925. ^{1}H-NMR: 0.82 (*s*, 3 H); 1.19 (*d*, *J* = 7, 1 H); 1.65 (*q*, *J* = 2, 3 H); 1.88 (*s*, 3 H); 1.9–2.0 (*m*, 3 H); 2.1–2.15 (*m*, 2 H); 2.2–2.4 (*m*, 2 H); 2.65–2.75 (*m*, 2 H); 5.21 (*m*, 1 H); 5.78 (br. *s*, 1 H); 5.99 (*s*, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(6')); 17.8 (*Me*–C(2)); 23.0 (*Me*–C(2')); 31.2 (C(4')); 31.6 (C(7')); 33.1 (C(5)); 33.7 (C(4)); 38.9 (C(5')); 41.0 (C(6')); 45.3 (C(1')); 116.6 (C(3')); 124.3 (C(1)); 144.2 (C(2')); 144.6 (C(2)); 202.8 (C(3)). MS: 218 (1, $M^{+\cdot}$), 204 (1), 132 (100), 119 (98), 105 (35), 93 (75), 77 (40), 69 (70), 41 (98). Green, opoponax, woody, oily.

(−)-(1'S,6'R)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpentan-3-one ((−)-**8**). A suspension of (−)-**7** (86.2 mg, 0.39 mmol) and *Raney*-Ni (1.8 mg) in EtOH (1 ml) was hydrogenated for 0.5 h (13 ml of H_2) prior to filtration over *Celite*, evaporation, and bulb-to-bulb distillation: pure (−)-**8** (81%).

A soln. of (−)-**7** (19.2 mg, 0.088 mmol) and Bu_3SnH (70 µl, 0.26 mmol) in toluene (1 ml) was refluxed for 20 h. The resulting mixture was evaporated and purified by CC (SiO_2 (8.0 g), toluene/AcOEt 9:1): pure (−)-**8** (21%).

Alternatively, a suspension of (−)-**9** (225 mg, 1.01 mmol), *Celite* (495 mg), and PCC (328 mg, 1.52 mmol) in CH_2Cl_2 (2.5 ml) was stirred at 20° for 16 h. Filtration through SiO_2 (20 g, Et_2O), evaporation, and bulb-to-bulb distillation afforded pure (−)-**8** (97%). B.p. 110–120°/0.17 Torr. $[\alpha]_D^{20} = -39.3$ (*c* = 1.65, $CHCl_3$). IR: 2925, 1713, 1465, 1445, 1375, 1070. ^{1}H-NMR: 0.81 (*s*, 3 H); 1.10 (*d*, *J* = 7, 6 H); 1.19 (*d*, *J* = 9, 1 H); 1.66 (*q*, *J* = 2,

3 H); 1.89 (*m*, 2 H); 1.98 (*m*, 1 H); 2.12 (*m*, 2 H); 2.25 (*m*, 1 H); 2.32 (*dt*, *J* = 5, 9, 1 H); 2.45 (*m*, 2 H); 2.65 (*sept.*, *J* = 7, 1 H); 5.21 (*m*, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(6′)); 18.4 (C(1)); 18.4 (*Me*–C(2)); 23.0 (*Me*–C(2′)); 31.2 (C(4′)); 31.6 (C(7′)); 32.1 (C(5)); 36.5 (C(4)); 38.8 (C(5′)); 40.8 (C(6′)); 41.0 (C(2)); 45.3 (C(1′)); 116.6 (C(3′)); 144.2 (C(2′)); 215.4 (C(3)). MS: 220 (1, $M^{+\cdot}$), 159 (13), 134 (96), 132 (68), 119 (100), 105 (30), 93 (70), 91 (60), 86 (17), 79 (38), 77 (39), 71 (57), 55 (24), 43 (89). Woody, slightly amber, cedar, rooty, natural.

