38. Syntheses and Absolute Configuration of (*E*)- and (*Z*)-α-Bisabolenes

by **François Delay** und **Günther Ohloff**

Firmenich SA, Research Laboratories, CH-1211 Geneva 8

Dedicated to Professor *E. Giovannini* on the occasion of his 70th birthday

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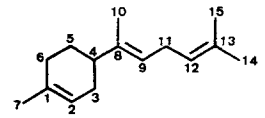
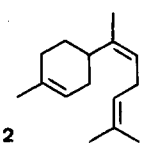
Summary

Stereospecific syntheses of (*E*)- and (*Z*)-α-bisabolenes have made revision of the configuration of natural (+)-α-bisabolene from *Opoponax* oil necessary. ^{13}C-NMR. spectroscopy has been used for the differentiation of these isomers.

α-Bisabolene has been known for some years with certainty to be a constituent of essential oils [1–7]. However, the geometry about the C(8) double bond[1]) has not been unambiguously established. The (*E*)-structure **1** has been assigned by *Wenninger* [1] to the hydrocarbon isolated from the oil of *Opoponax*. The α-bisabolene with a considerably longer retention time[2]) which was obtained by dehydrochlorination of bisabolene trihydrochloride, has been assigned the (*Z*)-configuration **2** on the basis of unpublished spectroscopic data[3]).



1



2

On the other hand, recent reports [7–9] state that these two isomers are very difficult to differentiate from their spectral properties. Finally, the stereospecific syntheses of (*E*)- and (*Z*)-α-bisabolenes by *Teisseire* [10] and *Vig* [11] respectively, are somewhat confusing, since both synthetic pathways involved *Wittig* reactions and gave exclusively 'abnormal' isomers [12].

The uncertainty arising from these results prompted us to re-examine the synthesis of both α-bisabolenes and to provide spectroscopic features allowing their facile structural assignment.

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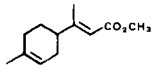
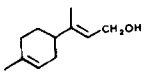
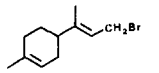
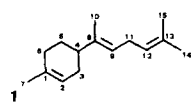
[1]) This skeleton was considered as a sesquimenthane and was therefore numbered from the numbering of *p*-menthane.

[2]) Capillary: UCON HB 5100 (this work) and [1].

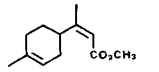
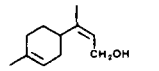
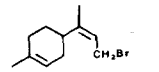
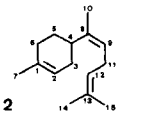
[3]) See ref. [7], footnote p. 1748.

Table 1. *^{1}H-NMR. data of the (E)-derivatives at 360 MHz*

	C(2)	C(3,4,5)	C(5)(a)[a]	C(5)(e)[b]	C(11)	C(9,12)	C(7,10,14,15)
 5	5.42 br. *s*	1.90–2.30 br. *m*	1.56 *m*	1.79 *m*	–	5.71 *s*	1.66 br. *s* 2.17 *s*
 7	5.42 br. *s*	1.86–2.18 br. *m*	1.50 *m*	1.76 *m*	4.20 *d* $^3J=7$	5.46 *t* $^3J=7$	1.66 br. *s* 1.68 *s*
 9	5.41 br. *s*	1.80–2.20 br. *m*	1.50 *m*	1.74 *m*	4.05 *d* $^3J=8$	5.58 *t* $^3J=8$	1.56 br. *s* 1.73 *s*
 1	5.41 br. *s*	1.82–2.12 br. *m*	1.46 *m*	1.66 *m*	2.70 br. *t* $^3J=7$	5.12/5.14 br. *t* $^3J=7$	1.61 *s* 1.63 *s* 1.64 *s* 1.69 *s*

[a]) Axial: $d\times d\times t$ ($^2J=12$, $^3J=6$, $^3J=12$ Hz).
[b]) Equatorial: $d\times d\times t$ ($^2J=12$, $^3J=5$, $^3J=4$ Hz).

