

124. Determination of the Chemical Structure of Linden Ether

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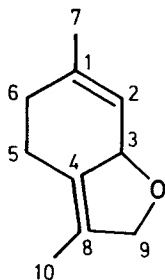
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The chemical structure of the novel monoterpene **1**, named 'linden ether' and isolated from linden honey and the blossoms of lime tree (*Tilia cordata*), was studied by two-dimensional NMR spectroscopy, by high-resolution MS as well as by hydrogenation experiments and by GC on a chiral phase. Thus, linden ether was identified as a racemic mixture, i.e. (7*aRS*)-2,4,5,7*a*-tetrahydro-3,6-dimethylbenzofuran.

Introduction. – The primary neutral odourants of linden honey have been recently compared [1] with those of honeys of other botanical origin. It was shown that 3,9-epoxy-1,4 (8)-*p*-menthadiene (**1**) and *cis*-rose oxide, both occurring also in the blossoms of the lime tree (*Tilia cordata*) [1], were typical odourants of the linden honey. Compound **1** smelled 'flowery, mint-like' and was named 'linden ether'; as to our knowledge, this monoterpene has not been described previously in the literature. The details of the identification of **1** are reported in the present paper.



1 (menthane numbering)

Results and Discussion. – *Spectroscopy.* The ¹H-NMR spectrum ((D₆)benzene) of **1** is shown in Fig. 1. Further NMR data are given in Tables 1–3 which are – as also the MS data – consistent with the proposed structure.

A double-quantum-filtered COSY experiment revealed two strongly coupled ¹H-spin systems comprising (i) the protons at 4.60 and 4.49 ppm with a high geminal coupling constant of ca. 12 Hz, indicating a CH₂ group substituted by a heteroatom and (ii) the signal at 2.25 ppm and the signals of the crowded region at 1.9–1.6 ppm. Homonuclear long-range couplings were detected by inspecting the 2D-matrix at a low level (Table 1). The ¹³C-NMR spectrum showed 10 signals. The results of ¹H,¹³C-correlation experiments are summarized in Table 2. Since the molecular formula, as determined by high-resolution MS, showed only 1 O-atom (see below), the fragment CH–O–CH₂ could be derived. Moreover, both CH₂ protons showed an exceptionally large long-range coupling with the proton at 5.23 ppm (*J* = 4.7 and = 4.4 Hz, resp.). Such a large coupling is normally not observed in a CH–O–CH₂ fragment with the exception of 2,5-dihydrofurans [2], where these groups are additionally linked by the double bond. This indicated the presence of a 2,5-dihydrofuran substructure. From the DQF-COSY

spectrum, it was apparent that the proton at 5.23 ppm also weakly coupled with both Me groups, indicating that it was in homoallylic position to both. Connectivities for the quaternary C-signals at 124.6, 131.4, and 135.3 ppm were established by heteronuclear multiple-bond/multiple-quantum coherence experiments, optimized for $^2J(\text{C},\text{H})$ and $^3J(\text{C},\text{H})$ coupling constants. These results are summarized in Table 2. NOE experiments were well in line with the bicyclic-ether structure **1** (Table 3).

