127. Conversion of Campholene- to Necrodane-Type Monoterpenes. A Short Stereoselective Synthesis of (–)-(*R,R*)-β-Necrodol and its Three Stereoisomers

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Dedicated to Dr. *G. Ohloff* on the occasion of his 65th birthday

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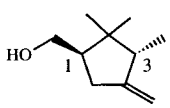
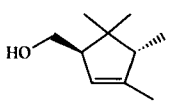
Application of a stereoselective *Prins/retro-Prins* rearrangement sequence from (–)-(*R*)-campholenyl acetate ((–)-**4**) opens a new access to the naturally occurring (–)-(*R,R*)-β-necrodol ((–)-**1**) and its three stereoisomers with high optical purity.

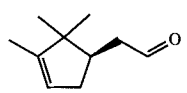
Introduction. – Discovered by *Eisner* and *Meinwald* in the defense spray of the carrion beetle [1], (–)-(*R,R*)-β-necrodol ((–)-**1**) and its α-isomer (–)-**2** constitute the first members of a new class of monoterpenes possessing the non-isoprenoid 1,2,2,3,4-pentamethylcyclopentane skeleton[1]). A first synthetic approach was developed by *Meinwald* and coworkers [2] who prepared both (–)-**1** and (–)-**2** starting from either (–)-camphoric anhydride or (–)-bornyl acetate. A stereoselective synthesis of (–)-**1**, based on an intramolecular Mg-ene reaction as the key step, has been achieved by *Oppolzer* and *Schneider* [3], while recently *Trost* and *Braslau* have reported a stereoselective access to (±)-**1** *via* a Pd-catalysed en-yne cyclisation [4].



(–)-**1** (–)-β-Necrodol



(–)-**2** (–)-α-Necrodol



(+)-**3** (+)-*R*-Campholenaldehyde

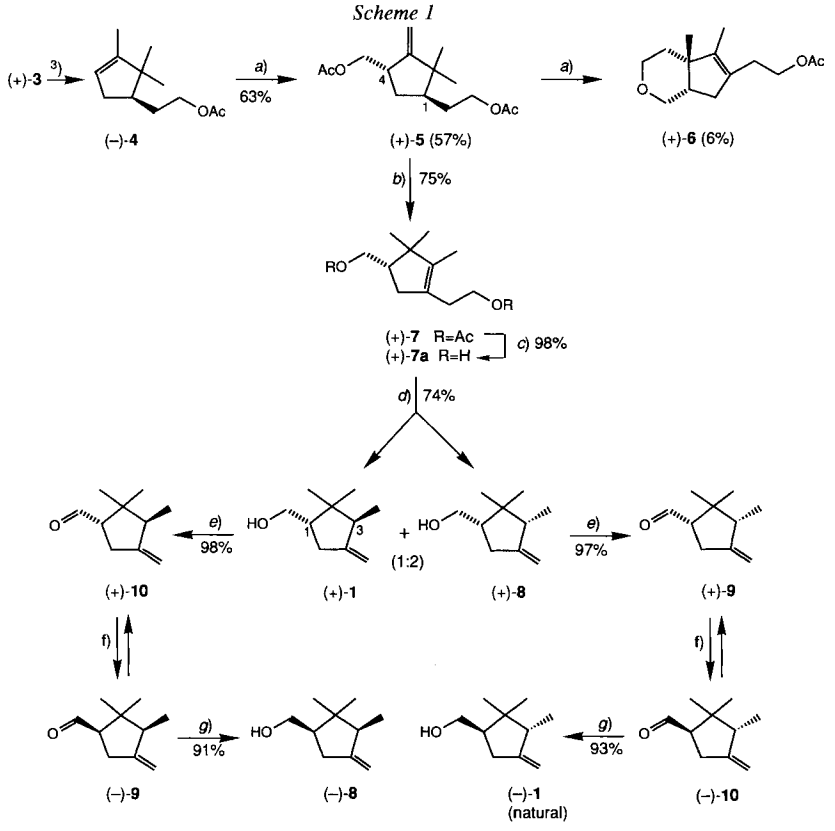
In the context of our general interest in the organoleptic properties of monoterpenoids, we now report an efficient, highly stereoselective synthesis of (–)-**1** and its three stereoisomers (+)-**1**, (+)-**8**, and (–)-**8**. This route takes advantage of the abundant availability of (+)-campholenaldehyde ((+)-**3**[2]) and establishes a direct correlation of the necrodane structure with the configurationally well defined campholenic monoterpenes [5][6]. As depicted in *Scheme 1*, our synthetic strategy involves a stereoselective *Prins/retro-Prins* rearrangement sequence which takes into account the known propensity of 1,2-CH_3 shifts in the campholenyl skeleton [6b].

