21. Synthesis of *Aristotelia*-Type Alkaloids

Part III[1])

(3*R*,4*R*)- and (3*R*,4*S*)-1-*p*-Menthene-3,8-diol and the Corresponding Racemates: Preparation and Assignment of Configuration

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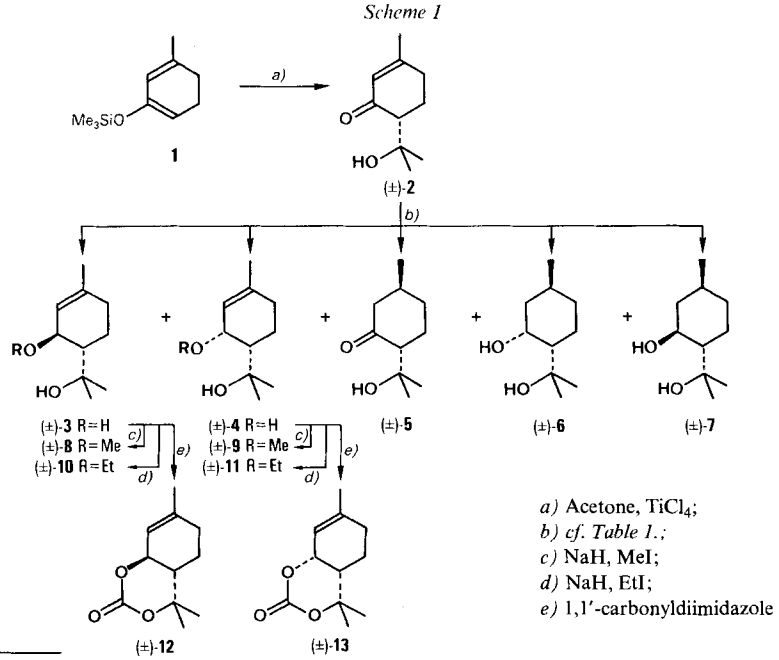
(20.XI.87)

A 1:1 mixture of the racemic *trans*- and *cis*-1-*p*-menthene-3,8-diols ((±)-**3** and (±)-**4**, resp.) was readily prepared in 3 steps starting from 3-methyl-2-cyclohexen-1-one. The relative configuration of the diols, purified *via* the corresponding cyclocarbonates, was assigned by ^{1}H-NMR spectroscopy and found to be at variance with tentative claims in the literature. Optically active samples of **3** and **4** were prepared by resolution of the racemates with (*R*)-1-phenylethylamine. The absolute configuration of the resulting diols was determined by chemical correlation with standards of known absolute configuration.

1. Introduction. – Recently, an efficient biomimetic route to the indole alkaloids (−)-hobartine and (+)-aristoteline was developed in our laboratory [2]. A prerequisite for

Scheme 1



[1]) Part II: [1].

[2]) Taken in part from the diploma works of *S.B.* (ETH Zürich, 1984) and *M.L.* (ETH Zürich, 1984/85).

an application of this synthetic scheme to some of the more highly oxidized members of the *Aristotelia*-alkaloid family [3], such as aristoserratine [4] and triabunnine [5], is easy access to either *trans*-1-*p*-menthene-3,8-diol (**3**) or the corresponding *cis*-isomer **4** *(Scheme 1)*. A literature search showed that no efficient synthesis of these compounds has been reported up to now.

In 1979, *Arbuzow et al.* isolated an optically active diol as a minor product from the oxidation of 2-carene (**17**) with $Hg(OAc)_2$ to which they tentatively assigned structure **4** [6]. The racemic diols (±)-**3** and -**4** have been reported to be formed during the acid-catalyzed decomposition of citral [7] [8]. However, these compounds were not fully characterized, nor has their relative configuration been firmly established. *Kimura et al.* [9] stated that the diols were extremely unstable in acid and isolated what they considered to be a 1:1 mixture of the two ethoxy alcohols **10** and **11**.

Obviously, a more satisfactory route to **3** and **4** had to be developed, and eventually the synthesis outlined in *Scheme 1* was adopted.

2. Preparation of Racemic Materials. – A $TiCl_4$-mediated crossed aldol condensation [10] with the readily available silyl enol ether **1** [11] and acetone produced the expected hydroxy ketone (±)-**2** in 70–80% yield when the pH of the mixture was carefully controlled during the workup. (±)-8-Hydroxypiperitone ((±)-**2**) has been prepared before in 5–7% yield by oxidation of racemic α-terpineol ((±)-**16**; see below) with *tert*-butyl chromate [12] and has been reported to be formed as a minor product in the microbiological oxidation of (±)-piperitone [13].

Table 1. *Reduction of (±)-2 with Various Reagents*[a])

Reagent[b])	Solvent	Conditions	Yield [%] of mixture	Products [%] of mixture[c])				
				(±)-**3**	(±)-**4**/(±)-**7**[d])	(±)-**5**	(±)-**6**	[e])
$LiAlH_4$	Et_2O	20 h, r.t.	97	40	40	11	1	8
$LiAlH_4/ZnCl_2$	Et_2O	2 h, −78°; 4 h, 0°	98	20	31	36	5	8
$LiAlH_4/TiCl_4$	Et_2O	4 h, −78°; 16 h, r.t.	98	11	31	27	12	19
DIBAH	Et_2O	3 h, −78°; 16 h, r.t.	95	27	44	21	1	7
$DIBAH/ZnCl_2$	Et_2O	7 h, 0°	81	25	37	29	6	3
$Zn(BH_4)_2$	Et_2O	2½ h, 0°	92	44	25	2	5	24
$LiBH_4$	THF	7 h, r.t.	87	23	40	0	10	27

[a]) No reaction was observed with AlH_3 [14] (1.6 equiv., 20 h, r.t.) and with 9-borabicyclo[3.3.1]nonane (9-BBN) [15] (1.1 equiv., 2 h, r.t.).

[b]) DIBAH = diisobutylaluminium hydride.

[c]) Analyzed *via* capillary GLC (*SE 54*, 140°).

[d]) In the GLC system employed, (±)-**4** and -**7** gave a single peak. However, they were readily separated on TLC (Et_2O/benzene 1:1). In preparative runs, a relation of *ca.* 6:1 in favour of (±)-**4** was generally observed.

[e]) Sum of additional unidentified products.