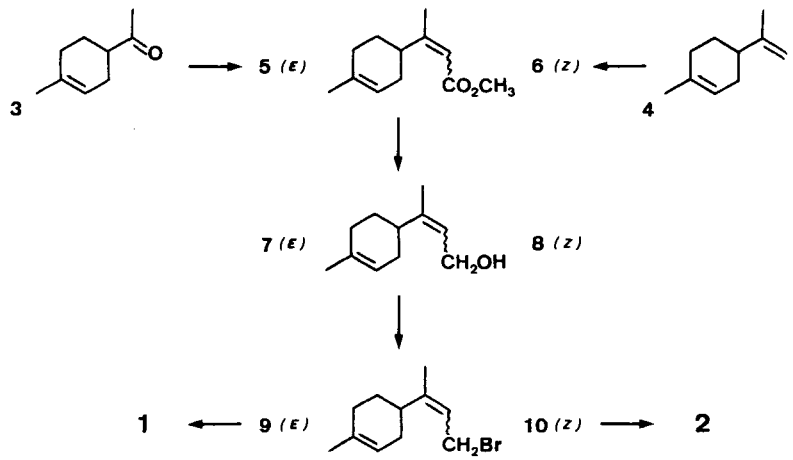
Table 2. *^{1}H-NMR. data of the (Z)-derivatives at 360 MHz*

	C(2)	C(4)	C(3,6)	C(5)(a)	C(5)(e)	C(11)	C(9,10)	C(7,10,14,15)
 6	5.38 br. *s*	3.78 *m*	2.00 br. *s*	1.58[a]) *m*	1.67 *m*	–	5.62 *s*	1.64 br. *s* 1.82 *s*
 8	5.39 br. *s*	2.66 *m*	2.00 br. *m*	1.58 *m*	1.78 *m*	4.16 *m*	5.39 *m*	1.66 br. *s* 1.70 *s*
 10	5.43 br. *s*	2.73 $t\times t$ $^3J=10$ $^3J=5$	1.98 br. *m*	1.50 *m*	1.80 *m*	4.05 *d* $^3J=8.2$	5.53 *t* $^3J=8.2$	1.67 br. *s* 1.70 *s*
 2	5.46 br. *s*	2.68 *m*	2.00 br. *m*	1.60 *m*	1.82 *m*	2.72 *t* $^3J=7$	5.11/5.13 br. *t* $^3J=7$	1.62 *s* 1.62 *s* 1.66 *s* 1.69 *s*

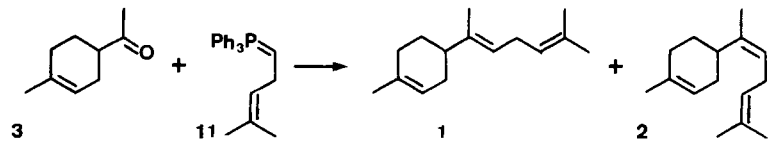
[a]) $d\times d\times t$ ($^2J=12$, $^3J=5.5$, $^3J=12$ Hz).

A 4:1 thermodynamic mixture of the methyl esters **5** and **6** was obtained either by the *Wittig-Horner* reaction [13] [14] on (±)-methyl 4-methyl-3-cyclohexenyl ketone (**3**) [15] or by the direct metallation and carbonation of limonene (**4**) [16] *(Scheme 1)*. Both isomers were readily separated by column chromatography and identified by NMR. spectroscopy (see *Table 1* and *2*, and [17]). Reduction of each methyl ester separately by means of lithium aluminium hydride gave the corresponding alcohols **7** and **8** in 80% yield. The latter were converted into their bro-

Scheme 1



Scheme 2



mides **9** and **10** with phosphorous tribromide in ether[4]). Finally, (*E*)- and (*Z*)-α-bisabolenes (**1** and **2**) were obtained by coupling the bromides **9** and **10** with lithium di-(2-methyl-1-propenyl)cuprate in 70% yield.

Alternatively, reaction of the ylid **11** with the methyl ketone **3** gave a low yield (25%) of a mixture containing 93% of the (*Z*)-isomer **2** *(Scheme 2)*. This stereoselectivity was not surprising in view of the size of the unstabilized ylid **11**.

Examination of the ^{1}H-NMR. data reproduced in the *Tables* and *Figure 1* reveals three salient features which allow the unambiguous differentiation between the (*E*)- and (*Z*)-α-bisabolenes (**1** and **2**). Firstly, the axial proton at C(5) appears at about 0.15 ppm higher field in the (*E*)-isomer **1** than the (*Z*)-isomer **2**. This proton can be seen quite distinctly at 360 MHz, but it is much less easily recognizable at 60 MHz (see *Fig. 1*). Secondly, there is a difference between the chemical shifts of the cyclic and non-cyclic olefinic protons: this is only 0.29 ppm in the (*E*)-isomer **1**, but 0.35 ppm in the (*Z*)-isomer **2**.

Finally, integration at 2.7 ppm corresponds to two doubly allylic protons at C(11) in the (*E*)-isomer **1**, but three protons in the(*Z*)-isomer **2**, the third one being the tertiary allylic proton at C(4)[5]). This is readily detectable in 60 MHz spectra and is thus the best way to differentiate the geometrical isomers.