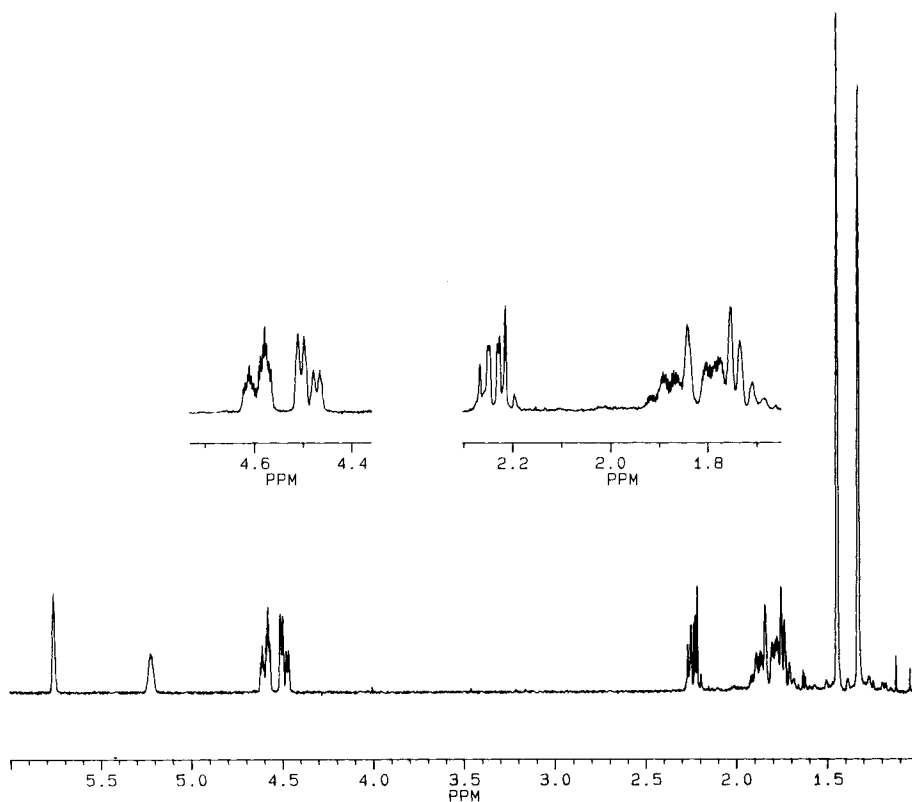


Fig. 1. ^1H -NMR spectrum of linden ether (**1**)

Table 1. Assignment of ^1H -NMR Signals of Linden Ether (**1**)

	δ [ppm]	J [Hz]	Connectivity ^{a)} with
H—C(2)	5.77	1.2	CH ₃ (7)
H—C(3)	5.23		H—C(9), H'—C(9), CH ₃ (7), CH ₃ (10)
H—C(9)	4.60	11.6, 4.4, 1.2	H'—C(9) ^{b)} , CH ₃ (10), H—C(3)
H'—C(9)	4.49	11.5, 4.7, 1.1	H—C(9) ^{b)} , CH ₃ (10), H—C(3)
H—C(5)	2.25		H'—C(5) ^{b)} , CH ₂ (6) ^{b)}
H'—C(5)	1.88		H—C(5) ^{b)} , CH ₂ (6) ^{b)}
CH ₂ (6)	1.77		H—C(5) ^{b)} , H'—C(5) ^{b)}
CH ₃ (7)	1.46	1.3	H—C(2), H—C(3)
CH ₃ (10)	1.34	1.2	H—C(9), H'—C(9), H—C(3)

^{a)} Observed homonuclear ^1H , ^1H connectivities by double-quantum-filtered COSY (DQF-COSY).

^{b)} Strong signal intensity.

Table 2. Assignment of ^{13}C -NMR Signals of Linden Ether (**1**)^{a)}

	δ [ppm]	DEPT analysis	Heteronuclear ^1H , ^{13}C multiple-quantum coherence	
			via $^1J(\text{C},\text{H})$	via $^{2,3}J(\text{C},\text{H})$
C(1)	135.3	C		$\text{CH}_3(7)$, $\text{H}-\text{C}(5)$
C(8) (C(4))	131.4	C		$\text{H}-\text{C}(5)$, $\text{CH}_3(10)$, $\text{H}-\text{C}(9)$, $\text{H}'-\text{C}(9)$
C(2)	125.9	CH	$\text{H}-\text{C}(2)$	$\text{CH}_3(7)$
C(4) (C(8))	124.6	C		$\text{CH}_3(10)$, $\text{H}'-\text{C}(9)$
C(3)	83.9	CH	$\text{H}-\text{C}(3)$	$\text{H}'-\text{C}(9)$, ($\text{H}-\text{C}(5)$)
C(9)	79.1	CH_2	$\text{H}-\text{C}(9)$, $\text{H}'-\text{C}(9)$	$\text{CH}_3(10)$
C(6)	31.8	CH_2	$\text{CH}_2(6)$	$\text{CH}_3(7)$, ($\text{H}'-\text{C}(5)$)
C(7)	23.2	CH_3	$\text{CH}_3(7)$	
C(5)	21.0	CH_2	$\text{H}-\text{C}(5)$, $\text{H}'-\text{C}(5)$	
C(10)	9.3	CH_3	$\text{CH}_3(10)$	

^{a)} Observed heteronuclear ^1H , ^{13}C connectivities in **1** by DEPT analysis and inverse ^1H , ^{13}C multiple-quantum coherence experiments.