The reduction of (±)-**2** was investigated in some detail (see *Table 1*) and led to the isolation of the five products (±)-**3** to (±)-**7**. For preparative purposes, the most efficient procedure turned out to be reduction with $LiAlH_4$ in Et_2O followed by treatment of the crude product with 1,1'-carbonyldiimidazole. The resulting mixture of cyclocarbonates was subsequently separated by column chromatography. Separate reductive cleavage of the purified derivatives (±)-**12** and (±)-**13** led to the desired allylic diols (±)-**3** and (±)-**4**, respectively. The latter were stable crystalline compounds and could be converted to the

Table 2. *^{1}H-NMR Chemical Shifts* (ppm, rel. to TMS in $CDCl_3$) *of 1-*p*-Menthene Derivatives (±)-***2*** to (±)-***4*** and (±)-***8*** to (±)-***13***

	H–C(2)	H–C(3)	H–C(4)	H_{ax}–C(5)	H_{eq}–C(5)	$H_{\psi ax}$–C(6)	$H_{\psi eq}$–C(6)	CH_3(7)	CH_3(9), CH_3(10)
(±)-**2**	5.86	–	2.33	1.71	2.09	2.41	2.31	1.97	1.21, 1.22
(±)-**3**	5.33	4.41	1.56	1.29	1.67	2.07	1.91	1.69	1.21, 1.30
(±)-**4**	5.60	4.44	1.70	1.28	1.75	1.99	2.11	1.71	1.24, 1.39
(±)-**8**	5.48	4.05	1.68	1.25	1.75	2.09	1.91	1.71	1.16, 1.22
(±)-**9**	5.75	3.92	1.78	1.24	1.76	1.98	2.13	1.74	1.21, 1.32
(±)-**10**	5.47	4.13	1.70	1.25	1.74	2.08	1.92	1.70	1.16, 1.22
(±)-**11**	5.70	4.03	1.82	1.28	1.81	1.97	2.12	1.72	1.21, 1.32
(±)-**12**	5.49	4.76	1.84	1.43	1.72	2.17	2.05	1.73	1.36, 1.48
(±)-**13**	5.63	4.99	1.72	1.50	1.88	2.03	2.15	1.77	1.43, 1.54

Table 3. *Selected ^{1}H-NMR Coupling Constants* (Hz) *of 1-*p*-Menthene Derivatives (±)-***2*** to (±)-***4*** and (±)-***8*** to (±)-***13***

	J(3, 4)	J(4, 5_{ax})	J(4, 5_{eq})	J(5_{ax}, $6_{\psi ax}$)	J(5_{ax}, $6_{\psi eq}$)	J(5_{ax}, 5_{eq})	J($6_{\psi ax}$, $6_{\psi eq}$)
(±)-**2**	–	13.9	4.6	11.5	5.3	13.0	18.5
(±)-**3**	9.0	13.1	2.6	11.5	5.5	13.0	17.5
(±)-**4**	3.3	12.3	3.3	11.2	5.5	13.1	18.5
(±)-**8**	9.5	12.7	2.7	11.5	5.4	12.9	17.5
(±)-**9**	4.0	13.0	2.5[a])	[b])	5.6[a])	13.1	17.5
(±)-**10**	9.4	13.1	2.6	11.5	5.0	12.5	17.0
(±)-**11**	3.2[a])	12.9[a])	2.8[a])	[b])	[b])	[b])	17.5
(±)-**12**	10.2	13.0	2.8	11.0	6.0	13.0	18.0
(±)-**13**	4.0	13.2	3.2	11.5	6.0	13.0	18.0

[a]) Values taken from spectra recorded in (D_6)benzene as solvent.
[b]) Signal overlap prevented determination of these coupling constants.

Table 4. *^{13}C-NMR Chemical Shifts* (ppm, rel. to TMS) *of 1-*p*-Menthene Derivatives (±)-***2*** to (±)-***4*** and (±)-***8*** to (±)-***13***

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9), C(10)
(±)-**2**	163.8	127.2	203.1	54.7	25.3	31.3	25.3	72.3	25.3, 28.2
(±)-**3**	136.1	125.3	69.8	54.1	24.3	30.8	22.8	74.8	24.1, 30.1
(±)-**4**	140.4	123.0	66.0	46.7	17.5	31.5	23.3	72.4	28.1, 29.1
(±)-**8**	137.9	120.4	79.4	48.4	24.3	30.8	22.9	73.0	24.7, 29.3
(±)-**9**	141.6	119.0	74.4	46.7	18.2	31.6	23.6	71.7	27.9, 29.1
(±)-**10**	137.7	121.1	78.2	48.7	24.4	30.9	23.0	73.2	24.7, 29.5
(±)-**11**	141.2	120.0	73.4	46.9	18.4	31.7	23.7	71.8	28.1, 29.3
(±)-**12**	138.9	119.5	74.3	44.0	21.5	30.2	22.7	85.8	22.7, 28.1
(±)-**13**	143.1	117.9	72.8	37.8	17.8	29.8	23.3	81.8	25.7, 27.5

ethers (±)-**8** and **-10** and (±)-**9** and **-11**, respectively. The relative configuration of the main products (±)-**3** and **-4** was determined with the aid of spectral data *(Tables 2–4)*.

First-order analyses of the ^{1}H-NMR spectra revealed that both (±)-**3** and **-4** (as well as all other 1-*p*-menthene derivatives described in this paper) adopt the usual half-chair conformation in which the bulky substituent at C(4) occupies the equatorial position. The axial nature of *H*–C(4) is supported by coupling constants of *ca.* 12–13 Hz with H_{ax}–C(5) and of 2.6–3.3 Hz with H_{eq}–C(5), respectively *(cf. Table 3)*. Concerning the coupling of *H*–C(4) with *H*–C(3), two sets of compounds are readily discerned: in (±)-**3**, **-8**, **-10**, and **-12**, *J* amounts to 9.0–10.2 Hz, while in (±)-**4**, **-9**, **-11**, and **-13**, the corresponding value is 3.2–4.0 Hz. Clearly, the size of the former coupling is consistent with an axial/pseudoaxial arrangement of *H*–C(3) and *H*–C(4), whereas the latter values are in accordance with an axial/pseudoequatorial interaction. The significant shielding (4–7 ppm) of C(5) in the ^{13}C-

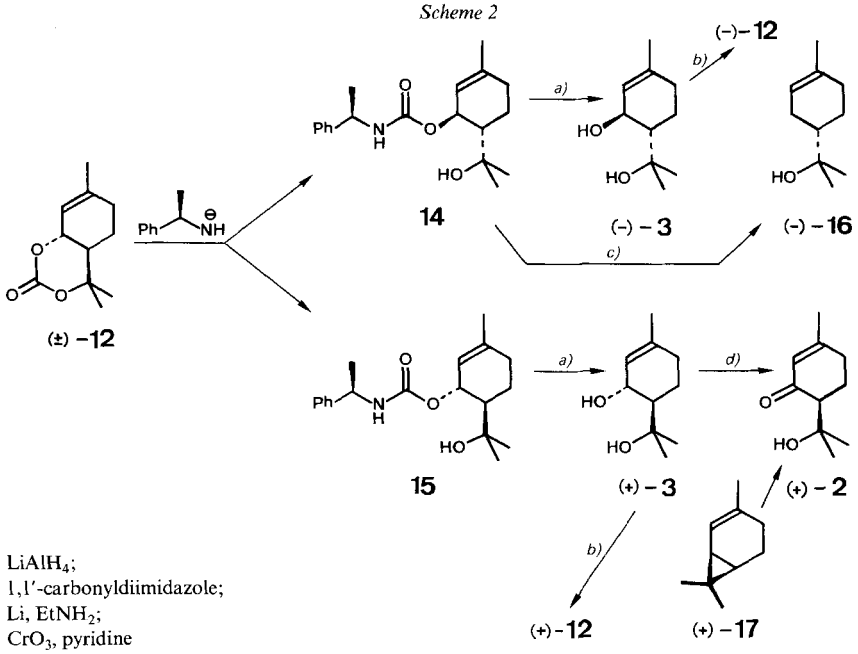
NMR spectra of the *cis*-isomers (±)-**4**, -**9**, -**11**, and -**13**, as compared to their *trans*-counterparts (±)-**3**, -**8**, -**10**, and -**12** *(cf. Table 4)*, which is caused most likely by a *syn*-γ effect [16] in the former case (pseudoaxial substituent at C(3)), is fully consistent with the above configurational assignments.