[1]) Trivial name according to [2]: necrodane.

[2]) Both (+)-**3** and (–)-**3** (*ca.* 80% ee) are commercialised by *Glidden Inc.* (USA).

Results. – The starting material, (–)-(*R*)-campholenyl acetate ((–)-**4**[3]) *ca.* 94% ee[4])), was treated with paraformaldehyde and $BF_3 \cdot Et_2O$ in the presence of Ac_2O (*Prins-Blomquist* conditions [7]) to afford stereoselectively the *trans*-diacetate (+)-**5** (*Scheme 1*)[5]). The latter could be isolated in *ca.* 57% yield, if the reaction was quenched after *ca.* 90% conversion of (–)-**4**. Otherwise, further reaction took place leading predominantly to the diacetate (+)-**7** and, in minor amounts, to the heterocyclic acetate (+)-**6**. Separate treatment of (+)-**5** with $BF_3 \cdot Et_2O$ in refluxing toluene gave (+)-**7** in 75% yield. The one-pot execution of the reactions (–)-**4** → (+)-**5** → (+)-**7** resulted in 30% overall yield. Structural confirmations of (+)-**5** and (+)-**7** were readily deduced from their characteristic NMR data (see *Exper. Part*), and additional proof of the *trans*-configuration of (+)-**5** was provided by the fact that the new chiral centre C(4) was subsequently shown to have (*R*)-configuration by correlation with (–)-**1**.

Scheme 1



a) Paraformaldehyde, $BF_3 \cdot Et_2O$, Ac_2O, CH_2Cl_2, 0°. *b*) $BF_3 \cdot Et_2O$, toluene, 60°. *c*) $LiAlH_4$, Et_2O, 0°. *d*) 450°, N_2, 1–5 s. *e*) PCC [8], CH_2Cl_2, 0°. *f*) $NaOCH_3$, CH_3OH, H_2O. *g*) $LiAlH_4$, Et_2O, 0°.

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[3]) Acetate (–)-**4** was freshly prepared from (–)-α-pinene ($[\alpha]_D^{20} = -47$ (neat)) *via* (+)-**3** ($[\alpha]_D^{20} = +9.6$ (neat)) following a known procedure [6]. Natural occurrence of (+)-**3** and its correlation with (–)-**4** has been reported [5].

[4]) The ee was determined for (+)-**3** by ^{1}H-NMR spectroscopy using chiral $Eu(hfbc)_3$ as shift reagent.

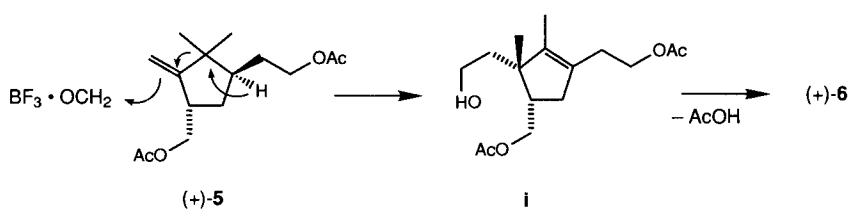
[5]) The corresponding *cis*-isomer of (+)-**5** was not detected in the crude product mixture obtained from the *Prins* reaction.