(−)-(1′S,6′R)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-2-methylpentan-3-ol ((−)-**9**). A soln. of (−)-**5** (1.1 g, 5.0 mmol) in EtOH (10 ml) was hydrogenated for 2 h (112 ml of H_2), in the presence of *Raney*-Ni (0.3 g). The resulting suspension was filtered, the filtrate evaporated, and the residue bulb-to-bulb distilled: pure (−)-**9** (91%). B.p. 110°/0.01 Torr. $[\alpha]_D^{20} = -34.0$. $n_D = 1.4891$, $d^{20} = 0.9444$. IR: 3350. ^{1}H-NMR: 0.81 (*s*, 3 H); 0.92 (*d*, *J* = 7, 3 H); 0.95 (*d*, *J* = 7, 3 H); 1.11 (*d*, *J* = 9, 33%, 1 H); 1.19 (*d*, *J* = 9, 66%, 1 H); 1.3–1.6 (*m*, 3 H); 1.67 (*q*, *J* = 1, 3 H); 1.7–1.85 (*m*, 2 H); 2.0 (*m*, 1 H); 2.15 (*m*, 2 H); 2.23 (*m*, 1 H); 2.29 (*m*, 1 H); 2.32 (*dt*, *J* = 7, 4, 1 H); 3.38 (*m*, 1 H); 5.21 (br. *s*, 1 H). ^{13}C-NMR: 17.0 (C(1)); 17.5 (*Me*–C(6′)); 19.0 (*Me*–C(2)); 23.0 (*Me*–C(2′)); 29.7 (C(4)); 31.2 (C(4′)); 31.6 (C(7′)); 33.4 (C(2)); 34.6 (C(5)); 39.0 (C(5′)); 41.0 (C(6′)); 45.5 (C(1′)); 77.5 (C(3)); 116.5 (C(3′)); 144.4 (C(2′)). MS: 222 (1, $M^{+\cdot}$). 204 (3), 189 (2), 179 (3), 161 (15), 134 (18), 119 (70), 105 (40), 93 (100), 79 (35), 69 (40), 41 (45). Without parfumistic interest.

(−)-(1′S,6′R,3R)/(1′S,6′R,3S)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-2,3-epoxy-2-methylpentane (= *(−)-(3RS)-3-{2-[(1S,6R)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]ethyl}-2,2-dimethyloxirane*; (−)-**10**). Under mechanical stirring, 40% AcOOH in AcOH (62 g, 326.3 mmol) was added dropwise to a suspension of (−)-**2** (93% pure; 51 g, 232.5 mmol) and AcONa (3 g, 36.6 mmol) in CH_2Cl_2 (150 ml) at 0–5°. After 18 h at 20°, the mixture was extracted with H_2O and sat. aq. $NaHCO_3$ soln., dried (Na_2SO_4), and distilled. The obtained 9:1 mixture of mono- and diepoxides was further purified by CC (SiO_2, cyclohexane/AcOEt 97:3): pure (−)-**10** (75%), 1:1 diastereoisomer mixture. B.p. 90°/0.01 Torr. $[\alpha]_D^{20} = -36.1$. $n_D = 1.4803$, d^{20} 0.9355. IR: 2990, 1450, ^{1}H-NMR: 0.82 (*s*, 3 H); 1.19 (*d*, *J* = 9, 1 H); 1.20 (*m*, 3 H); 1.23 (*m*, 3 H); 1.25 (*s*, 3 H); 1.26 (*m*, 3 H); 1.27 (*s*, 3 H); 1.67 (*d*, *J* = 2, 3 H); 2.7 (*m*, 1 H); 5.17 (*m*, 1 H). MS: 220 (1, $M^{+\cdot}$), 204 (1), 159 (3), 134 (30), 119 (55), 105 (30), 93 (100), 79 (30), 71 (30), 55 (30), 41 (50), 27 (70). Bergamot, green.

(−)-(1′S,6′R)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-2-methylpentan-2-ol ((−)-**11**). A soln. of (−)-**10** (2.2 g, 10 mmol) and $LiAlH_4$ (0.4 g, 10.5 mmol) in Et_2O (20 ml) was stirred for 18 h before quenching with sat. aq. NH_4Cl soln. The mixture was extracted with Et_2O, the org. phase dried (Na_2SO_4) and evaporated, and the residue bulb-to-bulb distilled: pure (−)-**11** (95%).