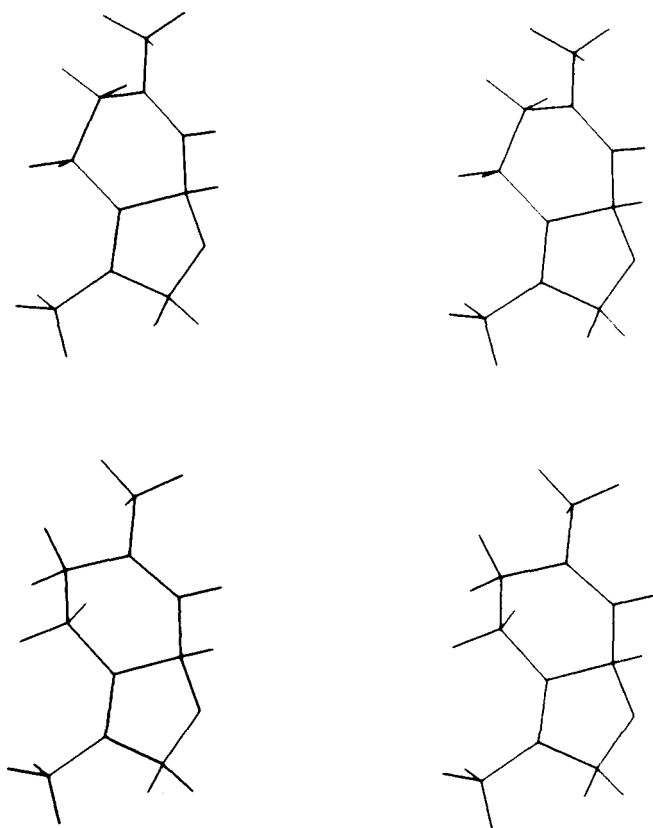


Fig. 2. Energy-minimized conformations of (3*S*)-linden ether ((3*S*)-**1**); stereo pairs. Top: dihedral angle of 93° for $\text{H}-\text{C}(2)$, $\text{H}-\text{C}(3)$; bottom: dihedral angle of 72° for $\text{H}-\text{C}(2)$, $\text{H}-\text{C}(3)$.

Table 3. NOE Observations and Time-Averaged Internuclear Proton-Proton Distances in Linden Ether (**1**)

Proton pair	Calculated internuclear distance [Å] ^a	NOE
H–C(3), CH ₃ (10)	4.74	
H–C(2), H–C(3)	2.76	++
H–C(2), CH ₃ (7)	2.97	++
H–C(3), H–C(9)	3.20	
H–C(3), H'–C(9)	3.92	
H–C(9), CH ₃ (10)	3.34	+
H'–C(9), CH ₃ (10)	3.20	+
H–C(6), CH ₃ (7)	3.33	} +
H'–C(6), CH ₃ (7)	3.03	
H–C(5), CH ₃ (10)	3.38	
H'–C(5), CH ₃ (10)	3.70	+

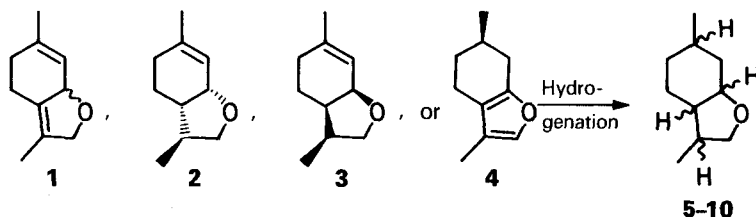
^a) Time average from molecular-dynamics simulation (DISCOVER).