Diacetate (+)-**7** was converted to (+)-**7a** by $LiAlH_4$ reduction (98% yield) from which a 1:2 mixture of the C(3)-epimeric alcohols (+)-**1** and (+)-**8** was obtained *via* a thermal *retro-Prins* reaction (450°, gas phase, N_2 [9]) in 74% yield. In contrast to the exclusive *trans*-stereoselectivity observed in the foregoing acid-catalysed *Prins* reaction (see (–)-**4** → (+)-**5**), this transformation was considerably less selective. Nevertheless, (+)-**1** and (+)-**8** were readily separated by either fractional distillation or chromatography, and (+)-**1** was shown to be spectrally identical to its enantiomer (–)-**1**[6]). On the other hand, (+)-**8** already possesses the natural (3*R*)-configuration and was transformed into (–)-**1** in the following manner: pyridinium-chlorochromate (PCC) oxidation [8] of (+)-**8** afforded aldehyde (+)-**9** in almost quantitative yield. Equilibration with NaOMe in Et_2O/MeOH then gave a 3:1 mixture of (+)-**9** and its *trans*-isomer (–)-**10** which could be separated by chromatographic methods. Reduction of (–)-**10** with $LiAlH_4$ finally yielded (–)-**1** in high chemical and optical purity (*ca.* 94%)[4]). Application of the same oxidation/epimerisation/reduction sequence to (+)-**1** provided (–)-**8** in comparable yield and purity. The specific optical rotation of (–)-**1** and (+)-**8** in $CHCl_3$ was $[\alpha]_D^{20} = -17.85$ and +81.7, respectively (reported values, see *Footnote 7*).

Thus, our synthetic scheme has led only indirectly to the naturally occurring enantiomer (–)-**1**, but it is evident that (–)-**1** would be directly available starting from (–)-**3**[8]) instead of (+)-**3**. Nevertheless, the present route has the advantage to provide the two aldehydes **9** and **10** which are interesting new members of the still relatively small group of necrodane monoterpenes.

The formation of (+)-**6** as by-product in the *Prins* reaction (–)-**4** → (+)-**5** may be rationalised as shown in *Scheme 2*. The diacetate (+)-**5** reacts with a BF_3-activated species of CH_2O by addition at the double bond and subsequent 1,2-CH_3 and H shift to give intermediate **i** which is stabilised under elimination of AcOH to yield (+)-**6**.

Scheme 2



Chiroptical Properties. All the transformations performed in our synthetic scheme can be considered to have proceeded with complete conservation of the original optical purity. The enantiomeric excess (*ca.* 94%)[4]) determined for (+)-**3** is, therefore, valid for all the chiral compounds prepared in this work. It also indicates that the optical rotations for enantiomerically pure (–)-(*R*,*R*)-β-necrodol ((–)-**1**) and its C(1)-epimer (+)-**8** are approximately $[\alpha]_D^{20} = -19.2$ and +87, respectively[7]).

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[6]) We thank Dr. *P. Schneider* (Université de Genève) for providing us with the NMR spectra of (–)-**1** and (+)-**8** [3].

[7]) Previously reported values are: (–)-(*R*,*R*)-**1**: $[\alpha]_D^{20} = -11.2$ (*c* = 0.6, $CHCl_3$) [2] and –10.74 (*c* = 1.48, $CHCl_3$) [3]; (+)-(*S*,*R*)-**8**: $[\alpha]_D^{20} = +53.9$ (*c* = 1.5, $CHCl_3$) [2] and +37.4 (*c* = 0.72, $CHCl_3$) [3].

[8]) Aldehyde (–)-**3** was not available with comparable high optical purity at the outset of our work.

Organoleptic Properties. Compounds **5**–**10** exhibit only a very weak odour whose character is woody herbal like for alcohols **1** and **8** and dominantly camphorous for the aldehydes **9** and **10**. Significant odour differences between the optical antipodes are not discernible [10].