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[4]) Carbon tetrabromide and triphenylphosphine as an alternative brominating agent gave the same results.

[5]) *Table 2* shows that this down-field shift of the proton at C(4) is general for all intermediates in the synthesis of (*Z*)-α-bisabolene (**2**).

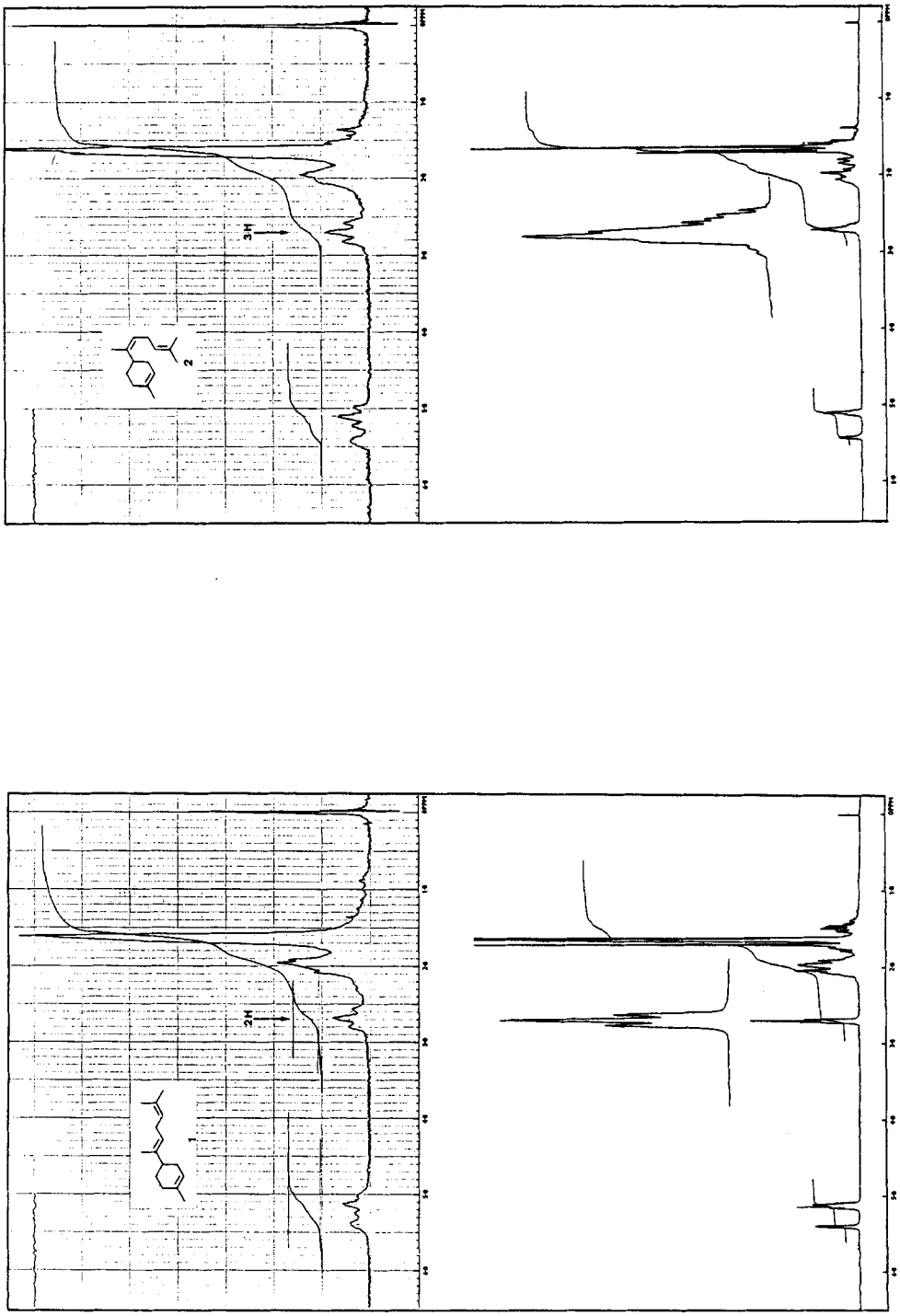


Fig. 1. *^{1}H-NMR. spectra* (60 and 360 MHz, $CDCl_3$) *of compounds* **1** *and* **2**

From a stereochemical point of view, this unusual down-field shift of an allylic proton implies a conformational constraint of the molecule, which either brings the isopropylidene double bond in the vicinity of the tertiary center, or places this proton in a *syn*-periplanar arrangement with the adjacent double bond. This last hypothesis was confirmed by examination of the ^{1}H-NMR. spectrum of the corresponding 12,13-dihydro derivative (**14** = 12,13-dihydro-**2**), prepared by the *Wittig* reaction (in analogy to *Scheme 2* by use of triphenyl (4-methylpentyl) phosphonium instead of **11**). In compound **14**, the H–C(4) signal appeared at 2.62 ppm, *vs.* 2.68 ppm in the case of compound **2**.

