222. Synthesis of (*R*)- and (*S*)-*p*-Mentha-1,8-dien-4-ols from (*R*)-Limonene

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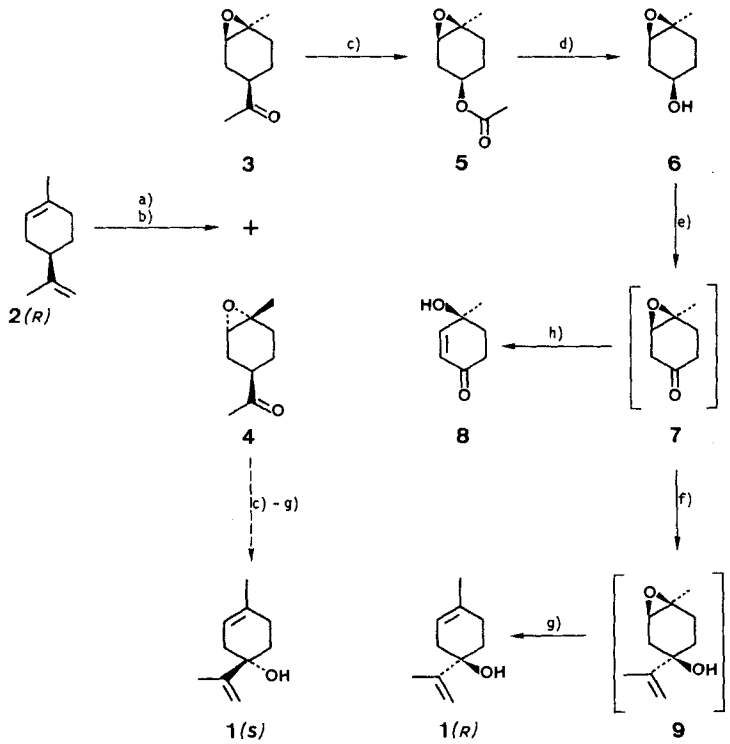
(15.VIII.79)

Summary

Synthesis of both enantiomers of *p*-mentha-1,8-dien-4-ol (**1**) from commercially available (+)-(*R*)-limonene (**2**) is described.

Among the known monoterpenes of the *p*-menthane family, natural *p*-mentha-1,8-dien-4-ol (**1**), which has been found in the essential oils of pepper [1], *Citrus junus* [2], *Citrus iyo* [3], spearmint [4] and *Ledum palustre* [5], is still of unknown

Scheme. *Synthesis of (R)- and (S)-p-mentha-1,8-dien-4-ols* (**1**)

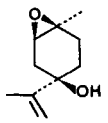


[a]) AcO_2H; [b]) O_3; [c]) *m*-CPBA; [d]) MeONa/MeOH; [e]) $(PyH)_2Cr_2O_7$; [f]) iso-C_3H_5Li; [g]) NaI–Zn–NaOAc–HOAc; [h]) H^+ or HO^-.

0018-019X/79/7/2168-06$01.00/0

absolute configuration. Even its optical rotation has not been measured. Needing an optically active sample of this compound, also known as an insect attractant [6], we looked for a convenient way to prepare it. Since all published syntheses invariably give the racemate [7–10], we devised a reaction sequence leading to both enantiomers from commercially available (+)-(*R*)-limonene (**2**) *(Scheme)*.

Two requirements were essential for the success of this approach. First, the isomers **3** and **4** had to be readily separable – a separation which we were able to effect by fractional distillation, and second, addition of iso-propenyllithium to the epoxyketone **7** had to proceed stereospecifically, or at least give separable diastereoisomers. The latter separation was examined by epoxidizing (±)-*p*-mentha-1,8-dien-4-ol (**1**) [11], when the two epoxides **9** and **10** (obtained in the ratio 83:17[1])) were readily purified. The synthesis was thus started with some confidence.