A comparison of the spectral data of *Clarke* and *Powell*'s diol [7] with our values leaves no doubt that their compound is identical with the racemic *trans*-diol (±)-**3**. This finding is at variance with the conclusion of the American authors who tentatively assigned structure **4** to their diol which was formed in 4.3% yield when citral was shaken with *aq.* HCl solution for 35 days. *Kimura et al.* [9] studied the decomposition of citral in the presence of EtOH and citric acid and isolated a compound (*'Peak 18'*) which was homogeneous on TLC and GLC, but which they considered to be a 1:1 mixture of the ethoxy alcohols **10** and **11**. A critical reevaluation of the reported spectroscopic data led us to the conclusion that the Japanese group actually had a single isomer in their hands since it displayed only 12 signals in the ^{13}C-NMR spectrum and since the ^{1}H-NMR signals for the EtO group are readily accounted for by analyzing this groups as an AMX_3 spin system with J_{AM} = 9 Hz. In fact, their data coincide within experimental error whith the values we obtained for the *trans*-isomer (±)-**10**, whereas (±)-**11** displays considerably different ^{1}H- and ^{13}C-NMR spectra *(cf. Tables 2–4)*.

The by-products (±)-**5** to (±)-**7** *(Scheme 1)* were identified as follows: the ^{1}H- and ^{13}C-NMR parameters of the saturated diols (±)-**6** and -**7** coincide within experimental error with the data reported for *cis*- and *trans-p*-menthane-3,8-diol, respectively [17]. Hydroxy ketone (±)-**5** has been isolated before as a *cis*/*trans*-mixture which could not be separated [18]; a single diastereoisomer of unspecified relative configuration has recently been obtained when pulegone epoxide was reduced with SmI_2 [19]. Whereas there is a satisfactory agreement ($\Delta\delta$ = ±0.2 ppm) between the ^{13}C-NMR spectra of the 1,4-reduction product (±)-**5** and the compound isolated by *Molander* and *Hahn* [19], the values of the ^{1}H-NMR chemical shifts of the 3 Me groups all differ by 0.25 ppm; presumably, a calibration error in the previous work is the reason for this discrepancy. The splitting patterns of the 3 protons next to the carbonyl group displayed in the ^{1}H-NMR spectrum (C_6D_6) and the δ_c of the secondary Me group point to equatorial positions of both substituents; therefore, the relative configuration of (±)-**5** is most likely represented as shown in *Scheme 1*.

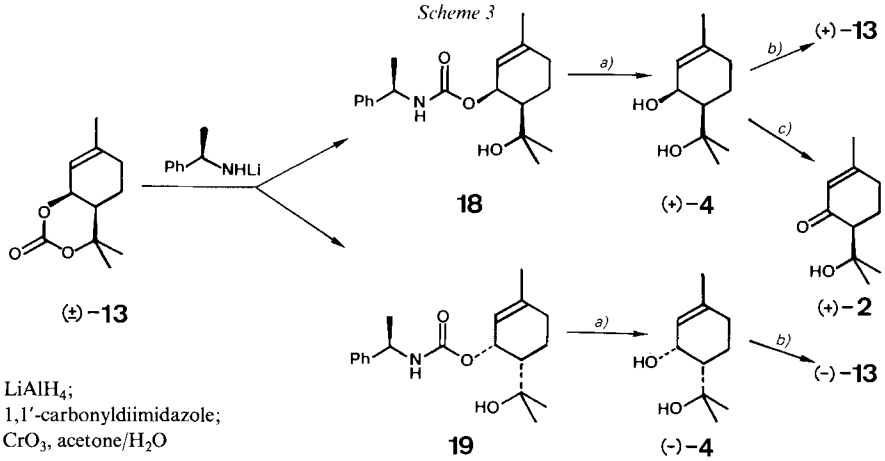
3. Preparation of Optically Active Materials. – In order to establish the absolute configuration of some of the *Aristotelia* alkaloids, optically pure samples of the diols **3** and **4** would be potentially useful. The following protocol provides an adequate route to

Scheme 2



a) $LiAlH_4$;
b) 1,1'-carbonyldiimidazole;
c) Li, $EtNH_2$;
d) CrO_3, pyridine

Scheme 3



a) $LiAlH_4$;
b) 1,1'-carbonyldiimidazole;
c) CrO_3, acetone/H_2O

these compounds (see *Schemes 2* and *3*): treatment of the racemic *trans*-cyclocarbonate (±)-**12** with the lithium salt of (*R*)-1-phenylethylamine at −78° resulted in a 1:1 mixture of the two 'secondary' urethanes **14** and **15** (combined yield *ca.* 60%) and a small amount of the corresponding 'tertiary' carbamates which were not investigated further. Parallel reductions of the separated 'secondary' urethanes with $LiAlH_4$ furnished the desired optically active, enantiomeric *trans*-diols (+)-**3** and (−)-**3**, respectively.

The absolute configuration of these diols was determined by two independent chemical correlations. First, the crystalline 'secondary' urethane **14** was cleaved reductively with Li in $EtNH_2$ [20] to give an optically active sample[3]) of (−)-α-terpineol ((−)-**16**), known to possess the (*S*)-configuration as shown in *Scheme 2* [21]. On the other hand, a sample of diol (+)-**3**, prepared from the oily carbamate **15** by reduction with $LiAlH_4$, was oxidized according to *Arbuzow et al.* [6] to yield a sample of (+)-**2** which had been obtained by these workers in 3 steps[4]) starting from (+)-2-carene (**17**). Since the crucial C(4)–C(8) bond is not affected during these transformations, it can safely be concluded that (+)-**3** has the absolute configuration shown in *Scheme 2*.

The two enantiomerically pure forms of the *cis*-diol (±)-**4** were prepared by the methodology described above (see **18** and **19** in *Scheme 3*). The absolute configuration of (+)-**4** was established by a chemical correlation with (+)-**2**.