^{13}C-NMR. data *(Scheme 3)* support our assignments. The key values are those of carbons C(4) and C(10), which are in full agreement with those expected for (*Z,E*)-isomers [19]. As would also be expected *a priori*, the signals of the cyclic carbon atoms in limonene (**4**) [20] compare favourably with those of the (*E*)-isomer **1** in which the side chain is directed away from the ring. The C(10) methyl group,

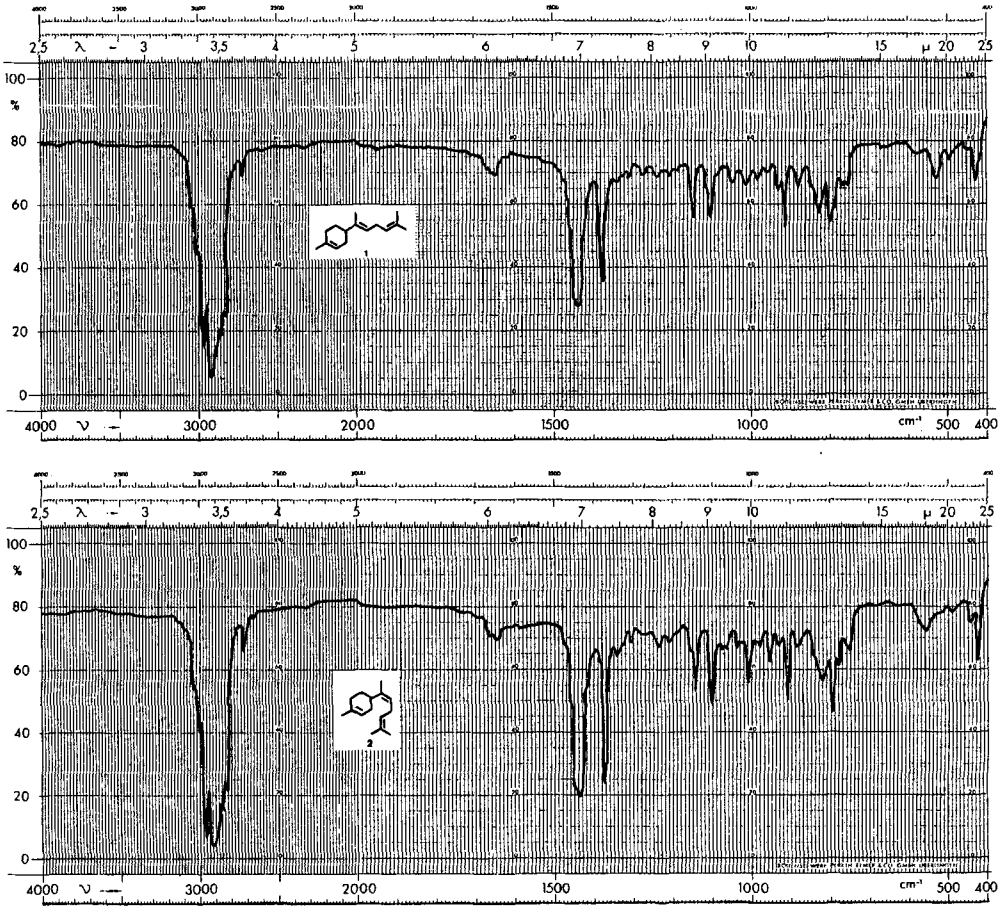
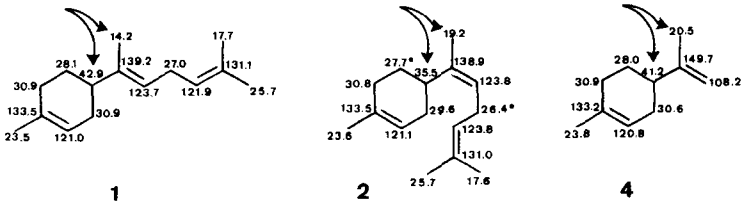


Fig. 2. *IR. spectra (film) of compounds* **1** *and* **2**. These spectra were reversed in [8].

Scheme 3. *^{13}C-NMR. data of compounds* **1**, **2** *and* **4**



however, is more similar to the corresponding signal in (*Z*)-*α*-bisabolene (**2**), since only in this case does the methyl group have no (*Z*)-substituent in the neighbourhood.