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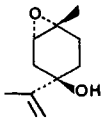

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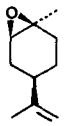


11

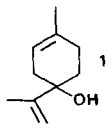
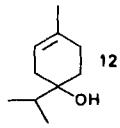
Epoxidation of (+)-(*R*)-limonene (**2**) followed by ozonolysis of the resulting 1:1 mixture of epoxides gave the methyl ketones **3** and **4** in the approximate ratio 40:60 [12]. The structures assigned to these diastereoisomers were confirmed by ozonolysis of pure (+)-(4*R*)-*trans*-1,2-epoxy-*p*-menth-8-ene (**11**) [14], which produced only **3**. Compound **3** was oxidized with *m*-chlorperbenzoic acid (*m*-CPBA) into the ester **5** in 76% yield and with retention of configuration at C(4) [15]. Base-catalyzed transesterification of the acetate **5** with methanol liberated quantitatively the epoxy-alcohol **6**.

A suspension of pyridinium dichromate [16] and sodium acetate in methylene chloride proved to be the most efficient oxidizing mixture for the next step, since the epoxy-ketone formed (**7**) was extremely sensitive to the pH of the medium. In the presence of traces of acid or base, **7** isomerized spontaneously into the α,β-unsaturated hydroxy ketone **8** [17], presumably *via* its enol form. Any attempt to purify it either by chromatography or by distillation failed. Therefore, the crude oxidation product, obtained after filtration of the chromium salts and evaporation of methylene chloride, was dissolved in dry ether and added rapidly to isopropenyllithium in ether at $-70°$. The reaction proved to be completely stereospecific in giving exclusively *cis*-1,2-epoxy-*p*-menth-8-en-4-ol (**9**) besides some heavier by-products. This stereospecificity not only paralleled but passed far beyond that observed during epoxidation of **1** (see above). Finally, the oxirane ring was removed directly from crude **9** to give (+)-(*R*)-*p*-mentha-1,8-dien-4-ol (**1***R*) ($[\alpha]_D^{20} = +10°$) in a 30% overall yield from the epoxy-alcohol **6** [18].

When the same sequence of reactions (*Scheme*, c to g) was carried out on methyl ketone **4**, (−)-(*S*)-*p*-mentha-1,8-dien-4-ol (**1***S*) ($[\alpha]_D^{20} = -9.8°$) was obtained.

[1]) The predominant formation of the *cis*-isomer has been discussed already in terms of hydrogen-bonding between the hydroxyl and the incoming peracid [13].

Table. $[\alpha]_D^{20}$ *values of compounds* **1** *and* **12**

	 **1**	 **12**
(*R*)-configuration	+ 10.0°	− 37.2° (− 33.7° [20])
(*S*)-configuration	− 9.8°	+ 40.2° (+ 46.7° [21])

Additional evidence for the assignment of this absolute configuration was provided by hydrogenation of the C(8),C(9) double bond of **1** over *Raney* nickel [19], giving the known menthen-4-ol **12** [20]. The *Table* shows that the optical rotations of the enantiomers (*R*)-**12** and (*S*)-**12** obtained from (*R*)-**1** and (*S*)-**1** respectively compare favourably with those reported [20] [21].

Being interested in structure/activity relationships in olfaction we investigated the odor of the two enantiomeric pairs of alcohols **1** and **12**. Each of the four components proved to have a specific character and could easily be distinguished from the others. (*R*)-*p*-Mentha-1,8-dien-4-ol ((*R*)-**1**) if highly diluted has a flowery smell reminiscent of freshly sliced cucumbers, but in high concentrations this is accompanied by an unpleasant metallic subnote. The odor of its enantiomer (*S*)-**1** is considerably stronger, and is dominated by a heavy, earthy, urinous-animal tonality reminiscent of decaying straw in a stable, the phenolic character being comparable to that of methyl 3,6-dimethylresorcylate obtained from the essential oil of oak moss. The commercially available (+)-menthen-4-ol ((*S*)-**12**) is known to have a 'warm-peppery, mildly earthy, musty-woody odor of moderate tenacity. The earthy-musty notes are pleasantly green' [22]. Its flowery character resembles that of *α*-terpineol [23]. In the stronger smelling (−)-menthen-4-ol ((*R*)-**12**) an intense herbal-green odor and a pronounced earthy note dominate the flowery tonality. However, the difference of odor between the enantiomers of **12** is not quite as pronounced as between the enatiomers of **1**. These observations are in agreement with previous investigations made on the olfactory differentiation of monoterpenoid enantiomers [24].