4. Conclusion. – The reaction sequences presented in the schemes provide easy access to the racemic and optically active forms of **3** and **4** with known relative and absolute configuration. At present, work is in progress [23] to convert these diols into the corresponding 8-amino derivatives which should represent valuable intermediates for the preparation of *exo*- and *endo*-15-hydroxyhobartine according to our established strategy [2].

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[3]) The observed value of the optical rotation ($[\alpha]_D^{25} = -86°$ as compared to −100° for optically pure (−)-**16** [22]) is somewhat low. This is probably due to the difficulties experienced in small-scale work of removing the last traces of solvent without excessive loss of material.

[4]) One of the intermediates in this sequence had m.p. 78–79° and $[\alpha]_D^{25} = +67°$ and was tentatively assigned structure (+)-**4**. In our hands, *cis*-diol (+)-**4** did not crystallize and showed a significantly higher rotation ($[\alpha]_D^{25} = +163°$), whereas there is a more satisfactory agreement between our *trans*-diol (+)-**3** (m.p. 78–79°, $[\alpha]_D^{25} = +52°$) and the scanty analytical data reported for the oxidation product of 2-carene [6].

The authors would like to express their thanks to Miss *F. Werren* for her excellent technical assistance. The support of part of this work by the *Swiss National Science Foundation* (project No. 2.105-0.86) and the *Stipendienfonds der Basler Chemischen Industrie* is gratefully acknowledged.

Experimental Part

General. See [1] [24]. Prep. HPLC: *Lichrosorb Si 60*, 7 μm; column 31 × 250 mm, flux 10 ml/min; AcOEt/cyclohexane 1:2; detector: *Knauer* refractometer *mod. 2025/50*. Anal. GLC: *Carlo Erba Fractovap*, series *2150*; capillary column: *SE 54*, 29 m; *T* 140°; carrier gas H_2 (0.8 bar). FC: flash chromatography.

1. General Procedures. – 1.1. *Formation of Cyclocarbonates.* Method, see [25]. To a soln. of the indicated diol in dry benzene were added 6 equiv. of 1,1'-carbonyldiimidazole *(Fluka, purum)*. After 24 h stirring at r.t., the solvent was evaporated and the residue filtered through 2 g of silica gel (Et_2O) and crystallized as indicated.

1.2. *Reduction of the Cyclocarbonates.* To a stirred chilled suspension of a 6-fold excess of $LiAlH_4$ in dry Et_2O, an Et_2O soln. of the indicated cyclocarbonate was added. After 1 h at 0°, excess reagent was destroyed by dropwise addition of H_2O. The resulting white suspension was dried (Na_2SO_4), filtered, evaporated, and recrystallized.

1.3. *Treatment of the Cyclocarbonates with Lithium (R)-1-Phenylethylamide.* To a stirred soln. of 6 equiv. of (*R*)-1-phenylethylamine *(Fluka, purum)* in dry THF were added 5 equiv. of 1.6M BuLi in hexane *(EGA)* at 0°. After 1 h at 0°, the yellow soln. was cooled to −78° and treated with 1 equiv. of the indicated cyclocarbonate dissolved in dry THF and stirred for 30 min. The mixture was poured onto cold 0.5N HCl and extracted with 3 portions of Et_2O. The combined org. layers were washed with brine, dried ($MgSO_4$), and evaporated. The oily residue was separated into its components by FC [26] or prep. HPLC as indicated.

1.4. *Reduction of the Carbamates.* To a 10-fold molar excess of $LiAlH_4$ in THF was added a soln. of the indicated carbamate in THF. When the evolution of H_2 had ceased, the mixture was heated at reflux for 10 h. Then, a slight excess of H_2O was added at 0°. The resulting suspension was diluted with twice its volume of Et_2O, dried (Na_2SO_4), and evaporated. The residue was filtered through silica gel (Et_2O) and crystallized as indicated.

1.5. *Preparation of Methyl Ethers.* To a chilled suspension of 2 equiv. of NaH (*Fluka, pract.*; washed with 4 portions of pentane) in dry THF, was added 1 equiv. of the indicated diol. After stirring for 30 min at r.t., 1.2 equiv. of freshly distilled MeI were added. After 4 h at r.t., the mixture was worked up with Et_2O and phosphate buffer (pH 6.5). The crude product was filtered through silica gel (Et_2O/hexane 1:1) and purified by bulb-to-bulb distillation (120°/0.1 Torr).

1.6. *Preparation of Ethyl Ethers. Procedure 1.5* was applied, but using freshly distilled EtI instead of MeI.

2. Racemic Materials. – 2.1. *(RS)-8-Hydroxy-1-*p*-menthen-3-one* ((±)-**2**). To a stirred soln. of 10.6 ml (144 mmol) of acetone (*Fluka, puriss.*; redistilled from freshly activated molecular sieves stored under Ar (*Union Carbide*, 3 Å, 1/16" pellets)) in 350 ml of CH_2Cl_2 (*Fluka, puriss.*; distilled over P_2O_5) which was kept at 0° under Ar were added 15.7 ml (143 mmol) of freshly distilled $TiCl_4$ *(Fluka, puriss.)*. To this mixture were added 21.86 g (110 mmol) of **1** (prepared in 88% yield according to [11]) in 100 ml of dry CH_2Cl_2 within 75 min. After stirring at 0° for 6 h, the dark red mixture was added dropwise to a vigorously stirred, ice-cold phosphate buffer soln. of pH 7.5 while continuously monitoring the pH of the mixture with a standard pH electrode. The pH was kept between 7.0 and 7.5 by adding 2.5N NaOH when necessary. The ensuing heterogeneous mixture was extracted with 500 and then 300 ml of Et_2O. The combined org. layers were washed once with brine, dried (Na_2SO_4), and evaporated at atmospheric pressure to yield 21.5 g of a yellow oil which was purified by FC (Et_2O/hexane 4:1). The product obtained (16.99 g) consisted of at least 95% pure (±)-**2** (yield: *ca.* 84%). Oil. IR (CCl_4): 3480, 1655, 1380, 1218, 1188. ^{1}H-NMR: 5.86 (*m*, 1 H); 5.17 (br. *s*, 1 H); 2.5–2.2 (*m*, 3 H); 2.09 (*ddt*, *J* = 13, 4.6, 2.7, 1 H); 1.97 (br. *s*, 3 H); 1.71 (*dddd*, *J* = 13.9, 13, 11.5, 5.3, 1 H); 1.22 (*s*, 3 H); 1.21 (*s*, 3 H). ^{13}C-NMR: 203.1 (*s*); 163.8 (*s*); 127.2 (*d*); 72.3 (*s*); 54.7 (*d*); 31.3 (*t*); 28.2 (*q*); 25.3 (*t*); 24.9 (*q*); 24.1 (*q*).