Scalar coupling might be expected between the protons at C(2) and C(3). However, H–C(3) appeared as a br. s (5.23 ppm), and no crosspeak was observed in the DQF-COSY experiment. A molecular-dynamics simulation suggested the existence of two energy minima characterized by the conformations shown in Fig. 2. The energy barrier between them appeared modest, and a dynamics simulation at 300 K gave a time average value of ca. 85° for the dihedral angle between H–C(2) and H–C(3). The Karplus equation would suggest a scalar coupling constant of less than 1 Hz between the two respective protons, in agreement with the experimental data.

The protonated molecular ion $[M+H]^+$ at m/z 151 in the CI-MS corroborated a molecular weight of 150. The elemental composition of C₁₀H₁₄O for M^+ , which was in agreement with structure **1**, was calculated from high-resolution MS data (not shown).

Hydrogenation. To further confirm structure **1**, hydrogenation experiments were performed. The chemical structure of **1** was related to that of (3*R*,4*S*,8*S*)-3,9-epoxy-1-*p*-menthene (= dill ether; **2**), its (3*S*,4*R*,8*S*)-diastereoisomer **3**, and (1*R*)-menthofuran (**4**; Scheme 1). Hydrogenation of each of these compounds afforded 3,9-epoxy-*p*-menthane and some secondary products. In the case of **1**, the conditions detailed in Table 4 yielded 3,9-epoxy-*p*-menthane (65%), *p*-menthan-9-ol (15%), and unknown compounds (20%).

Scheme 1



Theoretically, 16 3,9-epoxy-*p*-menthane stereoisomers, of which 14 are listed with their absolute configuration in Table 4 (see **5–11**), may result from the hydrogenation of **1–4**.

The products actually formed were analyzed by capillary GC on OV-1701 and SE-54, and the 3,9-epoxy-*p*-menthane isomers were identified by comparison of their EI-MS with those reported by Ohloff and coworkers [3] (Table 4). As expected, the hydrogenation of **2** and **3** yielded, in each case, two 3,9-epoxy-*p*-menthane stereoisomers, since a

Table 4. Hydrogenation of Linden Ether (**1**) and Related Compounds: Distribution of 3,9-Epoxy-*p*-menthane Stereoisomers

3,9-Epoxy- <i>p</i> -menthane stereoisomer ^{a)}	<i>RI</i>		Rel. proportion [%] of hydrogenation products from			
	(<i>OV-1701</i>)	(<i>SE-54</i>)	1 ^{b)}	2 (3 <i>R</i> ,4 <i>S</i> ,8 <i>S</i>) ^{c)}	3 (3 <i>S</i> ,4 <i>R</i> ,8 <i>S</i>) ^{c)}	4 ^{d)}
5a (1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i> ,8 <i>S</i>)				23 ^{e)}	–	3
b (1 <i>S</i> ,3 <i>R</i> ,4 <i>R</i> ,8 <i>R</i>)	1178	1129	9	–	–	–
6a (1 <i>R</i> ,3 <i>R</i> ,4 <i>S</i> ,8 <i>S</i>)			Traces	–	–	Traces
b (1 <i>S</i> ,3 <i>S</i> ,4 <i>R</i> ,8 <i>R</i>)	1200	1139	–	–	–	–
7a (1 <i>R</i> ,3 <i>S</i> ,4 <i>S</i> ,8 <i>R</i>)			–	–	–	64
b (1 <i>S</i> ,3 <i>R</i> ,4 <i>R</i> ,8 <i>S</i>)	1208	1154	26	–	13 ^{e)}	–
8a (1 <i>R</i> ,3 <i>R</i> ,4 <i>R</i> ,8 <i>R</i>)			3	–	–	8
b (1 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,8 <i>S</i>)	1229	1164	–	77 ^{e)}	–	–
9a (1 <i>R</i> ,3 <i>R</i> ,4 <i>R</i> ,8 <i>S</i>)			57	–	87 ^{e)}	25
b (1 <i>S</i> ,3 <i>S</i> ,4 <i>S</i> ,8 <i>R</i>)	1230	1172	–	–	–	–
10a (1 <i>R</i> ,3 <i>R</i> ,4 <i>S</i> ,8 <i>R</i>)			2	–	–	Traces
b (1 <i>S</i> ,3 <i>S</i> ,4 <i>R</i> ,8 <i>S</i>)	1243	1174	–	–	–	–
11a (1 <i>R</i> ,3 <i>S</i> ,4 <i>R</i> ,8 <i>S</i>)			3	–	–	–
b (1 <i>S</i> ,3 <i>R</i> ,4 <i>S</i> ,8 <i>R</i>)	1263	1195	–	–	–	–