Finally, the absolute configurations of both *α*-bisabolenes have been established by carrying out their syntheses separately from (+)-(*R*)-limonene ($[\alpha]_D^{20} = +116°$) and (−)-(*S*)-limonene ($[\alpha]_D^{20} = -89.4°$). Thus, while (*R*,*E*)-*α*-bisabolene proved to be dextrorotatory ($[\alpha]_D^{20} = +54.3°$), (*R*,*Z*)-*α*-bisabolene was levorotatory ($[\alpha]_D^{20} = -12°$). On the other hand, (−)-(*S*)-limonene led to (−)-(*S*,*E*)-*α*-bisabolene ($[\alpha]_D^{20} = -38.9°$) and to (+)-(*S*,*Z*)-*α*-bisabolene ($[\alpha]_D^{20} = +8.0°$)[6]).

As an example of application of this isomeric differentiation, we isolated *α*-bisabolene from the oil of *Opoponax*. After careful purification by column chromatography on 15% silver nitrate-silica and gas chromatography, it was identical with (+)-(*S*,*Z*)-*α*-bisabolene, with $[\alpha]_D^{20} = +4.15°$ ([1]: $[\alpha]_D^{20} = +3.8°$), and the previous assignment [1] must thus be revised.

The stereoisomeric bisabolenes **1** and **2** possess distinctly different odour qualities. The (*E*)-derivative **1** exhibits a woody-herbal odour with a green subnote, whereas the (*Z*)-compound **2** is more green and flowery. Furthermore, **1** has neither the rather fatty note, dominant in **2**, nor the resinous-varnish subnote vaguely reminiscent of *Asa foetida*. Whilst (*Z*)-bisabolene **2** remotely recalls the typical odour of *Opoponax*, there is no trace of it in (*E*)-bisabolene **1**. The scent of **2** is stronger than that of **1**, but the reverse is found for the intermediate alcohols **7** and **8**. However, the lily-of-the-valley note which they have in common, is more pleasant, purer and sweeter in the (*Z*)-alcohol **8**. (*E*)-Alcohol **7** has a heavy tonality and a subnote of dry crushed leaves.

We are grateful to Mr. *W. Thommen* for running the ^{1}H- and ^{13}C-NMR. spectra.

Experimental Part

(with the precious collaboration of Mr. *P. Janin*)

General. – ^{1}H- 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 tetramethylsilane. Coupling constants *J* are in Hz. Mass spectra were measured on an *Atlas* CH-4 mass spectrometer, using an inlet temperature of

[6]) Assuming that no racemization occurs throughout the synthesis, the optical purities are those of the starting materials, (+)-(*R*)- ($[\alpha]_D^{20}$(neat) = +122.9°) and (−)-(*S*-limonenes ($[\alpha]_D^{20}$(neat) = −92.6°), namely 97% and 76%, published values being $[\alpha]_D^{20}$(neat) = +125.6° and −122.1° [21]. The corrected $[\alpha]_D^{20}$ values of (*R*,*E*)- and (*S*,*E*)-*α*-bisabolenes are +55.9° and −51.2°; while those of the (*R*,*Z*)- and (*S*,*Z*)-isomers are −12.4° and +10.5°.

ca. 150° and electrons of 70 eV. Usually, only the ten most important fragments are reported as *m/e* (% base peak). IR. spectra were recorded as films on NaCl plates on a model A-21 *Perkin-Elmer* spectrophotometer. Specific rotations were measured in ethanol (1%) on a model 141 *Perkin-Elmer* polarimeter. Gas liquid 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.

Methyl (*E*)- and (*Z*)-3-(4-methyl-3-cyclohexenyl)-2-butenoates (5 and 6). – a) *The* Wittig-Horner *reaction* [14] [15]. Methyl dimethylphosphonoacetate (52.6 g; 0.289 mol) was added dropwise under argon over a period of 2.5 h to a suspension of NaH (6.95 g; 0.289 mol) in dry tetrahydrofuran (THF) (290 ml) at RT. To the resulting creamy mixture, (±)-methyl 4-methyl-3-cyclohexenyl ketone (**3**) (40 g; 0.289 mol) in dry THF (150 ml) was added slowly. The yellowish mixture was stirred for 2 h and after standing overnight, was heated 1.5 h at reflux and poured onto ice-water. The mixture was extracted with ether, the organic phase was washed ($3\times H_2O$), dried and concentrated. The crude product (48 g) consisted of a mixture of unreacted starting material (**3**; 33%) and the methyl esters **5** (15%) and **6** (52%). Column chromatography on silica, in hexane/ether 90:10 yielded pure samples of each ester (**5** and **6**, combined yield 57%).