2.2. *(±)-*cis*- and (±)-*trans*-1-*p*-Menthene-3,8-diyl Carbonate* ((±)-**13** and (±)-**12**). To a suspension of 2.09 g (55 mmol) of $LiAlH_4$ in 150 ml of dry Et_2O at 0° was added a soln. of 6.13 g (36.4 mmol) of (±)-**2** in 50 ml of Et_2O. After stirring for 24 h at r.t., the mixture was hydrolyzed by adding the required amount of H_2O. Following filtration, the residue was extracted with 3 × 30 ml of warm Et_2O. The combined filtrates were dried ($MgSO_4$) and evaporated. The residue was dissolved in 120 ml of dry benzene, combined with 12.5 g (77 mmol) of 1,1'-carbonyldiimidazole *(Fluka, purum)*, and stirred at r.t. for 24 h. The mixture was filtered, diluted with 100 ml of Et_2O, and washed with 2 × 130 ml of phosphate buffer (pH 6.5) which was back-washed twice with 100 ml of Et_2O. The combined org. layers were dried ($MgSO_4$) and evaporated to yield 6.45 g of an orange oil. Repeated chromatography (Et_2O/hexane 4:1), followed by recrystallization (Et_2O/hexane) furnished 3.065 g (42% from (±)-**2**) of (±)-**12** and (±)-**13**, ratio 1:1.

(±)-**12**: Less polar. M.p. 105–106°. IR (CCl_4): 1762, 1120, 1075. ^{1}H-NMR: 5.94 (*m*, 1 H); 4.76 (*ddq*, *J* = 10.2, 3.2, 1.5, 1 H); 2.17 (*m*, 1 H); 2.05 (*ddm*, *J* = 18, 6, 1 H); 1.84 (*ddd*, *J* = 13, 10.2, 2.8, 1 H); 1.8 (*m*, 1 H); 1.73 (br. *s*, 3 H); 1.48 (*s*, 3 H); 1.43 (*tdd*, *J* = 13, 11, 6,2, 1 H); 1.36 (*s*, 3 H). ^{13}C-NMR: 149.5 (*s*); 138.9 (*s*); 119.5 (*d*); 85.8 (*s*); 74.3 (*d*); 44.0 (*d*); 30.2 (*t*); 28.1 (*q*); 22.7 (2*q*); 21.5 (*t*). MS: 152 (2, M^{+-} – 44), 109 (12), 94 (25), 81 (71), 79 (29), 69 (100), 43 (58), 41 (40). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.34, H 8.18.

(±)-**13**: More polar. M.p. 84–85°. IR (CCl_4): 1755, 1261, 1205, 1129. ^{1}H-NMR: 5.63 (*m*, 1 H); 4.99 (*m*, 1 H); 2.15 (*ddm*, *J* = 18, 6, 1 H); 2.03 (*m*, 1 H); 1.88 (*m*, 1 H); 1.74 (br. *s*, 3 H); 1.72 (*dt*, *J* = 13.2, 4, 1 H); 1.54 (*s*, 3 H); 1.50 (*dddd*, *J* = 13.5, 13.2, 11.5, 6, 1 H); 1.43 (*s*, 3 H). ^{13}C-NMR: 148.9 (*s*); 143.1 (*s*); 117.9 (*d*); 81.8 (*s*); 72.8 (*d*); 37.8 (*d*); 29.8 (*t*); 27.5 (*q*); 25.7 (*q*); 23.3 (*q*); 17.8 (*t*). MS: 152 (1, M^{+-} – 44), 109 (14), 94 (43), 81 (100), 79 (56), 69 (90), 43 (50). Anal. calc. for $C_{11}H_{16}O_3$ (196.25): C 67.32, H 8.22; found: C 67.40, H 8.20.

2.3. *(3*RS,*4*RS*)-1-*p-*Menthene-3,8-diol* ((±)-**3**). According to *Procedure 1.2* from (±)-**12**. Yield 86%. M.p. 76° (Et_2O/hexane). IR (CCl_4): 3340, 1379, 1368, 1185, 1007, 990. IR (KBr): 1676, 1473, 1440, 1381, 1370, 1182, 1134, 1008, 994, 900, 881, 822. ^{1}H-NMR: 5.33 (*m*, 1 H); 4.41 (*m*, 1 H); 2.07 (*m*, 1 H); 1.91 (*ddm*, *J* = 18, 5.5, 1 H); 1.69 (br. *s*, 3 H); 1.65 (*m*, 1 H); 1.56 (*ddd*, *J* = 13,9, 2.6, 1 H); 1.30 (*s*, 3 H); 1.29 (*ddt*, *J* = 13, 11.5, 5.5, 1 H); 1.21 (*s*, 3 H). ^{1}H-NMR ((D_6)DMSO): 5.21 (br. *s*, 1 H); 5.10 (*d*, *J* = 3.7, 1 H); 5.06 (*s*, 1 H); 4.15 (*m*, 1 H); 1.61 (br. *s*, 3 H); 1.13 (*s*, 3 H); 1.09 (*s*, 3 H). ^{13}C-NMR: 136.1 (*s*); 125.3 (*d*); 74.8 (*s*); 69.8 (*d*); 51.1 (*d*); 30.8 (*t*); 30.1 (*q*); 24.3 (*t*); 24.1 (*q*); 22.8 (*q*). MS: 170 (0.4, M^{+}), 152 (14), 137 (23), 112 (14), 109 (18), 96 (30), 84 (34), 81 (100), 79 (55), 69 (71), 59 (90), 43 (59). Anal. calc. for $C_{10}H_{18}O_2$ (170.25): C 70.55, H 10.66; found: C 70.53, H 10.60.

2.4. *(3*RS,*4*SR*)-1-*p-*Menthene-3,8-diol* ((±)-**4**). According to *Procedure 1.2* from (±)-**13**. Yield 88%. M.p. 69° (hexane). IR (CCl_4): 3615, 3345, 1375, 953, 895. IR (KBr): 1475, 1450, 1430, 1415, 1375, 1368, 1282, 1162, 1140, 960, 905, 802. ^{1}H-NMR: 5.60 (*m*, 1 H); 4.45 (*m*, 1 H); 3.25 (br. *s*, 1 H); 2.11 (*ddm*, *J* = 18, 5.5, 1 H); 1.99 (*dddm*, *J* = 18, 11.5, 6.5, 1 H); 1.90 (br. *s*, 1 H); 1.71 (*s*, 3 H); 1.70 (*ddt*, *J* = 13, 11.5, 6, 1 H); 1.39 (*s*, 3 H); 1.28 (*dt*, *J* = 12.3, 3.3, 1 H); 1.24 (*s*, 3 H). ^{1}H-NMR ((D_6)DMSO): 5.47 (*m*, 1 H); 4.65 (br. *d*, *J* = 5.3, 1 H); 4.14 (*s*, 1 H); 4.13 (*m*, 1 H); 2.1–1.8 (*m*, 2 H); 1.63 (*s*, 3 H); 1.19 (*s*, 3 H); 1.13 (*s*, 3 H). ^{13}C-NMR: 140.4 (*s*); 123.0 (*d*); 72.4 (*s*); 66.0 (*d*); 46.7 (*d*); 31.5 (*t*); 29.1 (*q*); 28.1 (*q*); 23.3 (*q*); 17.5 (*t*). MS: 152 (6, M^{+-} – 18), 137 (10), 94 (100), 93 (25), 84 (25), 81 (33), 79 (70), 43 (58). Anal. calc. for $C_{10}H_{18}O_2$ (170.25): C 70.55, H 10.66; found: C 70.57, H 10.53.