Alternatively, (−)-**6** (2.2 g, 10 mmol) in EtOH (10 ml) was hydrogenated (220 ml of H_2) over 5% Pd/C (25 mg). Filtration, evaporation, and bulb-to-bulb distillation gave (−)-**11** (95%). B.p. 110°/0.01 Torr. $[\alpha]_D^{20} = -36.1$. $n_D = 1.4879$, $d^{20} = 0.9388$. IR: 3350. ^{1}H-NMR: 0.82 (*s*, 3 H); 1.18 (*d*, *J* = 9, 1 H); 1.20 (*s*, 6 H); 1.2–1.3 (*m*, 11 H); 1.46 (*s*, OH); 1.66 (*d*, *J* = 3, 3 H); 5.18 (*m*, 1 H). MS: 222 (1, $M^{+\cdot}$), 204 (5), 189 (3), 148 (6), 133 (14), 119 (48), 107 (30), 93 (100), 79 (25), 69 (25), 59 (25), 41 (35). Woody, sandalwood.

(−)-(1′S,6′R,E)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-2-methylpenta-1,3-diene (= *(−)-(1S,6R)-2,6-Dimethyl-6-[(E)-4-methylpenta-2,4-dienyl]bicyclo[3.1.1]hept-2-ene*; (−)-**12**). A mixture of (−)-**6** (10 g, 45.45 mmol) and $KHSO_4$ (0.5 g, 3.68 mmol) was heated at 120–130°/12 Torr in a flask equipped with a distillation bridge. The oily (−)-**12** (35%) thus obtained was 90% pure and was further purified by prep. GC (*Carbowax* column for anal.). $[\alpha]_D^{20} = -41.0$. IR: 3080, 1650, 1610, 965, 880. ^{1}H-NMR: 0.81 (*s*, 3 H); 1.2 (*d*, *J* = 7, 1 H); 1.65 (*d*, *J* = 2, 3 H); 1.8 (*d*, *J* = 1, 3 H); 1.9–2.7 (*m*, 7 H); 4.79 (*m*, 2 H); 5.16 (*m*, 1 H); 5.3–6.21 (*m*, 2 H). MS: 202 (3, $M^{+\cdot}$), 187 (7), 159 (5), 145 (13), 119 (60), 105 (38), 93 (100), 79 (35), 55 (25), 41 (45). Woody, fatty, rancid.

(−)-(1′S,6′R,2R,3R)/(1′S,6′R,2S,3R)/(1′S,6′R,2R,3S)/(1′S,6′R,2S,3S)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-1,2-epoxy-2-methylpentan-3-ol (= *3-[(1S,6R)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]-1-(2-methyloxiran-2-yl)propan-1-ol*; (−)-**13**). ^{t}BuOOH (70% in H_2O; 4.6 ml, 35.8 mmol) was introduced dropwise to a mixture of (−)-**5** (5.25 g, 23.8 mmol) and $[VO(acac)_2]$ (94.8 mg, 0.36 mmol) in toluene (90 ml) at 20°. After 4 h of mechanical stirring, the conversion was complete. The mixture was diluted with Et_2O (50 ml), the org. phase washed with H_2O and Na_2SO_3 soln., dried (Na_2SO_4), and evaporated, and the residue bulb-to-bulb distilled: (−)-**13** (88%). B.p. 90–100°/0.11 Torr. $[\alpha]_D^{20} = -41.1$ (*c* = 0.9 $CHCl_3$). IR: 3452, 2921, 1446, 1374, 1066, 890. ^{1}H-NMR: 0.81 (*s*, 3 H); 1.19 (*d*, *J* = 7, 1 H); 1.36 (*s*, 3 H); 1.40 (*m*, 2 H); 1.65 (*m*, 3 H); 1.68 (*m*, 2 H); 1.89 (*m*, 1 H); 2.0 (*m*, 1 H); 2.07 (br. *s*, OH); 2.15 (*m*, 1 H); 2.22 (*m*, 1 H); 2.32 (*m*, 1 H); 2.62 (*d*, *J* = 5, 1 H); 2.92 (*d*, *J* = 5, 1 H); 3.63 (*m*, 1 H); 5.21 (*m*, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(6′)); 18.2 (*Me*–C(2)); 23.0 (*Me*–C(2′)); 28.4 (C(4)); 31.2 (C(4′)); 31.6 (C(7′)); 34.1 (C(5)); 39.0 (C(5′)); 40.9 (C(6′)); 45.4 (C(1′)); 50.4 (C(1)); 59.2 (C(2)); 72.2 (C(3)); 116.5 (C(3′)); 144.4 (C(2′)). MS: 236 (0, $M^{+\cdot}$), 145 (8), 132 (34), 119 (62), 93 (100), 79 (42), 55 (30), 43 (43).