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Experimental Part

General. All reactions were run under N_2. B.p. are uncorrected. GC: *Varian* instrument, model *3500*; capillary columns *DB-1* and *DB-Wax* (15 m x 0.32 mm). Prep. GC: *Varian* Autoprep. model *700*, glass column packed with *Carbowax 20 M*, 10% on *Chromosorb W* (5 m). Polarimeter: *Perkin-Elmer 241*. IR: *Perkin-Elmer-297* spectrometer; band positions in cm^{-1}. ^{1}H-NMR (360 MHz) and ^{13}C-NMR (90 MHz): *Bruker WH 360*, chemical shifts δ in ppm rel. to TMS as internal standard; $CDCl_3$ as solvent. MS: *Finnigan 1020* automated GC/MS instrument, electron energy 70 eV, signals in *m/z* (%).

Starting Materials. Acetate (–)-**4** ($[\alpha]_D^{20}$ = –2.1 (neat)) [5] was prepared *via* campholenaldehyde ((+)-**3**; $[\alpha]_D^{20}$ = +9.6 (neat)) from (–)-α-pinene (*Aldrich*; $[\alpha]_D^{20}$ = –47, (neat)) as described in [6]. The enantiomeric excess of (+)-**3** was determined to be 94% by ^{1}H-NMR measurements using $Eu(hfbc)_3$ as a chiral shift reagent.

1. Prins-Blomquist *Reaction on (–)-**4**: Formation of (+)-**5**, (+)-**6**, and (+)-**7***. $BF_3 \cdot Et_2O$ (11 ml) was added dropwise at 0° to a stirred mixture of (–)-**4** (557 g, 2.8 mol), paraformaldehyde (100.5 g, 1.12 mol), Ac_2O (420 ml), and 2,6-di(*tert*-butyl)-4-methylphenol (1.5 g) as inhibitor in CH_2Cl_2 (2000 ml). The mixture was stirred overnight at r.t. and then poured onto brine, the org. phase washed with sat. aq. $NaHCO_3$ and NaCl soln., dried (Na_2SO_4), and evaporated. GC: 12% of (–)-**4**, 5% of (+)-**6**, 65% of (+)-**5**, and 7% of (+)-**7**. Distillation at 65–150°/0.3 Torr afforded a colourless oil (677 g). Fractional distillation using a 20-cm column packed with stainless steel helices at 0.5 Torr gave 64 g of (–)-**4** (b.p. 72°), 25 g of (+)-**6** (b.p. 75°), and 385 g of (+)-**5**/(+)-**7** (b.p. 90–112°; ratio 9:1; 57% yield). The compounds were purified by flash chromatography (silica gel, cyclohexane/$(i\text{-}Pr)_2O$ 6:4).

(+)-2-[(1R,4S)-4-(Acetoxymethyl)-2,2-dimethyl-3-methylidenecyclopentyl]ethyl Acetate ((+)-**5**). $[\alpha]_D^{20}$ = +43.4 (*c* = 3.45, $CHCl_3$). IR: 2950, 1710, 1360, 1240, 1020, 890. ^{1}H-NMR: 0.86 (*s*, 3 H); 1.07 (*s*, 3 H); 1.36–1.85 (*m*, 5 H); 2.06 (*s*, 3 H); 2.07 (*s*, 3 H); 2.93 (*m*, 1 H); 3.87 (*dd*, *J* = 8.3, 10.8, 1 H); 4.01–4.2 (*m*, 3 H); 4.91 (*m*, 2 H). ^{13}C-NMR: 171.2 (2 *s*); 161.4 (*s*); 105.7 (*t*); 67.8 (*t*); 63.9 (*t*); 44.9 (*s*); 44.4 (*d*); 40.7 (*d*); 31.8 (*t*); 28.8 (*t*); 26.7 (*q*); 23.8 (*q*); 21 (2 *q*). MS: 268 (0, $M^{+\cdot}$), 148 (47), 133 (73), 121 (62), 105 (53), 91 (27), 79 (15), 67 (9), 55 (10), 43 (100).