We are grateful to Dr. *A. F. Thomas* for his advice and for his constant interest in this work.

Experimental Part

(with the technical assistance of Mrs. *L. Limacher* and Mr. *P. Janin*)

General. – Boiling points are uncorrected. Specific rotations were measured in ethanol (1%) on a model 141 *Perkin-Elmer* polarimeter. IR. spectra were recorded as films on NaCl plates on a model A-21 *Perkin-Elmer* spectrophotometer (max. in cm^{-1}). ^1H- and ^{13}C-NMR. spectra were recorded in $CDCl_3$ on a *Bruker* WH-360 instrument. Chemical shifts (δ) are given in ppm downfield from TMS. Coupling constants *J* are in Hz. Mass spectra were measured on an *Atlas* CH-4 mass spectrometer, using an inlet temperature of *ca.* 150° and electrons of 70 eV. Usually, only the ten most important fragments are reported as *m/z* (% base peak). Gas chromatography (GC.) was performed on model 2200 (analytical) or model 2450 (semi-preparative) *Carlo-Erba* instruments, using 20% SE-30 or 5% Carbowax 20M as liquid phases on Chromosorb W (80–100 mesh ASTM, acid washed and silanized). – Abbreviations: RT. = room temperature, equiv. = equivalent.

Ozonolysis of *cis*- and *trans*-(4*R*)-1,2-epoxy-*p*-menth-8-enes [12]. – A 1:1 mixture of both epoxides (30 g; 0.195 mol; $[\alpha]_D^{20} = +65.2°$) was ozonized in dry methylene chloride (500 ml) and then added to an ice-cold solution of triphenylphosphine (122 g; 0.466 mol) in methylene chloride (300 ml). The mixture was allowed to reach RT. and the solvent was evaporated. On addition of ether, tri-

phenylphosphine oxide precipitated and was filtered off. This treatment was repeated until no more triphenylphosphine oxide cristallized. The resulting oily residue was a mixture of methyl ketones **3** and **4** in the ratio 40:60. Distillation under reduced pressure (0.01 Torr) on a *Fischer* column gave pure **3** (b.p. 32–34°) and **4** (b.p. 36–38°) in 59% overall yield.

(+)-(*4*R)-c-*4-Acetyl*-r-*1,2-epoxy-1-methylcyclohexane* (**3**). $[\alpha]_D^{20} = +88.7°$. – IR.: 2920*s*, 1705*s*, 1430*m*, 1375*m*, 1350*m*, 1150*m*, 1095*w*, 1015*w*, 950*w*, 835*m* and 748*w*. – ^{1}H-NMR.: 1.32 (*s*, 3 H); 2.12 (*s*, 3 H); 2.24 (*m*, 1 H) and 3.01 (*d*, $^3J = 4.5$, 1 H). – ^{13}C-NMR.: 22.9 and 27.7 (2 *qa*, 2 CH_3); 21.7, 26.0 and 29.7 (3 *t*, C(5), C(6) and C(3)); 46.3 and 58.1 (2 *d*, C(4) and C(2)); 57.3 and 209.9 ppm (2 *s*, C(1) and C(8)). – MS.: 154 (1, M^+), 136 (1), 121 (2), 111 (9), 96 (23), 83 (15), 71 (13), 55 (15) and 43 (100).