b) *Metallation of limonene* [16]. To a stirred solution of 1.58N butyllithium in hexane (305 ml; 0.482 mol) under argon was added dropwise *N,N,N',N'*-tetramethylethylene diamine (56 g; 0.482 mol). To the resulting yellow solution, (+)- or (−)-limonene (136 g; 1 mol) was added slowly and the mixture was stirred overnight at RT. The solution of metallated limonene was added rapidly to a slurry of dry ice (1 kg) in ether (1000 ml). When the mixture had warmed to RT., water was added, the layers separated, and the aqueous layer was extracted with ether. Unreacted limonene was recovered from the ethereal phase, while the aqueous phase was acidified with 10% aqueous HCl-solution, extracted three times with ether, dried and evaporated to yield the crude acid (44 g). A solution of this in methanol (700 ml) containing concentrated sulfuric acid (7 ml) was refluxed for 3 h and poured into water. Usual work-up and evaporation of the solvent gave crude β,γ-unsaturated ester (~40 g). Isomerization of the double bond was carried out by refluxing the crude ester with sodium methoxide (36 g) in dry methanol (750 ml) for 1 h. Again, the reaction mixture was worked up the usual way to give 24 g of a brownish residue, which contained the (*E*)- and (*Z*)-esters in the ratio 82:18. Isolation of these isomers was carried out as described above. The overall yield based on butyllithium was 16%.

Methyl (E)-3-(4-methyl-3-cyclohexenyl)-2-butenoate (**5**). – $[\alpha]_D^{20}=+84.8°$ from (+)-(*R*)-limonene ($[\alpha]_D^{20}=+116°$); $[\alpha]_D^{20}=-65.7°$ from (−)-(*S*)-limonene ($[\alpha]_D^{20}=-89.4°$). – IR.: max. at 3040*w*, 3010*m*, 1715*s*, 1641*s*, 1225*s*, 1203*s* and 1143*s* cm^{-1}. – ^{13}C-NMR.: 17.2, 23.4 and 50.7 (3*qa*, 3 CH_3); 27.4 and 2×30.3 (3*t*, C(5), C(3), C(6)); 44.3 (*d*, C(4)); 114 and 120 (2*s*, C(9), C(2)); 133.8 and 164.2 (2*s*, C(1), C(8)) and 167.5 ppm (*s*, C(11)). – MS.: 194 (17, M^+), 162 (22), 135 (30), 125 (39), 111 (33), 101 (66), 94 (78), 68 (100), 67 (56) and 41 (42).

Methyl (Z)-3-(4-methyl-3-cyclohexenyl)-2-butenoate (**6**). – $[\alpha]_D^{20}=-25.2°$ from (+)-(*R*)-limonene ($[\alpha]_D^{20}=+116°$); $[\alpha]_D^{20}=+14.8°$ from (−)-(*S*)-limonene ($[\alpha]_D^{20}=-89.4°$). – IR.: max. at 3040*w*, 3010*m*, 1715*s*, 1635*s*, 1230*s*, 1200*s* and 1150*s* cm^{-1}. – ^{13}C-NMR.: 20.5, 23.5 and 50.7 (3*qa*, 3 CH_3), 27.3, 29.3 and 30.3 (3*t*, C(5), C(3), C(6)); 36.1 (*d*, C(4)); 115.7 and 120.3 (2*d*, C(9), C(2)); 133.4 and 164.0 (2*s*, C(1), C(8)) and 166.2 ppm (*s*, C(11)). – MS.: 194 (90, M^+), 162 (85), 147 (94), 125 (56), 95 (55), 94 (100), 79 (60), 68 (86), 67 (68) and 41 (75).

Reduction of the esters 5 and 6 with lithium aluminium hydride (LAH). – The ester **5** or **6** (4.0 g; 21 mmol) in dry ether (10 ml) was added dropwise to a suspension of LAH (0.4 g; 11 mmol) in dry ethyl ether (10 ml). The mixture was refluxed for 4 h and cooled. The excess LAH was destroyed by careful addition of water and the white precipitate was filtered off. The filtrate was dried (Na_2SO_4) and the solvent evaporated. Distillation of the colorless residue (bulb. b.p. 100–110°/0.1 Torr) gave the alcohol **7** or **8** in 80% yield.