*(+)-[(4aS)-1,3,4,4a,7,7a-Hexahydro-4a,5-dimethyl-*cis*-cyclopenta[c]pyran-6-yl]ethyl Acetate* ((+)-**6**). $[\alpha]_D^{20}$ = + 32.4 (*c* = 2.48, $CHCl_3$). IR : 2900, 1730, 1220. 1120, ^{1}H-NMR: 1.0 (*s*, 3 H); 1.54 (*s*, 3 H); 1.44–1.62 (*m*, 2 H); 1.78–1.92 (*m*, 2 H); 2.03 (*s*, 3 H); 2.28–2.45 (*m*, 3 H); 3.23 (*dd*, *J* = 7.2, 11.2, 1 H); 3.38 (*m*, 1 H); 3.59 (*m*, 1 H); 3.69 (*dd*, *J* = 5, 11.2, 1 H); 4.08 (*m*, 2 H). ^{13}C-NMR: 171.0 (*s*); 140.3 (*s*); 129.6 (*s*); 68.4 (*t*); 64.7 (*t*); 62.7 (*t*); 46.0 (*s*); 43.0 (*d*); 35.8 (*t*); 33.4 (*t*); 28.2 (*t*); 24.5 (*q*); 21.0 (*q*); 9.6 (*q*). MS: 238 (1, $M^{+\cdot}$), 178 (70), 163 (80), 147 (12), 134 (100), 119 (82), 105 (69), 97 (11), 91 (45), 79 (22), 55 (12), 43 (81).

(+)-2-[(4S)-4-(Acetoxymethyl)-2,3,3-trimethylcyclopent-1-enyl]ethyl Acetate ((+)-**7**). $[\alpha]_D^{20}$ = +6 (*c* = 2, $CHCl_3$). IR: 2900, 1720, 1430, 1360, 1250, 1030. ^{1}H-NMR: 0.83 (*s*, 3 H); 1.05 (*s*, 3 H); 1.51 (*s*, 3 H); 2.03 (*s*, 3 H); 2.06 (*s*, 3 H); 2.1 (*m*, 1 H); 2.26–2.42 (*m*, 4 H); 4.02–4.19 (*m*, 4 H). ^{13}C-NMR: 171.2 (*s*); 170.9 (*s*); 142.0 (*s*); 127.9 (*s*); 65.7 (*t*); 62.7 (*s*); 47.8 (*s*); 46.8 (*d*); 36.9 (*t*); 28.2 (*t*); 26.7 (*q*); 21.0 (*q*); 20.9 (*q*); 19.8 (*q*); 9.3 (*q*). MS: 268 (0, $M^{+\cdot}$), 208 (8), 148 (10), 133 (100), 119 (5), 105 (22), 91 (11), 79 (4), 55 (5), 43 (42).

2. *Diacetate (+)-**7** from (+)-**5***. $BF_3 \cdot Et_2O$ (50 ml) was added dropwise at r.t. to a stirred soln. of (+)-**5** (383 g, 1.43 mol) in toluene (2000 ml) and then heated at 60°. After 6 h, more $BF_3 \cdot Et_2O$ (20 ml) was added and heating continued for another 4 h. The black mixture was cooled to r.t., washed with sat. aq. $NaHCO_3$ and NaCl soln., dried (Na_2SO_4), and evaporated. Distillation afforded (+)-**7** as a colourless oil (286 g, 75%). B.p. 120–125°/0.1 Torr.