(−)-(1′S,6′R,3R)/(1′S,6′R,3S)-5-(2′,6′-Dimethylbicyclo[3.1.1]hept-2′-en-6′-yl)-3,4-epoxy-2-methylpentan-2-ol (= *2-{3-{[(1S,6R)-2,6-Dimethylbicyclo[3.1.1]hept-2-en-6-yl]methyl}oxiran-2-yl}propan-2-ol* (−)-**14**). As described for (−)-**13**, with ^{t}BuOOH (70% in H_2O; 9.4 ml; 68.8 mmol), (−)-**6** (10.1 g, 45.9 mmol), $[VO(acac)_2]$

(183 mg, 0.69 mmol), and toluene (350 ml; 6 h). Workup with Et_2O (100 ml): (−)-**14** (89%). B.p. 100°/0.11 Torr. $[\alpha]_D^{20} = -42.4$ ($c = 0.9$, $CHCl_3$). IR: 3450, 2922, 1446, 1375, 1188, 959, 911. ^{1}H-NMR: 0.95 (*s*, 3 H); 1.22 (*d*, $J = 7$, 1 H); 1.26 (*s*, 3 H; 50% diast. A); 1.27 (*s*, 3 H; 50% diast. B); 1.31 (*s*, 3 H); 1.68 (*m*, 3 H); 1.78 (br. *s*, OH); 1.8 (*m*, 1 H); 1.98 (*m*, 2 H); 2.12 (*m*, 1 H); 2.18 (*m*, 1 H); 2.25 (*m*, 1 H); 2.32 (*m*, 1 H); 2.72 (*d*, $J = 2$, 1 H); 3.09 (*td*, $J = 7$, 2, 1 H); 5.22 (*m*, 1 H). ^{13}C-NMR: 18.1 (*Me*–C(6')); 22.9 (*Me*–C(2')); 25.0 (C(1)); 27.9 (*Me*–C(2)); 31.0 (C(4')); 31.3 (C(7')); 39.2 (C(5')); 40.3 (C(5)); 40.6 (C(6')); 45.4 (C(1')); 53.9 (C(4)); 65.0 (C(3)); 67.7 (C(2)); 116.6 (C(3')); 143.7 (C(2')). MS: diast. B: 236 (0, $M^{+\cdot}$), 185 (4), 146 (16), 131 (26), 119 (100), 105 (78), 93 (84), 77 (42), 59 (94), 43 (63); diast. A: 236 (0, $M^{+\cdot}$), 185 (4), 146 (15), 131 (28), 119 (100), 105 (76), 93 (84), 77 (42), 59 (90), 43 (62).