(E)-3-(4-Methyl-3-cyclohexenyl)but-2-en-1-ol (**7**). – (*R*)-configurated: $[\alpha]_D^{20}=+84.8°$; (*S*)-configurated: $[\alpha]_D^{20}=-65.7°$. – IR.: max. at 3340*s* br., 3040*w*, 3010*m*, 1660*m*, 995*s*, 795*m*, 785*m* and 772*w* cm^{-1}. – ^{13}C-NMR.: 14.5 and 23.4 (2*qa*, 2 CH_3), 27.9, 2×30.7 and 59.3 (4*t*, C(5), C(3) and C(6), C(11)); 42.8 (*d*, C(4)); 120.7 and 122.3 (2*d*, C(2), C(9)); 133.7 and 143.3 ppm (2*s*, C(1), C(8)). – MS.: 166 (11, M^+), 148 (28), 133 (19), 107 (25), 93 (66), 83 (52), 69 (100), 55 (44), 43 (42) and 41 (61).

(Z)-3-(4-Methyl-3-cyclohexenyl)but-2-en-1-ol (**8**). – (*R*)-configurated: $[\alpha]_D^{20} = +26.5°$; (*S*)-configurated: $[\alpha]_D^{20} = -21.5°$. – IR.: max. at 3340*s* br., 3035*w*, 3000*m*, 1652*m*, 1005*s*, 795*m* and 780*m* cm^{-1}. – ^{13}C-NMR.: 19.3 and 23.5 (2*qa*, 2 CH_3); 27.7, 30.1, 30.5 and 58.5 (4*t*, C(5), C(3) and C(6), C(11)); 35.8 (*d*, C(4)); 120.6 and 124.1 (2*d*, C(2), C(9)); 133.9 and 144.0 ppm (2*s*, C(1), C(8)). – MS.: 166 (4, M^+), 148 (74), 133 (68), 119 (16), 106 (42), 93 (68), 83 (60), 69 (100), 55 (55) and 41 (67).

Treatment of the alcohols 7 and 8 with phosphorous tribromide. – A mixture of the alcohol **7** or **8** (2.8 g; 16 mmol) and PBr_3 (1.51 g; 5.5 mmol) in ether (60 ml) was refluxed 3 h in the dark. The solution was poured onto ice/water and extracted with ether. The organic phase was washed twice with 5% aqueous $NaHCO_3$-solution, H_2O and sat. NaCl-solution. Evaporation of the solvent and distillation of the residue *in vacuo* (bulb: b.p. 80°/0.2 Torr) gave the bromide **9** or **10** (3.1 g; 13.5 mmol) in 84% yield.

(E)-3-(4-Methyl-3-cyclohexenyl)but-2-enyl bromide (**9**). – (*R*)-configurated: $[\alpha]_D^{20} = +43°$; (*S*)-configurated: $[\alpha]_D^{20} = -47.9°$. – IR.: max. at 3040*w*, 3010*m*, 1645*m*, 1199*s* and 580*s* cm^{-1}. – ^{13}C-NMR.: 14.2 and 23.4 (2*qa*, 2 CH_3); 27.5, 29.5 and 2×30.4 (4*t*, C(5), C(11), C(3), C(6)); 42.8 (*d*, C(4)); 119.3 and 120.3 (2*d*, C(2), C(9)); 133.6 and 147.6 ppm (2*s*, C(1), C(8)). – MS.: 230 and 228 (0.4, M^+, 2 Br), 148 (96), 133 (78), 119 (63), 105 (91), 91 (95), 79 (100), 67 (29), 55 (34) and 41 (43).

(Z)-3-(4-Methyl-3-cyclohexenyl)but-2-enyl bromide (**10**). – (*R*)-configurated: $[\alpha]_D^{20} = +12.1°$; (*S*)-configurated: $[\alpha]_D^{20} = -10.6°$. – IR.: max. at 3030*w*, 3000*m*, 1635*m*, 1196*s* and 542*s* cm^{-1}. – ^{13}C-NMR.: 19.5 and 23.4 (2*qa*, 2 CH_3); 27.2, 28.5, 29.4 and 30.4 (4*t*, C(5), C(11), C(3), C(6)); 35.4 (*d*, C(4)); 120.4 and 120.9 (2*d*, C(2), C(9)); 133.9 and 140 ppm (2*s*, C(1), C(8)). – MS.: 230 and 228 (2, M^+, 2 Br), 149 (53), 133 (35), 119 (33), 105 (59), 93 (77), 79 (100), 67 (41), 55 (30), 41 (59).