^{a)} The absolute configuration of the 3,9-epoxy-*p*-menthane stereoisomers is given in parentheses.

^{b)} Rh/alumina, H₂: 5 bar, 1 h.

^{c)} Rh/alumina, H₂: 3 bar, 1 h.

^{d)} Pd/C, H₂: 10 bar, 6 h.

^{e)} Hydrogenation of the C(1)=C(2) bond changes the priority (*Cahn-Ingold-Prelog* system) of the substituents at C(3).

new chiral center was formed at C(1). The assignment (1*R*) or (1*S*) presented in Table 4 was based on the comparison with the stereoisomers formed by hydrogenation of **4**. *Ohloff* and coworkers [3] have found that **4** is predominantly hydrogenated with *cis*-specificity to the stereoisomers **7a** and **9a**, in a ratio of 1 to 3. Using other conditions (catalyst, solvent), these stereoisomers were also primarily produced (Table 4), but in the reverse ratio of 2.5 to 1.

The stereoisomers **7a/b** and **9a/b** obtained by hydrogenation of **1** were isolated. The data of their ¹H-NMR spectra (Table 5) agreed with those reported in [3] for the (+)-(1*S*,3*S*,4*S*,8*R*)- and the (+)-(1*R*,3*S*,4*S*,8*R*)-3,9-epoxy-*p*-menthane, respectively. The small differences in the δ values of the Me group are most likely caused by the different solvents used ((D₆)benzene *vs.* CCl₄). Hydrogenation of the C(4)=C(8) bond of **1** changed the difference of the diastereoisotopic protons of the CH₂O group. This difference increased from 0.11 ppm (Table 1, H–C(9), H'–C(9)) to 0.44 ppm (Table 5).

Table 5. ¹H-NMR Data of the 3,9-Epoxy-*p*-menthane Isomers **7a/b** and **9a/b**. δ in ppm, *J* in Hz.

		Isomer 7a/b		Isomer 9a/b	
H–C(3)	(CH–O)	3.88	(<i>m</i> , <i>J</i> $\approx$ 3)	3.92	(<i>q</i> , <i>J</i> = 4.4)
CH ₃ (7)	(CH ₃)	0.72	(<i>d</i> , <i>J</i> = 6.8)	1.13	(<i>d</i> , <i>J</i> = 7.0)
H–C(9)	(CH ₂ –O)	3.41	(<i>dd</i> , <i>J</i> = 9.9, 7.9)	3.36	(<i>dd</i> , <i>J</i> = 9.2, 8.1)
H'–C(9)	(CH ₂ –O)	3.84	(<i>m</i> , <i>J</i> = 8.4)	3.81	(<i>t</i> , <i>J</i> = 8.2)
CH ₃ (10)	(CH ₃)	0.85	(<i>d</i> , <i>J</i> = 6.7)	0.73	(<i>d</i> , <i>J</i> = 6.9)

CD measurements were performed in order to establish the chirality at C(3). However, no unequivocal evidence for optical activity was obtained. The presence of a racemic mixture was subsequently confirmed by a detailed GC study using a chiral phase. As shown in Fig. 3, **1** was resolved into two peaks appearing in a ratio of 1:1 at *RI* 1281 and 1285, whereas experiments on various non-chiral phases (*SE-54*, *OV-1701*, *Carbowax*) consistently showed only one peak.