(−)-(1'S,6'R,2R,3R)/(1'S,6'R,2S,3R)/(1'S,6'R,2R,3S)/(1'S,6'R,2S,3S)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpentane-1,2,3-triol ((−)-**15**). A mixture of (−)-**13** (1.8 g, 7.6 mmol) in DMSO (18 ml), H_2O (0.7 ml), and KOH (0.5 g, 8.4 mmol) was refluxed for 1 h. The cold soln. was extracted twice with Et_2O, the org. phase washed with sat. aq. NaCl soln., dried (Na_2SO_4), and evaporated; and the residue purified by CC (SiO_2 (200 g), toluene/AcOEt 8:2 → 6:4): (−)-**15** (73%), 1:1 diastereoisomer mixture. $[\alpha]_D^{20} = -28.6$ ($c = 0.6$, $CHCl_3$). IR: 3452, 2920, 1446, 1373, 1097. ^{1}H-NMR: 0.82 (*s*, 3 H); 1.12 (*s*, 3 H); 1.18 (*m*, 3 H); 1.35 (*m*, 1 H); 1.57 (br. *s*, 3 OH); 1.67 (*s*, 3 H); 1.95 (*m*, 1 H); 2.13 (*m*, 2 H); 2.21 (*m*, 1 H); 2.3 (*m*, 2 H); 3.5 (*m*, 1 H); 3.6 (*m*, 2 H); 5.21 (br. *s*, 1 H). ^{13}C-NMR: diast. A: 17.6 (*Me*–C(6')); 20.7 (*Me*–C(2)); 23.0 (C(2')); 25.4 (C(4)); 31.2 (C(4')); 31.6 (C(7')); 36.0 (C(5)); 38.9 (C(5')); 41.0 (C(6')); 45.4 (C(1')); 70.8 (C(1)); 74.6 (C(2)); 74.8 (C(3)); 116.6 (C(3')); 144.3 (C(2')); diast. B: 15.3 (*Me*–C(6)); 21.7 (*Me*–C(2)); 23.0 (C(2')); 25.7 (C(5)); 31.6 (C(4'), (C(7')); 35.7 (C(4)); 39.0 (C(5')); 41.0 (C(6')); 45.4 (C(1')); 70.6 (C(1)); 74.6 (C(3)); 73.8 (C(2)); 116.5 (C(3')); 144.4 (C(2')). MS: 254 (0, $M^{+\cdot}$), 219 (9), 201 (14), 159 (21), 145 (26), 132 (38), 119 (58), 93 (85), 81 (59), 69 (38), 55 (57), 43 (100).

(−)-(1'S,6'R,3R,4R)/(1'S,6'R,3S,4R)/(1'S,6'R,3R,4S)/(1'S,6'S,3S,4S)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-2-methylpentane-2,3,4-triol ((−)-**16**). As described for (−)-**15**, with (−)-**14** (100 mg, 0.424 mmol), DMSO (1 ml), H_2O (65 µl), and KOH (26.1 mg, 0.466 mmol). CC (SiO_2 (15 g), toluene/AcOEt 8:2, then 7:3, then 6:4) afforded (−)-**16** (59%; 1:1 diastereoisomer mixture). B.p. 120–150°/0.095 Torr. $[\alpha]_D^{20} = -34.5$ ($c = 1.4$, $CHCl_3$). IR: 3567, 3028, 2924, 2849, 1445, 1381, 1167, 1042, 953. ^{1}H-NMR: 0.94 (*s*, 3 H, 50% diast. A); 0.96 (*s*, 3 H, 50% diast. B); 1.23 (*m*, 2 H); 1.31 (*s*, 6 H, 50% diast. B); 1.32 (*s*, 6 H, 50%, diast. A); 1.68 (br. *s*, 3 H); 1.8–2.4 (*m*, 9 H); 3.3 (*m*, 1 H); 3.95 (*m*, 1 H); 5.22 (br. *s*, 1 H). ^{13}C-NMR: 18.2 (*Me*–C(6')); 23.0 (*Me*–C(2')); 25.7 (C(1)); 26.9 (*Me*–C(2)); 31.1 (C(4')); 31.1 (C(7')); 39.7 (C(5')); 39.9 (C(5') (2nd diast.)); 40.6 (C(6')); 42.3 (C(5)); 42.4 (C(5) (2nd diast.)); 46.1 (C(1')); 46.4 (C(1') (2nd diast.)); 72.5 (C(4)); 73.0 (C(4) (2nd diast.)); 73.5 (C(2)); 79.5 (C(3)); 116.6 (C(3')); 116.7 (C(3') (2nd diast.)); 144.0 (C(2')). MS: 254 (0, $M^{+\cdot}$), 236 (6), 131 (26), 119 (70), 105 (50), 93 (100), 79 (36), 72 (34), 59 (76), 55 (38), 43 (53).