2.5. *(3*RS,*4*RS*)-3-Ethoxy-1-*p-*menthen-8-ol* ((±)-**10**). According to *Procedure 1.6* from (±)-**3**. Yield 80%. Oil. n_D^{20} = 1.469. IR (CCl_4): 3480, 1379, 1200, 1168, 1110, 1075, 990, 930. ^{1}H-NMR: 5.47 (*m*, 1 H); 4.94 (*s*, 1 H); 4.13 (*m*, 1 H); 3.77 (*dq*, *J* = 9, 7, 1 H); 3.46 (*dq*, *J* = 9, 7, 1 H); 2.08 (*m*, 1 H); 1.92 (*m*, 1 H); 1.8–1.65 (*m*, 2 H); 1.70 (br. *s*, 3 H); 1.25 (*m*, 1 H); 1.22 (*t*, *J* = 7, 3 H); 1.22 (*s*, 3 H); 1.16 (*s*, 3 H); identical with a published spectrum [9], assigned to a 1:1 mixture **10**/**11**. ^{13}C-NMR: 137.7 (*s*); 121.1 (*d*); 78.2 (*d*); 73.1 (*s*); 62.9 (*t*); 48.7 (*d*); 30.9 (*t*); 29.5 (*q*); 24.7 (*q*); 24.4 (*t*); 23.0 (*q*); 15.6 (*q*). MS: 152 (2, M^{+-} – 46), 134 (25), 119 (52), 109 (32), 94 (100), 93 (39), 91 (74), 79 (98), 77 (42), 59 (95). Anal. calc. for $C_{12}H_{22}O_2$ (198.29): C 72.68, H 11.18; found: C 72.57, H 10.99.

2.6. *(3*RS,*4*SR*)-3-Ethoxy-1-*p-*menthen-8-ol* ((±)-**11**). According to *Procedure 1.6* from (±)-**4**. Yield 82%. Oil. n_D^{20} = 1.467. IR (CCl_4): 3520, 1671, 1380, 1200, 1141, 1122, 1076, 966, 941. ^{1}H-NMR: 5.71 (*m*, 1 H); 4.03 (br. *t*, *J* = 4.5, 1 H); 3.89 (*s*, 1 H); 3.74 (*dq*, *J* = 9, 7, 1 H); 3.41 (*dq*, *J* = 9, 7, 1 H); 2.12 (*m*, 1 H); 1.97 (*m*, 1 H); 1.9–1.75 (*m*, 2 H); 1.72 (br. *s*, 3 H); 1.32 (*s*, 3 H); 1.28 (*m*, 1 H); 1.21 (*s*, 3 H); 1.21 (*t*, *J* = 7, 3 H). ^{13}C-NMR: 141.2 (*s*); 120.0 (*d*); 73.4 (*d*); 71.8 (*s*); 63.4 (*t*); 46.9 (*d*); 31.7 (*t*); 29.3 (*q*); 28.1 (*q*); 23.7 (*q*); 18.4 (*t*); 15.8 (*q*). MS: 152 (2, M^{+-} – 46), 134 (18), 119 (37), 109 (49), 94 (> 100), 91 (69), 79 (> 100), 59 (> 100). Anal. calc. for $C_{12}H_{22}O_2$ (198.29): C 72.68, H 11.18; found: C 72.35, H 11.14.

2.7. *(3*RS,*4*RS*)-3-Methoxy-1-*p-*menthen-8-ol* ((±)-**8**). According to *Procedure 1.5* from (±)-**3**. Yield 86%. Oil. IR (CCl_4): 3490, 1680, 1370, 1169, 1080. ^{1}H-NMR: 5.48 (*m*, 1 H); 4.74 (*s*, 1 H); 4.05 (*m*, 1 H); 3.39 (*s*, 3 H); 2.09 (*m*, 1 H); 1.91 (*m*, 1 H); 1.8–1.6 (*m*, 2 H); 1.71 (br. *s*, 3 H); 1.25 (*m*, 1 H); 1.22 (*s*, 3 H); 1.16 (*s*, 3 H). ^{13}C-NMR: 137.9 (*s*); 120.4 (*d*); 79.4 (*d*); 73.0 (*s*); 54.5 (*q*); 48.4 (*d*); 30.8 (*t*); 29.3 (*q*); 24.7 (*q*); 24.3 (*t*); 22.9 (*q*). MS: 166 (19, M^{+-} – 18), 151 (35), 138 (11), 126 (19), 123 (20), 111 (24), 98 (100), 94 (70), 93 (32), 83 (56), 79 (78), 59 (72). Anal. calc. for $C_{11}H_{20}O_2$ (184.28): C 71.70, H 10.94; found: C 71.62, H 10.52.

2.8. *(3*RS,*4*SR*)-3-Methoxy-1-*p-*menthen-8-ol* ((±)-**9**). According to *Procedure 1.5* from (±)-**4**. Yield 83%. Oil. IR (CCl_4): 3530, 1677, 1393, 1381, 1210, 1141, 1080, 946, 900. ^{1}H-NMR: 5.75 (*m*, 1 H); 3.92 (*m*, 1 H); 3.69 (*s*, 1 H); 3.38 (*s*, 3 H); 2.13 (*m*, 1 H); 1.98 (*m*, 1 H); 1.85–1.75 (*m*, 2 H); 1.74 (br. *s*, 3 H); 1.32 (*s*, 3 H); 1.24 (*m*, 1 H); 1.21 (*s*, 3 H). ^{13}C-NMR: 141.6 (*s*); 119.1 (*d*); 74.7 (*d*); 71.7 (*s*); 55.4 (*q*); 46.8 (*d*); 31.6 (*t*); 29.1 (*q*); 27.9 (*q*); 23.6 (*q*); 18.2 (*t*). MS: 152 (2, M^{+-} – 32), 134 (15), 119 (25), 109 (26), 94 (75), 91 (48), 79 (98), 73 (100), 59 (91). Anal. calc. for $C_{11}H_{20}O_2$ (184.28): C 71.70, H 10.94; found: C 71.58, H 11.21.

3. Optically Active Compounds. – 3.1. *Treatment of* (±)-**12** *with Lithium (*R*)-Phenylethylamide. Procedure 1.3* was applied to 294 mg (1.5 mmol) of (±)-**12**. Chromatography (benzene/Et_2O 2:1) gave – in the order of elution –

94 mg (20%) of a mixture of 'tertiary' carbamates which was not investigated further, 163 mg (34%) of **14**, and 168 mg (35%) of **15**.