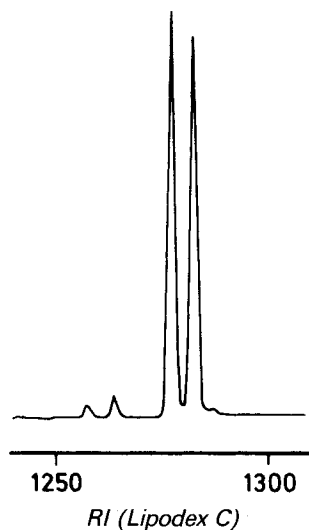
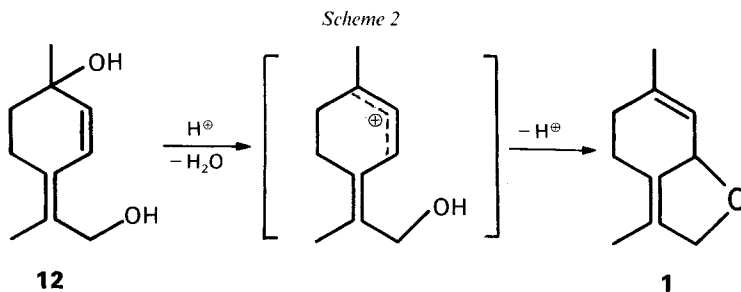


Fig. 3. Separation of linden ether (**1**) into enantiomers by capillary GC on a chiral stationary phase

The formation of the racemic mixture could be due to the mechanism of the ring closure. We propose tentatively that linden ether (**1**) could be formed by an acid-catalyzed cyclization of the intermediate **12** via an allylic carbocation (Scheme 2). Under mild conditions (pH 4), such a reaction occurs spontaneously as shown for dill ether (**2**) [1] [3]. However, the proposed intermediate **12** has not yet been detected.



Conclusion. – NMR and MS data as well as hydrogenation experiments indicated that compound **1**, isolated from linden honey and lime blossoms, was the racemic (7a*RS*)-2,4,5,7a-tetrahydro-3,6-dimethylbenzofuran.