(−)-(1S,6R)-2,6-Dimethylbicyclo[3.1.1]hept-2-ene-6-propanal ((−)-**17**). A soln. of (−)-**15** (100 mg, 0.39 mmol) in toluene (0.1 ml) was added to a suspension of $Pb(OAc)_4$ (349 mg, 0.79 mmol) in toluene (1 ml). After 5 h at 20°, the mixture was extracted with Et_2O. The org. phase was washed with H_2O, dried (Na_2SO_4), and evaporated and the residue purified by CC (SiO_2 (30 g), toluene/Et_2O 8:2, then 6:4): (−)-**17** (51%). B.p. 150°/0.24 Torr. $[\alpha]_D^{20} = -53.1$. IR: 2991, 2928, 2851, 2710, 1742, 1446, 1382, 1016, 955. ^{1}H-NMR: 0.79 (*s*, 3 H); 0.83 (*m*, 1 H); 1.20 (*d*, $J = 7$, 1 H); 1.22 (*m*, 1 H); 1.65 (*q*, $J = 2$, 3 H); 1.95 (*m*, 2 H); 2.12 (*m*, 1 H); 2.23 (*m*, 1 H); 2.3 (*m*, 1 H); 2.45 (*m*, 2 H); 5.22 (*m*, 1 H); 9.83 (*t*, $J = 2$, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(6)); 22.9 (*Me*–C(2)); 30.2 (C(β)); 31.2 (C(4)); 31.5 (C(7)); 38.8 (C(5)); 40.4 (C(α)); 40.8 (C(6)); 45.3 (C(1)); 116.7 (C(3)); 144.1 (C(2)); 203.0 (CHO). MS: 178 (1, $M^{+\cdot}$), 145 (19), 119 (58), 93 (100), 77 (46), 41 (33). Very pleasant.

(−)-(1S,6R)-2,6-Dimethylbicyclo[3.1.1]hept-2-ene-6-acetaldehyde ((−)-**18**). Under mechanical stirring, a soln. of (−)-**16** (10.95 g, 43.1 mmol) in toluene (10 ml) was added dropwise to a suspension of $Pb(OAc)_4$ (38.2 g, 86.2 mmol) and K_2CO_3 (25.6 g, 185.4 mmol) in toluene (230 ml), maintaining the temp. below 30°. After 20 min at 20°, the mixture was filtered over *Celite*, the filtrate evaporated, and the residue purified by bulb-to-bulb distillation: (−)-**18** (98%). B.p. 90°/0.28 Torr. $[\alpha]_D^{20} = -66.6$ ($c = 1.25$, $CHCl_3$). IR: 3030, 2927, 2851, 2709, 1736, 1445, 1383, 1086, 1021. ^{1}H-NMR: 0.85 (*m*, 3 H); 1.00 (*s*, 3 H); 1.29 (*d*, $J = 7$, 1 H); 1.68 (*q*, $J = 2$, 3 H); 2.16 (*m*, 1 H); 2.2–2.4 (*m*, 3 H); 2.7 (*m*, 2 H); 5.26 (*m*, 1 H); 9.83 (*t*, $J = 2$, 1 H). ^{13}C-NMR: 18.5 (*Me*–C(6)); 22.9 (*Me*–C(2)); 30.8 (C(4)); 31.0 (C(7)); 39.3 (C(5)); 39.8 (C(6)); 45.5 (C(1)); 51.7 (CH_2–C(6)); 116.9 (C(3)); 143.2 (C(2)); 203.7 (CHO). MS: 164 (1, $M^{+\cdot}$), 131 (43), 120 (52), 105 (76), 93 (100), 77 (68), 55 (26), 41 (44), 39 (48).

(−)-(1'S,6'R,E)-6-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)-hex-3-en-2-one ((−)-**19**). A soln. of (−)-**17** (190 mg, 1.07 mmol) and 1-(triphenylphosphoranylidene)propan-2-one (679 mg, 2.13 mmol) in toluene (10 ml) was refluxed for 90 min. The ice-cold soln. was filtered, diluted with cyclohexane (15 ml), filtered, and evaporated and the residue purified by CC (SiO_2 (20 g), toluene/AcOEt 95:5): (−)-(*E*)-**19** (43%). B.p. 120°/0.16 Torr. $[\alpha]_D^{20} = -40.6$ ($c = 3.0$, CCl_4). IR: 2922, 1878, 1626, 1435, 1361, 1256, 981. ^{1}H-NMR: 0.85 (*s*, 3 H); 1.20 (*d*, $J = 7$, 1 H); 1.66 (*q*, $J = 1$, 3 H); 1.77 (*m*, 2 H); 2.0 (*t*, $J = 5$, 1 H); 2.17 (*m*, 2 H); 2.22 (*s*, 3 H); 2.25 (*m*, 4 H); 5.22 (*m*, 1 H); 6.11 (*dt*, $J = 15$, 1, 1 H); 6.86 (*dt*, $J = 15$, 7, 1 H). ^{13}C-NMR: 17.4 (*Me*–C(6')); 23.0 (*Me*–C(2')); 26.8