3. *(+)-(4S)-4-(Hydroxymethyl)-2,3,3-trimethylcyclopent-1-ene-1-ethanol* ((+)-**7a**) *from* (+)-**7**. To a stirred suspension of $LiAlH_4$ (38 g, 1 mol) in dry Et_2O (1000 ml), a soln. of (+)-**7** (177 g, 0.66 mol) in dry Et_2O (510 ml) was added dropwise. During the addition, the temp. rose to reflux, and the mixture was stirred for 2 h and cooled to 0° with an ice bath. H_2O (38 ml), NaOH (15%, 38 ml), and H_2O (114 ml) were then added successively and dropwise under vigorous stirring. The mixture was stirred for further 30 min and filtered. The filtrate was evaporated and distilled *i.v.* (90°/0.1 Torr): **7a** as a colourless oil (119 g, 98%). $[\alpha]_D^{20}$ = +17.0 (*c* = 3.18, $CHCl_3$). IR: 3290, 2850, 1440, 1020. ^{1}H-NMR (+D_2O): 0.86 (*s*, 3 H); 1.05 (*s*, 3 H); 1.58 (*s*, 3 H); 1.92–2.45 (*m*, 5 H); 3.56–3.68 (*m*, 3 H); 3.75 (*m*, 1 H). ^{13}C-NMR: 142.5 (*s*); 128.6 (*s*); 64.0 (*t*); 60.8 (*t*); 50.3 (*d*); 47.7 (*s*); 36.9 (*t*); 32.0 (*t*); 27.0 (*q*); 20.1 (*q*); 9.4 (*q*). MS: 184 (19, M^+), 169 (32), 151 (3), 139 (61), 133 (12), 121 (60), 105 (32), 95 (100), 91 (31), 79 (22), 67 (11), 55 (15), 41 (31).

4. *Pyrolysis of Diol (+)-***7a**: *(+)-***1** *and (+)-***8**. Diol **7a** (118 g, 0.64 mol) was pyrolysed at 6 ml/h through a *Pyrex* column (Ø 1 cm × 10 m), heated at 450° using N_2 as carrier gas. The mixture (+)-**1**/(+)-**8** (ratio *ca.* 35:65) was condensed in a dry-ice trap. Distillation of the condensate afforded 73.5 g (74%) at b.p. 52–65°/0.6 Torr as a pale yellow oil which was separated into (+)-**1** and (+)-**8** by prep. chromatography (5-m *Carbowax* column). Identification by comparison with authentic samples [3][6].

(+)-(1S,3S)-2,2,3-Trimethyl-4-methylidenecyclopentane-1-methanol ((+)-**1**). $[\alpha]_D^{20}$ = +18.05 (*c* = 1.59, $CHCl_3$). IR: 3300, 2900, 1640, 1360, 1000, 860. ^{1}H-NMR (+D_2O): 0.83 (*s*, 3 H); 0.94 (*s*, 3 H); 0.94 (*d*, *J* = 7.2, 3 H); 1.85 (*m*, 1 H); 2.16 (*m*, 1 H); 2.27 (*m*, 1 H); 2.6 (*m*, 1 H); 3.46 (*dd*, *J* = 8.2, 10.8, 1 H); 3.77 (*dd*, *J* = 5.4, 10.8, 1 H); 4.78 (*m*, 1 H); 4.86 (*m*, 1 H). MS: 154 (2, M^+), 139 (62), 121 (100), 107 (18), 93 (33), 81 (22), 67 (27), 55 (23), 41 (40).

(+)-(1S,3R)-2,2,3-Trimethyl-4-methylidenecyclopentane-1-methanol ((+)-**8**). $[\alpha]_D^{20}$ = +81.7 (*c* = 1.2, $CHCl_3$). IR: 3300, 2880, 1640, 1200, 1000, 870, 750. ^{1}H-NMR (+D_2O): 0.53 (*s*, 3 H); 0.92 (*d*, *J* = 7.2 Hz); 1.07 (*s*, 3 H); 1.83 (*m*, 1 H); 2.05 (*m*, 2 H); 2.66 (*m*, 1 H); 3.54 (*dd*, *J* = 8.2, 10.8); 3.79 (*dd*, *J* = 5.4, 10.8); 4.75 (*m*, 1 H); 4.85 (*m*, 1 H). MS: 154 (5, M^+), 139 (20), 136 (7), 121 (100), 107 (22), 93 (30), 81 (20), 67 (23), 55 (21), 41 (50).