Experimental Part

General. *Linden ether* (= (7*a*RS)-2,4,5,7*a*-tetrahydro-3,6-dimethylbenzofuran; **1**) was isolated from lime honey by simultaneous distillation/extraction and purified by column chromatography (CC) on silica gel and, in addition, by HPLC [1]. The following compounds were obtained commercially: (–)-(S)-limonene, (+)-1-*p*-menthen-9-ol, soln. (0.5 mol/l) of 9-borabicyclo[3.3.1]nonane (9-BBN) in hexane, Pt^{IV} oxide (Aldrich, Steinheim, FRG), Rh on activated alumina (Fluka, Buchs, Switzerland), Pd/C (10% Pd; Merck, Darmstadt, FRG), (+)-(R)-menthofuran (**4**)¹⁾ (Roth, Karlsruhe, FRG). (3*R*,4*S*,8*S*)-3,9-Epoxy-*p*-menthene ('dill ether'; **2**) was a gift of Dr. R. Emberger (Haarmann & Reimer, Holzminden, FRG). Pentane, hexane, and MeOH were 'for spectroscopy' (Merck, Darmstadt, FRG). (D₆)Benzene (99.96% D) was from MSD Isotopes (IC Chemicals, Munich, FRG). Capillary GC: SE-54 and OV-1701, as described [1]; separation of the enantiomers of **1** on a borosilicate glass capillary (50 × 0.25 mm) coated with a chiral stationary phase (Lipodex C; Macherey & Nagel, Düren, FRG); application of the sample by split injection (1:5, *v/v*); He flow 2.0 ml/min, temp. 100°; retention indices (*RI*) were calculated [1]. CD spectra: solns. in pentane (up to 0.1 μmol); spectropolarimeter Jasco J 500-A (Biotronik, Maintal, FRG) equipped with a H₂O-cooled 450-W Xe lamp; at 22° in a 1-mm quartz cell, at 400–190 nm. NMR spectra: Bruker-AM-360-FT-NMR spectrometer; at 298 K in (D₆)benzene in a Wilmad 535-PP tube; the sample tube was carefully degassed by repeated evacuation and subsequently sealed to avoid decomposition (by O₂). ¹H-NMR: transmitter frequency 360.13 MHz; 30° pulse, 3 μs; repetition time 3.2 s; spectral width 7.2 kHz; 32 K data set; for resolution enhancement, the FID was multiplied with a Lorentz Gauss function prior to Fourier transformation; δ rel. to (D₆)benzene (7.15 ppm). ¹³C-NMR: transmitter frequency 90.56 MHz; 30° pulse, 2 μs; repetition time 2.5 s; spectral width 21.7 kHz; 64 K data set; ¹H composite pulse decoupling (WALTZ-16); 1-Hz line broadening; δ rel. to (D₆)benzene (128.0 ppm); for spectral editing of the ¹³C-signals, the 135°- and 90°-DEPT experiments were used. ¹H-NOE difference spectroscopy: longitudinal relaxation times (*T*₁) by the inversion-recovery technique; irradiation time 2.5 × *T*₁; relaxation delay 3 × *T*₁; for each irradiated frequency, 96 scans were acquired. ¹H-COSY: a phase-sensitive double-quantum-filtered COSY was performed (DQF-COSY); relaxation delay 2 s; 512 experiments of 32 scans per *t*₁ value; 4 dummy scans, spectral width 1968 Hz in *F*₂; size: 1K in *F*₂, zero-filled to 2 K; zero-filling in *F*₁ to 2 K; resolution 2 Hz/point in both dimensions, sine-bell multiplication in *F*₂ and *F*₁; the sample was not rotated. ¹H-Detected multiple-quantum heteronuclear chemical-shift correlation: the pulse sequence described by Bax *et al.* [6], with an additional bilinear (BIRD) pulse to suppress protons which are not coupled to ¹³C, was used; 3 experiments with magnetization transfer optimized for coupling constants of 135, 6, and 4 Hz, giving delays of 3.7, 85, and 125 ms, resp.: delay time between experiments 3 s; the heteronuclear multiple-quantum coherence experiment was started 400 ms after the BIRD pulse; 256 scans preceded by 4 dummy scans were recorded for 100 *t*₁ values and zero-filled to 256; spectral width 2525 Hz in *F*₂ and 6234 Hz in *F*₁; spectra calculated in magnitude mode with sine-bell apodization in *F*₂; no digital filtering in the *t*₁ dimension; the sample was not rotated to avoid *t*₁ noise.

(–)-(4*S*,8*RS*)-1-*p*-Menthen-9-ol (= (1'*S*,2*RS*)-2-(4'-Methylcyclohex-3'-enyl)propanol. (–)-(4*S*)-Limonene (16.5 mmol) was hydroborated with a soln. of 9-BBN in hexane (30 ml), according to the general procedure [4]. After cooling with an ice-bath, the organoboranes were oxidized by adding, successively, EtOH (9 ml), 6*N* NaOH (3 ml), and 30% (*w/v*) H₂O₂ (6 ml). The mixture was heated at 50° for 1 h and then cooled and the aqueous layer saturated with Na₂CO₃. The org. layer was separated, the H₂O phase extracted with Et₂O (2 × 20 ml), and the combined org. phase dried (Na₂SO₄) and concentrated. Fractional distillation at (118°/15 mbar) afforded the alcohol which was further purified by CC (silica gel, 30 × 1.6 cm, Et₂O/pentane 1:1). CD (pentane): Θ = –7700°/cm²·decimol at λ = 202 nm. ¹H-NMR (360 MHz, (D₆)benzene): 0.82 (*d*, *J* = 7, CH₃(10)); 0.85 (*d*, *J* = 7, CH₃(10)); 1.63 (*s*, CH₃(7)); 3.26 (*m*, *J* = 6.7, 1.9, 1 H, CH₂(9)); 3.43 (*m*, *J* = 2.7, 1 H, CH₂(9)); 5.4 (*br. s*, H–C(2)); 1.0–1.9 (*m*, 9 H, CH₂(3), H–C(4), CH₂(5), CH₂(6), H–C(8), OH). ¹³C-NMR (DEPT, 90 MHz): 133.7, 133.8 (C(1)); 121.4, 121.5 (C(2)); 66.2, 66.0 (C(9)); 40.5, 40.3 (C(8)); 35.5, 35.6 (C(4)); 31.1, 31.0 (CH₂); 28.1, 30.3 (CH₂); 27.7, 25.9 (CH₂); 23.7 (C(7)); 13.5, 14.0 (C(10)). The 1:1 ratio of the *d* at 0.82 and 0.85 ppm (CH₃) and some of the ¹³C-signals, indicated the presence of two diastereoisomers. EI-MS: 94 (100), 79 (68), 93 (60), 67 (45), 95 (42), 68 (42), 121 (40), 107 (40), 41 (38), 55 (31), 81 (26), 154 (24, *M*⁺), 91 (22), 39 (22), 136 (20).