*N-[(R)-1-Phenylethyl]-O-[(3S,4S)-8-hydroxy-1-*p*-menthen-3-yl]urethane* (**14**): M.p. 141–142° ($CHCl_3$/hexane). $[\alpha]_D^{25} = +107°$ ($c = 0.45$, $CHCl_3$). IR (CCl_4): 3449, 3340, 1719, 1491, 1380, 1214, 1125, 1044, 697, 672. ^{1}H-NMR: 7.4–7.2 (*m*, 5 H); 5.4–5.3 (*m*, 2 H); 4.96 (*m*, 1 H); 4.86 (*m*, 1 H); 1.70 (br. *s*, 3 H); 1.48 (*d*, $J = 6.8$, 3 H); 1.20 (*s*, 3 H); 1.18 (*s*, 3 H). ^{13}C-NMR: 155.4 (*s*); 143.6 (*s*); 139.1 (*s*); 128.6 (2*d*); 127.2 (*d*); 125.8 (2*d*); 121.7 (*d*); 72.5 (*d*); 72.5 (*s*); 50.7 (*d*); 48.5 (*d*); 29.9 (*t*); 28.1 (*q*); 27.2 (*q*); 23.5 (*t*); 23.0 (*q*); 22.6 (*q*). MS: 152 ($M^+ - 165$), 137 (13), 109 (16), 106 (100), 94 (36), 79 (61), 59 (55), 43 (39). Anal. calc. for $C_{19}H_{27}NO_3$ (317.43): C 71.89, H 8.57; N 4.41; found: C 71.61, H 8.63, N 4.37.

*N-[(R)-1-Phenylethyl]-O-[(3R,4R)-8-hydroxy-1-*p*-menthen-3-yl]urethane* (**15**): Resinous oil. $[\alpha]_D^{25} = -40°$ ($c = 1.29$, $CHCl_3$). IR (CCl_4): 3450, 3372, 1715, 1494, 1380, 1221, 1160, 1041, 696, 674. ^{1}H-NMR: 7.4–7.2 (*m*, 5 H); 5.34 (*m*, 1 H); 5.31 (br. *s*, 1 H); 5.00 (*m*, 1 H); 4.84 (*m*, 1 H); 2.34 (*m*, 1 H); 2.03 (*m*, 1 H); 1.91 (*m*, 1 H); 1.87 (*m*, 1 H); 1.73 (*ddd*, $J = 11.6$, 8.2, 3.3, 1 H); 1.68 (br. *s*, 3 H); 1.46 (*d*, $J = 6.8$, 3 H); 1.20 (*m*, 6 H). ^{13}C-NMR: 155.5 (*s*); 143.3 (*s*); 139.1 (*s*); 128.7 (2*d*); 127.3 (*d*); 125.9 (2*d*); 121.8 (*d*); 72.6 (*s*); 72.4 (*d*); 50.8 (*d*); 48.6 (*d*); 29.9 (*t*); 28.3 (*q*); 26.8 (*q*); 23.7 (*t*); 23.0 (*q*); 22.7 (*q*). MS: 299 (1, $M^+ - 18$), 152 (47), 137 (46), 109 (23), 106 (100), 105 (41), 95 (41), 94 (86), 79 (75), 77 (38), 59 (96), 43 (51).

*(3S,4S)-1-*p*-Menthene-3,8-diol* ((−)-**3**). *Procedure 1.4* was applied to **14**. Yield 85%. M.p. 77–78° (hexane). $[\alpha]_D^{25} = -56°$ ($c = 0.7$, $CHCl_3$).

*(3S,4S)-1-*p*-Menthene-3,8-diyl Carbonate* ((−)-**12**). *Procedure 1.1* was applied to (−)-**3**. Yield 92%. M.p. 96–97° (Et_2O/hexane). $[\alpha]_D^{25} = -101°$ ($c = 1$, $CHCl_3$).

*(3R,4R)-1-*p*-Menthene-3,8-diol* ((+)-**3**). *Procedure 1.4* was applied to **15**. Yield 91%. M.p. 77–78° (hexane). $[\alpha]_D^{25} = +52°$ ($c = 1.3$, $CHCl_3$).

*(3R,4R)-1-*p*-Menthene-3,8-diyl Carbonate* ((+)-**12**). *Procedure 1.1* was applied to (+)-**3**. Yield 93%. M.p. 95–96° (Et_2O/hexane). $[\alpha]_D^{25} = +96°$ ($c = 2$, $CHCl_3$).

(S)-α-Terpineol ((−)-**16**). To a stirred soln. of 56 mg (0.176 mmol) of **14** in 2 ml of $EtNH_2$ at 0° were added small portions of powdered Li containing 0.5% Na *(Fluka)* until the blue colour persisted for 5 min. Standard workup with Et_2O and 1N HCl gave 38 mg of crude material which was chromatographed (Et_2O/pentane 3:7): 9.6 mg (35%) of (−)-**16**. $[\alpha]_D^{25} = -86°$ ($c = 0.55$, EtOH; [20]: $[\alpha]_D = -100°$ ($c = 20$, EtOH)).

*(S)-8-Hydroxy-1-*p*-menthen-3-one* ((+)-**2**). Oxidation of (+)-**3** (40 mg, 0.23 mmol) with CrO_3/pyridine according to [6] gave 16 mg of crude (+)-**2** which was purified by prep. TLC (benzene/Et_2O 1:2): 8 mg (21%) of (+)-**2**. $[\alpha]_D^{25} = +136°$ ($c = 0.59$, EtOH; [6]: $[\alpha]_D = +156°$ ($c = 10.4$, EtOH)).

3.2. *Treatment of (±)-***13** *with Lithium (R)-Phenylethylamide. Procedure 1.3* was applied to 744 mg (3.79 mmol) of (±)-**13**. The resulting mixture was separated by prep. HPLC (AcOEt/cyclohexane 1:2). Besides 83 mg of a mixture of 'tertiary' carbamates were isolated 370 mg (31%) of crystalline **18** and 340 mg (28%) of the oily, more polar **19**.

*N-[(R)-1-Phenylethyl]-O-[(3S,4R)-8-hydroxy-1-*p*-menthen-3-yl]urethane* (**18**). M.p. 106° (Et_2O/hexane). $[\alpha]_D^{25} = +231°$ ($c = 0.93$, $CHCl_3$). IR (CCl_4): 3450, 1722, 1700 (sh), 1491, 1380, 1220, 1046, 1029, 697. ^{1}H-NMR: 7.4–7.2 (*m*, 5 H); 5.64 (*m*, 1 H); 5.34 (br. *s*, 1 H); 5.03 (*m*, 1 H); 4.85 (*m*, 1 H); 2.71 (br. *s*, 1 H); 2.2–1.9 (*m*, 2 H); 1.72 (br. *s*, 3 H); 1.47 (*d*, $J = 6.9$, 3 H); 1.22 (*s*, 3 H); 1.13 (*s*, 3 H). ^{13}C-NMR: 155.5 (*s*); 143.6 (*s*); 141.4 (*s*); 128.6 (2*d*); 127.2 (*d*); 125.8 (2*d*); 120.2 (*d*); 71.7 (*s*); 69.4 (*d*); 50.8 (*d*); 47.7 (*d*); 31.6 (*t*); 28.8 (*q*); 27.3 (*q*); 23.3 (*q*); 22.4 (*q*); 19.4 (*t*). MS: 166 ($M^+ - 151$), 152 (6), 109 (22), 106 (100), 94 (65), 79 (88), 77 (34), 59 (64), 43 (33). Anal. calc. for $C_{19}H_{27}NO_3$ (317.43): C 71.89, H 8.57, N 4.41; found: C 71.82, H 8.53, N 4.37.