(C(1)); 28.5 (C(5)); 31.2 (C(4')); 31.5 (C(7')); 36.9 (C(6)); 38.9 (C(5')); 41.2 (C(6')); 45.4 (C(1')); 116.6 (C(3')); 131.0 (C(3)); 144.2 (C(2')); 149.2 (C(4)); 198.7 (C(2)). MS: 218 (1, $M^{+\cdot}$), 134 (14), 119 (100), 105 (22), 93 (98), 84 (52), 77 (50), 55 (34), 43 (67). Woody, vaguely sandalwood, pine, oily, fatty.

(−)-(1'S,6'R,E)-5-(2',6'-Dimethylbicyclo[3.1.1]hept-2'-en-6'-yl)pent-3-en-2-one ((−)-**1**). As described for (−)-**19**, with (−)-**18** (3.0 g, 18.3 mmol), 1-(triphenylphosphoranylidene)propan-2-one (11.65 g, 36.6 mmol) and toluene (180 ml; 7 h). Workup with cyclohexane (200 ml). CC (SiO_2 (500 g), toluene/AcOEt 95:5) gave (−)-**1** 3.2 g, 86%). B.p. 120°/0.23 Torr, $[\alpha]_D^{20} = -62.6$ (*c* = 2.1, $CHCl_3$). IR: 2990, 2927, 2850, 1697, 1632, 1441, 1363, 1247, 1176, 1119, 981. ^{1}H-NMR ($CDCl_3$): 0.85 (*s*, 3 H); 1.23 (*d*, *J* = 7, 1 H); 1.68 (*q*, *J* = 1, 3 H); 2.04 (*t*, *J* = 5, 1 H); 2.19 (*m*, 2 H); 2.24 (*s*, 3 H); 2.31 (*m*, 1 H); 2.53 (*m*, 2 H); 5.23 (br. *s*, 1 H); 6.12 (*dt*, *J* = 15, 1, 1 H); 6.83 (*dt*, *J* = 7, 5, 15, 1 H). ^{13}C-NMR (C_6D_6): 17.9 (*Me*–C(6')); 23.0 (*Me*–C(2')); 26.9 (C(1)); 31.4 (C(4')); 31.5 (C(7)); 39.1 (C(5')); 41.3 (C(5)); 41.5 (C(6')); 45.7 (C(1')); 117.2 (C(3')); 133.2 (C(3)); 143.9 (C(2')); 144.8 (C(4)); 196.5 (C(2)). ^{13}C-NMR ($CDCl_3$): 18.0 (*Me*–C(6')); 22.9 (*Me*–C(2')); 27.1 (C(1)); 31.0 (C(4')); 31.3 (C(7')); 38.9 (C(5')); 41.4 (C(5)); 41.5 (C(6')); 45.4 (C(1')); 116.9 (C(3')); 132.8 (C(3)); 143.8 (C(2')); 146.2 (C(4)); 198.4 (C(2)). MS: 204 (1, $M^{+\cdot}$), 131 (14), 119 (41), 105 (39), 93 (100), 79 (41), 77 (43), 43 (79). Fatty, nitrile, oily.