(–)-(3*S*,4*R*,8*S*)-3,9-Epoxy-1-*p*-menthene (= (3*S*,3*aR*,7*aS*)-2,3,3*a*,4,5,7*a*-Hexahydro-3,6-dimethylbenzofuran; **3**). A mixture of (3*S*,4*R*,8*RS*)-3,9-epoxy-1-*p*-menthenes was prepared by photooxidation of (–)-(4*S*,8*RS*)-1-*p*-menthen-9-ol [1] [3]. The diastereoisomers were separated by capillary GC (SE-54) [1]: *RI* 1187 for (3*S*,4*R*,8*R*)

¹⁾ A positive molar ellipticity Θ = +6400°/cm²·decimol at λ = 225 nm was calculated from the CD curve.

and *R*_I 1235 for (3*S*,4*R*,8*S*); the (3*S*,4*R*,8*S*)-diastereoisomer was isolated by prep. GC [1]. CD (pentane): $\theta = -23700^\circ/\text{cm}^2 \cdot \text{decimol}$ at $\lambda = 199 \text{ nm}$. ¹H-NMR: 0.72 (*d*, *J* = 6.9, CH₃(10)); 1.58 (*s*, CH₃(7)); 2.24 (*m*, *J* = 9, H–C(8)); 3.42 (*dd*, *J* = 7.8, 9.8, 1 H–C(9)); 3.89 (*t*, *J* = 8.1, 1 H–C(9)); 4.21 (*m*, *J* = 1, H–C(3)); 5.77 (br. *s*, H–C(2)); 1.1–1.7 (*m*, H–C(4), CH₂(5), CH₂(6)). ¹³C-NMR (DEPT, 90 MHz): 138.3 (C(1)); 122.0 (C(2)); 76.3 (C(3)); 72.4 (C(9)); 40.6 (C(4) or C(8)); 37.4 (C(4) or C(8)); 30.0 (C(5) or C(6)); 23.7 (C(7)); 19.6 (C(5) or C(6)); 11.7 (C(10)). The abs. configuration was determined as 8*S*, due to the rather small ¹³C-NMR shift of CH₃(10) (11.7 ppm; shielding of the Me group by the O-atom). In contrast, CH₃(10) of the (3*S*,4*R*,8*R*) stereoisomer appeared at 17.6 ppm. MS: in agreement with that of dill ether [5].

Catalytic Hydrogenation. Catalysts and exper. conditions for hydrogenations are given in Table 4. Linden ether (1), dill ether (2), (+)-(*R*)-menthofuran (4); and (–)-(3*S*,4*R*,8*S*)-3,9-epoxy-1-*p*-menthene (3) were hydrogenated using MeOH (20 ml) as solvent. At the end of the reaction, H₂O (10 ml) was added, and the substances were extracted with pentane (2 × 20 ml). The pentane soln. was washed with brine (50 ml), dried (Na₂SO₄), and then concentrated to 200 μ l by distillation of the solvent on a Vigreux column (50 × 1 cm), and finally by micro distillation [7].

Molecular Dynamics Calculation. Molecular dynamics simulation was performed with the software packages INSIGHT and DISCOVER from Biosym Inc. (Munich) using an IRIS 4D 70GT workstation from Silicon Graphics.

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