5. *Aldehydes (+)-***9** *and (+)-***10**. A soln. of (+)-**1** or (+)-**8** (3.7 g, 0.024 mol) in CH_2Cl_2 (30 ml) was added dropwise to a stirred suspension of PCC (7.5 g, 0.035 mol) in CH_2Cl_2 (70 ml) [8]. The dark-brown mixture was stirred for 1 h at r.t., filtered through a column packed with SiO_2, washed with Et_2O, evaporated, and purified by bulb-to-bulb distillation (oven temp. 130°/3 Torr) to afford (+)-**9** (3.58 g, 98%) and (+)-**10** (3.54 g, 97%) as colourless oils.

(+)-(1S,3R)-2,2,3-Trimethyl-4-methylidenecyclopentane-1-carbaldehyde ((+)-**9**). $[\alpha]_D^{20}$ = +89.3 (*c* = 4.4, $CHCl_3$). IR: 2900, 2700, 1710, 1650, 1550, 1450, 1370, 890. ^{1}H-NMR: 0.67 (*s*, 3 H); 0.94 (*d*, *J* = 7.2, 3 H); 1.25 (*s*, 3 H); 2.18 (*m*, 1 H); 2.51 (*m*, 2 H); 2.75 (*m*, 1 H); 4.82 (br. *s*, 1 H); 4.93 (br. *s*, 1 H); 9.80 (*d*, *J* ≈ 3.6, 1 H). ^{13}C-NMR: 204.3 (*d*); 153.2 (*s*); 105.7 (*t*); 60.0 (*d*); 50.8 (*d*); 44.8 (*s*); 29.5 (*t*); 26.5 (*q*); 16.1 (*q*); 10.1 (*q*). MS: 152 (18, M^+), 137 (28), 121 (100), 109 (50), 93 (28), 91 (32), 81 (44), 79 (28), 67 (67), 65 (14), 55 (29), 53 (27), 51 (11), 43 (19), 41 (67), 39 (42).

(+)-(1S,3S)-2,2,3-Trimethyl-4-methylidenecyclopentane-1-carbaldehyde ((+)-**10**). $[\alpha]_D^{20}$ = +30.7 (*c* = 1.68, $CHCl_3$). IR: 2900, 1710, 1550, 1440, 1370, 890. ^{1}H-NMR: 0.93 (*s*, 3 H); 0.96 (*d*, *J* = 7.2, 3 H); 1.09 (*s*, 3 H); 2.19 (*m*, 1 H); 2.43–2.57 (*m*, 2 H); 2.79 (*m*, 1 H); 4.86 (br. *s*, 1 H); 4.94 (br. *s*, 1 H); 9.79 (*d*, *J* = 3.6, 1 H). MS: 152 (17, M^+), 137 (63), 134 (13), 121 (100), 109 (96), 95 (41), 93 (33), 91 (40), 81 (56), 79 (35), 77 (22), 69 (20), 67 (92), 55 (43), 53 (31), 43 (29), 41 (86), 39 (53).

6. *Base-Catalysed Equilibration of (+)-***9** *and (+)-***10**. A soln. of (+)-**9** or (+)-**10** (3.1 g, 0.02 mol) in Et_2O (60 ml) was heated at reflux with CH_3ONa (1 ml, 30% in CH_3OH) for 1 h. GC: *ca.* 1:3 mixture (+)-**9**/(–)-**10** and *ca.* 3:1 mixture (+)-**10**/(–)-**9**, resp.; ratios remained unchanged on further heating. After cooling to r.t., the mixture was washed with sat. aq. NH_4Cl soln., dried (Na_2SO_4), evaporated, and purified by bulb-to-bulb distillation (oven temp. 130°/3 Torr) to afford (+)-**9** and (–)-**10** (2.39 g, 77%) and (–)-**10** and (+)-**9** (2.23 g, 72%). Both mixtures were separated on a g scale by prep. GC (5-m *Carbowax* column). (–)-**9**: $[\alpha]_D^{20}$ = +88.2 (*c* = 1.8, $CHCl_3$), spectrally identical with (+)-**9**. (–)-**10**: $[\alpha]_D^{20}$ = +30.3 (*c* = 1.8, $CHCl_3$), spectrally identical with (+)-**10**.