(−)-(1S,2R,6R)-2,6-Dimethylbicyclo[3.1.1]heptane-6-ethanol ((−)-**20**). A soln. of (−)-**18** (109.6 mg, 0.67 mmol) in AcOH (1.5 ml) was hydrogenated for 13 h (32 ml of H_2) in the presence of PtO_2 (1.2 mg). The filtrated soln. was partitioned between H_2O and Et_2O, the org. phase washed with H_2O, 15% aq. NaOH soln., and H_2O, dried (Na_2SO_4), and evaporated, and the residue purified by CC (SiO_2 (20 g), cyclohexane/Et_2O 95:5): (−)-**20** (25%). $[\alpha]_D^{20} = -11.5$ (*c* = 0.35, CCl_4). ^{1}H-NMR: 0.85 (*m*, 2 H); 0.91 (*d*, *J* = 7, 1 H); 1.01 (*d*, *J* = 7, 3 H); 1.03 (*s*, 3 H); 1.42 (*m*, 1 H); 1.48 (*m*, 2 H); 1.75–2.0 (*m*, 4 H); 2.15 (*m*, 1 H); 2.35 (*m*, 1 H); 3.72 (*t*, *J* = 7, 2 H). ^{13}C-NMR: 20.3 (*Me*–C(6)); 22.8 (*Me*–C(2)); 23.8 (C(3)); 26.3 (C(4)); 33.8 (C(7)); 35.7 (C(2)); 40.0 (C(5)); 40.9 (C(6)); 42.7 (C(β)); 46.6 (C(1)); 60.5 (C(α)). MS: 168 (0, $M^{+\cdot}$), 135 (13), 124 (25), 95 (100), 81 (81), 67 (89), 55 (68), 41 (84), 31 (53).

(−)-(1S,2R,6R)-2,6-Dimethylbicyclo[3.1.1]heptane-6-acetaldehyde ((−)-**21**). A soln. of (−)-**20** (105.7 mg, 0.63 mmol) in CH_2Cl_2 (0.5 ml) was added to a suspension of PCC (203.4 mg, 0.94 mmol) in CH_2Cl_2. After 1 h, the mixture was purified by CC (SiO_2 (45 g), Et_2O): (−)-**21** (77%).

Alternatively, a soln. of (−)-**18** (119.6 mg, 0.73 mmol) in EtOH (10 ml) was hydrogenated for 22 h (16.3 ml of H_2) over 5% Pd/C (1.2 mg). The resulting mixture was evaporated and hydrolysed with 15% aq. HCl soln. (2 ml) in THF (8 ml) at 20° for 1.5 h. The mixture was extracted with THF, the org. phase washed with H_2O, dried (Na_2SO_4), and evaporated, and the residue purified as above: (−)-**21** (89%). $[\alpha]_D^{20} = 2.1$, $[\alpha]_{365}^{20} = -4.1$ (*c* = 0.1, $CHCl_3$). IR: 3020, 1730, 1524, 1426, 1210, 929. ^{1}H-NMR: 0.86 (*m*, 2 H); 1.0 (*m*, 2 H); 1.04 (*d*, *J* = 7, 3 H); 1.18 (*s*, 3 H); 1.45 (*m*, 1 H); 1.9 (*m*, 1 H); 2.0 (*m*, 1 H); 2.1 (*m*, 1 H); 2.35 (*m*, 1 H); 2.61 (*ABd*, *J* = 2, 15, 2 H); 9.82 (*t*, *J* = 2, 1 H). ^{13}C-NMR: 21.1 (*Me*–C(6)); 22.7 (*Me*–C(2)); 23.8 (C(3)); 26.0 (C(4)); 33.4 (C(7)); 35.5 (C(2)); 40.0 (C(5)); 40.9 (C(6)); 46.6 (C(1)); 53.1 (CH_2–C(6)); 204.1 (CHO). MS: 166 (1, $M^{+\cdot}$), 151 (5), 133 (11), 122 (34), 107 (26), 93 (47), 81 (59), 67 (63), 55 (84), 41 (100), 29 (50).

*(−)-(1S,2R)-*cis*-Pinane* (= *(1S,2R)-2,6,6-Trimethylbicyclo[3.1.1]heptane*; (−)-**22**). A soln. of (−)-**21** (60.9 mg, 0.37 mmol) and *Wilkinson* catalyst (39.4 mg, 0.37 mmol) in toluene (0.6 ml) was refluxed for 15 min. EtOH (1 ml) was then added and the soln. filtered twice through *Celite*. Evaporation and purification by CC (SiO_2 (3.0 g), pentane) afforded a 95:5 mixture of (−)-*cis*/(−)-*trans*-pinane (95%), identified by MS and coinjections with authentic material on achiral and chiral GC columns[10]). $[\alpha]_D^{20} = -52.7$ (*c* = 0.004, toluene). MS: 138 (2, $M^{+\cdot}$), 123 (28), 109 (9), 95 (100), 82 (66), 67 (65), 55 (74), 41 (54).

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