*N-[(R)-1-Phenylethyl]-O-[(3R,4S)-8-hydroxy-1-*p*-menthen-3-yl]urethane* (**19**). Resinous oil. $[\alpha]_D^{25} = -170°$ ($c = 1$, $CHCl_3$). IR (CCl_4): 3448, 1720, 1698, 1491, 1379, 1220, 1046, 1029, 798. ^{1}H-NMR: 7.4–7.2 (*m*, 5 H); 5.59 (br. *s*, 1 H); 5.37 (br. *s*, 1 H); 5.06 (*m*, 1 H); 4.86 (*m*, 1 H); 2.88 (br. *s*, 1 H); 2.2–1.9 (*m*, 2 H); 1.70 (*s*, 3 H); 1.47 (*d*, $J = 6.7$, 3 H); 1.35–1.15 (*m*, 7 H). ^{13}C-NMR: 155.7 (*s*); 143.5 (*s*); 141.6 (*s*); 128.2 (2*d*); 127.5 (*d*); 126.1 (2*d*); 120.2 (*d*); 71.8 (*s*); 69.5 (*d*); 51.0 (*d*); 48.0 (*d*); 31.7 (*t*); 29.1 (*q*); 27.3 (*q*); 23.4 (*q*); 22.6 (*q*); 19.6 (*t*). MS: 166 (24, $M^+ - 151$), 152 (19), 137 (19), 106 (15), 105 (41), 95 (59), 94 (100), 59 (61).

*(3S,4R)-1-*p*-Menthene-3,8-diol* ((+)-**4**). *Procedure 1.4* was applied to **18**. Yield 75%. Oil. $[\alpha]_D^{25} = +163°$ ($c = 0.7$, EtOH).

*(3S,4R)-1-*p*-Menthene-3,8-diyl Carbonate* ((+)-**13**). *Procedure 1.1* applied to (+)-**4** gave 64% of (+)-**13**. M.p. 93–94°. $[\alpha]_D^{25} = +103°$ ($c = 0.7$, $CHCl_3$).

*(3R,4S)-1-*p*-Menthene-3,8-diol* ((−)-**4**). *Procedure 1.4* was applied to **19**. Yield 90%. Oil. $[\alpha]_D^{25} = -164°$ ($c = 0.5$, EtOH).

*(3R,4S)-1-*p*-Menthene-3,8-diyl Carbonate* ((−)-**13**). *Procedure 1.1* applied to (−)-**4** gave 76% of (−)-**13**. M.p. 94–95° (Et_2O/hexane). $[\alpha]_D^{25} = -107°$ ($c = 0.85$, $CHCl_3$).

Correlation of (+)-**4**. Oxidation [28] of (+)-**4** (35 mg) gave 21 mg of crude (+)-**2** which was purified by chromatography (Et_2O/pentane 4:1) to yield 15 mg (42%) of (+)-**2**. $[\alpha]_D^{25} = +147°$ ($c = 0.9$, EtOH; [6]: $[\alpha]_D = +156°$ ($c = 10.4$, EtOH)).

4. Reduction of (±)-2 with Various Reagents. – 4.1. *(1RS,4SR)-8-Hydroxy-*p*-menthan-3-one* ((±)-**5**). Oil. IR (CCl_4): 3540, 1704, 1388, 1377, 1170. ^{1}H-NMR ($CDCl_3$): 3.0 (br. *s*, 1 H); 2.36 (*m*, 2 H); 2.14 (*m*, 1 H); 2.02 (*ddd*, $J = 12.8, 12.0, 1.3$, 1 H); 1.9 (*m*, 2 H); 1.56 (*qd*, *J ca.* 13, 3.2, 1 H); 1.40 (*m*, 1 H); 1.23 (*s*, 3 H); 1.22 (*s*, 3 H); 1.03 (*d*, $J = 6.2$, 3 H); [19]: 3.8 (*s*, 1 H); 0.98 (*s*, 6 H); 0.79 (*d*, $J = 5.4$, 3 H, see text). ^{1}H-NMR (C_6D_6): 3.96 (*s*, 1 H); 2.12 (*ddd*, $J = 12.5, 3.3, 2.4$, 1 H); 1.95 (*ddd*, $J = 13.2, 5.5, 1.2$, 1 H); 1.71 (*m*, 1 H); 1.45 (*ddd*, $J = 13, 12.5, 1.2$, 1 H); 1.4–1.25 (*m*, 2 H); 1.23 (*s*, 3 H); 1.22 (*s*, 3 H); 0.78 (*m*, H); 0.61 (*d*, $J = 6.1$, 3 H). ^{13}C-NMR: 215.2 (*s*); 71.4 (*s*); 58.8 (*d*); 51.5 (*t*); 35.5 (*d*); 34.0 (*t*); 28.7 (*t*); 28.5 (*q*); 25.7 (*q*); 22.3 (*q*); agreement with the reported data [19]: ±0.2 ppm. MS: 155 (15, $M^+ - 15$), 113 (15), 112 (100), 97 (32), 70 (59), 69 (31), 59 (54), 43 (80).

4.2. *(1RS,3SR,4RS)-*p*-Menthane-3,8-diol* ((+)-**6**). M.p. 81–82° ([17]: 81–82.5°). IR (CCl_4): 3630, 3350, 1361, 1163, 1037, 935. ^{1}H-NMR: agreement within 0.01 ppm with the values reported [17]. ^{13}C-NMR: agreement with the reported data [17]: ±0.1 ppm. MS: 157 (3, $M^+ - 15$), 154 (6), 139 (9), 96 (66), 95 (15), 81 (100), 68 (24), 59 (99), 43 (62).

4.3. *(1RS,3RS,4RS)-*p*-Menthane-3,8-diol* ((±)-**7**). M.p. 77–78° ([27]: 77–78°). IR (CCl_4): 3320, 1380, 1369, 1186, 1161, 1009, 907, 881. ^{1}H-NMR: values agree within 0.2 ppm with the reported data [17] [27]. ^{13}C-NMR: agreement with reported data [17]: ±0.1 ppm. MS: 157 (3, $M^+ - 15$), 154 (2), 139 (8), 96 (56), 95 (13), 81 (86), 59 (100), 43 (47).

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