(+)-(*4*R)-t-*4-Acetyl*-r-*1,2-epoxy-1-methylcyclohexane* (**4**). $[\alpha]_D^{20} = +51.2°$. – IR.: 2930*s*, 1707*s*, 1432*m*, 1377*m*, 1352*m*, 1163*s*, 1125*w*, 1023*w*, 840*m* and 755*w*. – ^{1}H-NMR.: 1.30 (*s*, 3 H); 2.14 (*s*, 3 H); 2.57 (*t* × *m*, $^3J = 11$, 1 H) and 3.09 (*t*, $J \simeq 2$, 1 H). – ^{13}C-NMR.: 23.9 and 28.1 (2 *qa*, 2 CH_3); 22.9, 26.8 and 28.0 (3 *t*, C(5), C(6) and C(3)); 43.5 and 59.6 (2 *d*, C(4) and C(2)) and 57.2 ppm (*s*, C(1)). – MS.: 154 (1, M^+), 136 (1), 121 (2), 111 (15), 96 (43), 83 (20), 71 (7), 55 (18) and 43 (100).

***Baeyer-Villiger* oxidation of 3 and 4.** – A solution of *m*-Chloroperbenzoic acid (85%; 12.3 g; 0.08 mol) in chloroform (170 ml) was added dropwise to a stirred solution of methyl ketone **3** (or **4**) (7.3 g; 0.47 mol) in chloroform (50 ml) at –10° under argon. The mixture was then allowed to reach RT. overnight. After addition of 2N aqueous NaOH the organic phase was separated, washed with $NaHCO_3$- and NaCl-solutions, dried and concentrated. Distillation of the residue (b.p. 85–88°/0.01 Torr) gave the acetate **5** (or **13**) in 76% yield.

(+)-(*4*R)-c-*4-Acetoxy*-r-*1,2-epoxy-1-methylcyclohexane* (**5**). $[\alpha]_D^{20} = +64.9°$. – IR.: 2960*s*, 1733*s*, 1425*m*, 1367*m*, 1240*s*, 1210*m*, 1055*s*, 1045*s*, 1025*s* and 832*m*. – ^{1}H-NMR.: 1.31 (*s*, 3 H); 2.01 (*s*, 3 H); 2.93 (*d*, $^3J = 5$, 1 H) and 4.64 ppm (*d* × *d* × *d*, $^3J = 15$, 10, 7, 1 H). – ^{13}C-NMR.: 21.1 and 22.6 (2 *qa*, 2 CH_3); 24.7, 28.5 and 30.2 (3 *t*, C(5), C(6) and C(3)); 57.8 and 69.1 (2 *d*, C(2) and C(4)); 57.1 and 170.4 ppm (2 *s*, C(1) and CO). – MS.: 170 (0, M^+), 127 (2), 110 (9), 100 (1), 91 (5), 82 (14), 68 (10), 67 (10), 55 (6) and 43 (100).

(–)-(*4*R)-t-*4-Acetoxy*-r-*1,2-epoxy-1-methylcyclohexane* (**13**). $[\alpha]_D^{20} = -13.9°$. – IR.: 2960*s*, 1732*s*, 1425*m*, 1367*m*, 1240*s*, 1210*m*, 1055*s*, 1045*s*, 1023*s* and 831*m*. – ^{1}H-NMR.: 1.35 (*s*, 3 H); 2.04 (*s*, 3 H); 2.98 (*d*, $^3J = 4$, 1 H) and 4.88 ppm (*d* × *d* × *d*, $^3J = 9$, 5, 4, 1 H). – ^{13}C-NMR.: 21.3 and 23.2 (2 *qa*, 2 CH_3); 24.0, 25.1 and 30.4 (3 *t*, C(5), C(6) and C(3)); 57.5 and 66.9 (2 *d*, C(2) and C(4)); 57.3 and 170.3 ppm (2 *s*, C(1) and CO). – MS.: 170 (0, M^+), 127 (1), 110 (10), 100 (2), 91 (13), 82 (11), 81 (13), 68 (8), 55 (7) and 43 (100).