(*E*)- and (*Z*)-α-Bisabolenes (1 and 2). – 2-Methyl-1-propenyl bromide (6.0 g; 44.5 mmol) in dry ether (10 ml) was added dropwise under argon to a suspension of clean lithium (0.61 g; 87 mmol) in dry ether (200 ml) at RT. The reaction started slowly and the solvent refluxed gently. After complete solution of the lithium, the mixture was cooled to −10° and added slowly to a cold suspension of cuprous iodide (4.2 g; 22 mmol) in ether (50 ml). A yellow precipitate appeared first, but dissolved completely in the dark-red solution after a few minutes. Stirring was continued for 0.5 h and the bromide **9** or **10** (2.0 g; 8.7 mmol) in ether (10 ml) was added rapidly. The mixture was stirred at −10° overnight, poured into ice-cold 10% chlorhydric acid (300 ml) and filtered through *Celite*. The organic phase was separated and the aqueous phase was extracted three times with ether. The combined ethereal phases were washed with water and sat. NaCl-solution, dried and the solvent evaporated. The yellowish residue (2.5 g) was chromatographed over silica (100 g) in hexane and distilled under reduced pressure (bulb: b.p. 90°/0.1 Torr) to give α-bisabolene **1** or **2** (1.24 g; 6 mmol; 70%).

(E)-α-Bisabolene (**1**). – (*R*)-configurated: $[\alpha]_D^{20} = +54.3°$; (*S*)-configurated: $[\alpha]_D^{20} = -38.9°$. – MS.: 204 (34, M^+), 189 (7), 175 (1), 161 (7), 148 (4), 136 (12), 121 (36), 119 (36), 109 (34), 93 (100), 80 (32), 69 (21), 59 (21), 55 (19), 41 (36).

(Z)-α-Bisabolene (**2**). – (*R*)-configurated: $[\alpha]_D^{20} = -12°$; (*S*)-configurated: $[\alpha]_D^{20} = +8.0°$. – MS.: 204 (52, M^+), 189 (9), 175 (1), 161 (12), 148 (11), 133 (19), 121 (33), 119 (28), 109 (38), 93 (100), 79 (27), 67 (24), 55 (20), 41 (41).

(*E*)- and (*Z*)-α-Bisabolenes 1 and 2 by the *Wittig* reaction. – 1.5N Butyllithium (14 ml; 21 mmol) in hexane was added to a suspension of triphenyl(4-methyl-3-pentenyl)phosphonium iodide [22] (7.5 g; 16 mmol) in dry THF (100 ml) under argon at RT. The resulting red solution was stirred for 4 h and cooled to +10°. The methyl ketone **3** (2.4 g; 17 mmol) in THF (10 ml) was added dropwise and the mixture was stirred overnight at RT. Addition of cold water and usual work-up gave a yellowish oil, which was distilled in a bulb apparatus. A fraction containing 93% of (*Z*)-α-bisabolene (**2**) and 5% of (*E*)-α-bisabolene (**1**) (0.85 g; 4.1 mmol; 25%) distilled at 95° (0.15 mm).

(±)-(*E*)- and (*Z*)-12,13-Dihydro-α-bisabolenes (13 and 14). – The *Wittig* reaction was carried out as described above, starting from the methyl ketone **3** (0.6 g; 4.4 mmol) and triphenyl(4-methylpentyl)-phosphonium bromide (1.75 g; 4.1 mmol; m.p. 197°). The resulting crude mixture (0.3 g) contained the 2 isomers **13** and **14** in the ratio 23:77, together with several decomposition products. Compounds **13** and **14** were separated by GC. on SE-30 (20% on chromosorb W, 2.5 m, 180°).

(±)-*(E)-12,13-Dihydro-α-bisabolene* (**13** = 12,13-dihydroderivative of **1**). – ^{1}H-NMR.: 0.87 (*d*, ^3J = 6.5 Hz, 6 H); 1.20 (*qa*, ^3J = 7 Hz, 2 H); 1.40–1.75 (br. *m*, 3 H); 1.57 and 1.63 (2br. *s*, 2×3 H); 1.97 (br. *m*, 7 H); 5.14 (*t*, ^3J = 7 Hz, 1 H) and 5.40 ppm (br. *s*, 1 H).

(±)-*(Z)-12,13-Dihydro-α-bisabolene* (**14** = 12,13-dihydroderivative of **2**). – ^{1}H-NMR.: 0.87 (*d*, ^3J = 6.5 Hz, 6 H); 1.20 (*qa*, ^3J = 7 Hz, 2 H); 1.46–1.72 (br. *m*, 2 H); 1.60 and 1.66 (2br. *s*, 2×3 H); 1.80 (*m*, 1 H); 1.90–2.18 (br. *m*, 6 H); 2.63 (*t*×*t*, ^3J = 5 Hz and 10 Hz, 1 H); 5.11 (*t*, ^3J = 7 Hz, 1 H) and 5.42 ppm (br. *s*, 1 H).

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