7. *Reduction of (–)-***9** *and (–)-***10**; *(–)-3-Epi-β-necrodol* (= *(–)-(1R,3S)-2,2,3-Trimethyl-4-methylidenecyclopentane-1-methanol*; (–)-**8**) *and (–)-(R,R)-β-Necrodol* (= *(–)-(1R,3R)-2-2-3-Trimethyl-4-methylidenecyclopentane-1-methanol*; (–)-**1**). A soln. of (–)-**9** or (–)-**10** (1 g, 6.6 mmol) in dry Et_2O (10 ml) was added dropwise to a suspension of $LiAlH_4$ (0.27 g, 7 mmol) in dry Et_2O (15 ml). During the addition, the temp. rose to 35°, and the mixture was stirred at 35° for 30 min, then cooled to 0° (ice bath), and H_2O (0.27 ml), NaOH (15%, 0.27 ml), and H_2O (0.81 ml) were successively added dropwise under vigorous stirring. The mixture was stirred for further 30 min, filtered, and the filtrate concentrated *i.v.* Bulb-to-bulb distillation (oven temp.: 130°/

3 Torr) afforded (–)-**8** (0.92 g, 91%) and (–)-**1** (0.94 g, 93%). (–)-**8**: $[\alpha]_D^{20} = -80.7$ (c = 1.14%, $CHCl_3$). (–)-**1**: $[\alpha]_D^{20} = -17.85$ (c = 1.68% $CHCl_3$). Both (–)-**8** and (–)-**1** were spectrally identical to (+)-**8** and (+)-**1**, resp., and to authentic samples [3][6]).

REFERENCES

[1] T. Eisner, J. Meinwald, *Psyche* **1982**, *89*, 357; T. Eisner, M. Deyrup, R. Jacobs, J. Meinwald, *J. Chem. Ecol.* **1986**, *12*, 1407; J. Meinwald, *Ann. N. Y. Acad. Sci.* **1986**, *471*, 197.

[2] R. Jacobs, G. Feutrill, J. Meinwald, *Tetrahedron Lett.* **1983**, *24*, 2441, and unpublished work, communicated to A. F. Thomas (*Firmenich SA*, Geneva), quoted in A. F. Thomas, Y. Bessière, 'The Synthesis of Monoterpenes', in 'The Total Synthesis of Natural Products', Ed. J. W. ApSimon, Wiley, New York, 1988, Vol. 7.

[3] W. Oppolzer, P. Schneider, *Helv. Chim. Acta* **1986**, *69*, 1817.

[4] B. M. Trost, R. Braslau, *Tetrahedron Lett.* **1988**, *29*, 1231.

[5] A. F. Thomas, *Helv. Chim. Acta* **1972**, *55*, 815; E. Gildemeister, F. Hoffmann, 'Ätherische Öle', Akad. Verlag, Berlin, 1960, Bd. III.

[6] a) A. Bhati, *J. Indian Sci.* **1953**, *35*, 43; b) J.B. Lewis, G. W. Hedrich, *J. Org. Chem.* **1965**, *30*, 4271; D. J. Goldsmith, C. J. Cheer, *ibid.* **1965**, *30*, 2264.

[7] A. T. Blomquist, R. J. Himics, *J. Org. Chem.* **1968**, *33*, 1156.

[8] E. J. Corey, W. Suggs, *Tetrahedron Lett.* **1975**, 2647.

[9] D. R. Adams, J. P. Bhatnagar, *Synthesis* **1977**, 661; H. M. R. Hoffmann, *Angew. Chem.* **1969**, *81*, 597.

[10] G. Ohloff, 'Odorous properties of enantiomeric compounds', in 'Olfaction and Taste IV', Ed. D. Schneider, Wissenschaftliche Verlagsgesellschaft, Stuttgart, 1972, pp. 156–160; G. Ohloff, *Experientia* **1986**, *42*, 271.