Base-catalyzed transesterification of acetates 5 and 13. – Sodium (73 mg; 3.17 mmol) was dissolved in dry methanol (35 ml) and the solution was cooled to 0°. The acetate **5** (or **13**) (5.4 g; 31.7 mmol) was added slowly under argon and the mixture was stirred at 0° for 4 h. A few drops of acetic acid were added to neutralise the reaction mixture and the solution was concentrated. Distillation of the residue (bulb to bulb, b.p. 70°/0.01 Torr) gave the alcohol **6** (or **14**) (3.9 g; 30.5 mmol; 96%), as a colorless viscous liquid.

(+)-(*4*R)-c-*4-Hydroxy*-r-*1,2-epoxy-1-methylcyclohexane* (**6**). $[\alpha]_D^{20} = +71.2°$. – IR.: 3400br., 2930*s*, 1431*s*, 1377*s*, 1205*m*, 1098*s*, 1078*s*, 1045*s*, 975*m*, 843*s* and 755*m*. – ^{1}H-NMR.: 1.33 (*s*, 3 H); 2.42 (*d*, $^3J = 8$, OH); 3.05 (*m*, 1 H) and 3.74 ppm (br. *m*, 1 H). – ^{13}C-NMR.: 23.4 (*qa*, CH_3); 26.9, 28.1 and 33.1 (3 *t*, C(5), C(6) and C(3)); 59.6 and 66.0 ppm (2 *d*, C(2) and C(4)). – MS.: 128 (1, M^+), 110 (2), 95 (2), 84 (20), 71 (64), 58 (28), 43 (100) and 41 (26).

(–)-(*4*R)-t-*4-Hydroxy*-r-*1,2-epoxy-1-methylcyclohexane* (**14**). $[\alpha]_D^{20} = -9.0°$. – IR.: 3440br., 2930*s*, 1440*s*, 1375*s*, 1210*s*, 1065*s*, 1045*s*, 945*m* and 875*m*. – ^{1}H-NMR.: 1.34 (*s*, 3 H); 1.52 (br. *s*, OH); 2.99 (*d*, $^3J = 4$, 1 H) and 3.89 ppm (*m*, 1 H). – ^{13}C-NMR.: 23.4 (*qa*, CH_3); 25.2, 27.6 and 33.0 (3 *t*, C(5), C(6) and C(3)); 58.6 and 63.5 (2 *d*, C(2) and C(4)) and 57.5 ppm (*s*, C(1)). – MS.: 128 (1, M^+), 110 (3), 95 (4), 84 (16), 71 (59), 58 (33), 43 (100) and 41 (30).

***p*-Mentha-1,8-dien-4-ol** (**1**). – The epoxy alcohol **6** (or **14**) (0.5 g; 3.9 mmol) was added under argon at RT. to a suspension of pyridinium dichromate (2.18 g; 5.85 mmol) and sodium acetate (0.5 g) in dry methylene chloride (15 ml) [16]. The reaction, which was monitored by GC. (10% Carbowax 20M, 1.5 m, 160°), was completed in 2–3 h. The black mixture was diluted with ether, the chromium salts were filtered off and the solvent evaporated. The treatment was repeated until no more salt was precipitated (*ca.* 3×). The yellowish residue, which contained traces of pyridine and

the epoxy ketone **7**[2]), was dissolved in dry ether (5 ml) and added rapidly to a 0.54M solution of isopropenyllithium in ether (25 ml) at −70°. The temperature was allowed to rise to 0° and a saturated NH_4Cl-solution was added slowly. The organic phase was separated, dried and concentrated. The GC. of the residue indicated that *cis*-1,2-epoxy-*p*-menth-8-en-4-ol (**9**) was obtained in about 40% yield, accompanied by some heavier by-products (presumably polyhydroxy compounds). Most of these impurities disappeared during the elimination of the oxirane ring. Thus, the crude mixture containing **9** was stirred with zinc (0.7 g), sodium acetate (1.6 g), sodium iodide (4.7 g), acetic acid (1.6 ml) and methylene chloride (4 ml) at RT. for 2 h. After filtration, the solution was diluted with water, neutralized with 2N NaOH and extracted with ether. The organic phase was washed with diluted NaOH- (2×) and saturated aqueous NaCl-solutions, dried and concentrated. The residue was chromatographed over silica gel (40 g) in ether/hexane 10:90 to give pure *p*-mentha-1,8-dien-4-ol (**1**) (0.18 g; 1.2 mmol). The overall yield from the epoxy-alcohol **6** (or **14**) was *ca.* 30%.

p-*Mentha-1,8-dien-4-ol* (**1**). (*R*)-configuration: $[\alpha]_D^{20} = +8.2°$; (*S*)-configuration: $[\alpha]_D^{20} = -8.0°$[3]). – IR.: 3380br., 3085*m*, 3040*w*, 3005*m*, 2910*s*, 1670*w*, 1640*m*, 1440*s*, 1370*s*, 1085*s*, 1065*s*, 1020*s* and 895*m*. – ^{1}H-NMR.: 1.69 (*s*, 3 H); 1.81 (*s*, 3 H); 4.84 (*m*, 1 H); 5.11 (*s*, 1 H) and 5.32 ppm (br. *s*, 1 H). – ^{13}C-NMR. [26]: 18.7 and 23.2 (2 *qa*, C(7) and C(10)); 27.4, 32.1 and 37.2 (3 *t*, C(6), C(5) and C(3)); 72.1 (*s*, C(4)); 109.7 (*t*, C(9)); 118.4 (*d*, C(2)); 133.6 and 150.4 ppm (2 *s*, C(1) and C(8)). – MS.: 152 (0.5, M^+), 134 (40), 132 (41), 119 (100), 117 (43), 105 (10), 91 (50), 77 (12), 65 (11), 55 (7) and 41 (14).

Isolation of the oxidation product of (−)-(4*R*)-*t*-4-hydroxy-*r*-1,2-epoxy-1-methyl-cyclohexane (14). – Oxidation of **14** ($[\alpha]_D^{20} = -9.0°$) with pyridinium dichromate (see above) and purification of the product by chromatography on silica gel in ether gave exclusively the isomerized ketone (*S*)-**8**: *(+)-(4S)-4-hydroxy-4-methyl-2-cyclohexenone.* $[\alpha]_D^{20} = +40.0°$. – IR.: 3400br., 3030*w*, 2970*s*, 1675*s*, 1210*s*, 1185*s*, 1125*s*, 989*m*, 920*m* and 800*m*. – ^{1}H-NMR. (60 MHz): 1.45 (*s*, 3 H); 1.95–2.75 (*m*, 4 H); 5.85 (*d*, $^3J = 9.7$, 1 H) and 6.81 ppm (*d*, $^3J = 9.7$, 1 H). – ^{13}C-NMR.: 27.0 (*qa*, 1 CH_3); 34.8 and 36.9 (2 *t*, C(5) and C(6)); 68.0 (*s*, C(4)); 127.3 and 156.0 (2 *d*, C(2) and C(3)) and 199.9 ppm (*s*, C(1)). – MS.: 126 (0.5, M^+), 111 (2), 98 (7), 91 (3), 84 (5), 72 (15), 59 (65), 43 (35), 31 (100) and 29 (40).

Epoxidation of (±)-*p*-mentha-1,8-dien-4-ol (1). – *m*-Chloroperbenzoic acid (85%; 6.7 g; 33 mmol) in chloroform (90 ml) was added to a solution of **1** (5.0 g; 32.9 mmol) in chloroform (35 ml) at −10° under argon. The mixture was then stirred overnight at RT. After addition of 2N NaOH (40 ml) the organic phase was separated, washed with 10% Na_2CO_3- and saturated NaCl-solutions, dried an concentrated. The two epoxides **9** and **10** (83:17) were separated by chromatography over silica gel (350 g) in ether/hexane of increasing polarities (from 5:95 to 50:50). The combined yield of **9** and **10** was 91%.

(±)-cis-*1,2-Epoxy*-p-*menth-8-en-4-ol* (**9**). IR.: 3450br., 3080*w*, 2950*s*, 1640*m*, 1440*s*, 1050*s*, 895*s*, 845*m*, 827*m* and 765*m*. – ^{1}H-NMR.: 1.34 (*s*, 3 H); 1.77 (*d*, $^4J = 1.5$, 3 H); 3.20 (*m*, 1 H), 4.86 (*m*, 1 H) and 4.97 ppm (br. *s*, 1 H). – MS.: 168 (5, M^+), 150 (7), 139 (9), 123 (10), 107 (23), 95 (24), 84 (44), 69 (88), 55 (31), 43 (100) and 41 (75).

(±)-trans-*1,2-Epoxy*-p-*menth-8-en-4-ol* (**10**). IR.: 3440br., 3070*w*, 2940*s*, 1640*m*, 1440*s*, 1370*s*, 1110*s*, 1020*m*, 825*m* and 755*m*. – ^{1}H-NMR.: 1.31 (*s*, 3 H); 1.71 (br. *s*, 3 H); 2.95 (*d*, $^3J = 4.5$, 1 H); 4.78 (*m*, 1 H) and 4.95 ppm (*s*, 1 H). – MS.: 168 (0.5, M^+), 150 (4), 135 (3), 122 (4), 107 (27), 95 (20), 82 (11), 69 (24), 55 (16), 43 (100) and 41 (35).

Hydrogenation of (+)-(*R*)- and (−)-(*S*)-*p*-mentha-1,8-dien-4-ols (1) [19]. – The dienol (*R*)-**1** (or (*S*)-**1**) (0.1 g) was hydrogenated in ethanol (2 ml) over *Raney* nickel (50 mg). After quantitative absorption of 1 equiv. of H_2, the catalyst was filtered off and the solvent evaporated. The residue consisted of a single product (**12**), which was further purified by GC. (10% SE-30, 3*m*, 150°) to measure its specific rotation.

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[2]) Epoxy ketone **7**. – IR.: 1710*s* cm^{-1}. – ^{1}H-NMR.: 1.45 (*s*, 3 H); 2.25 (br. *s*, 4 H); 2.76 (*m*, 2 H) and 3.14 ppm (*m*, 1 H).

[3]) The optical purity of the starting (+)-(*R*)-limonene being 82% ($[\alpha]_D^{20} = +103.3°$ (neat), compared with the published value of +125.6° (neat) [25]), the corrected $[\alpha]_D^{20}$ values of (*R*)-**1** and (*S*)-**1** are +10.0° and −9.8° respectively.

Menthen-4-ol (**12**). (*R*)-configuration: $[\alpha]_D^{20} = -37.3°$[4]); (*S*)-configuration: $[\alpha]_D^{20} = +40.2°$[4]). – IR.: 3400br., 2960*s* and 1665*w*. – ^{1}H-NMR. (90 MHz): 0.95 (*d*, $^3J = 7$, 6 H); 1.72 (br. *s*, 3 H) and 5.28 ppm (br. *s*, 1 H). – MS.: 154 (1, M^+), 136 (26), 134 (52), 119 (100), 105 (20), 93 (75), 91 (75), 77 (33), 65 (16), 51 (13) and 41 (35).

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4) Corrected values (see footnote 3).