260. A Convergent Synthesis of (±)-α- and β-Himachalenes[1])

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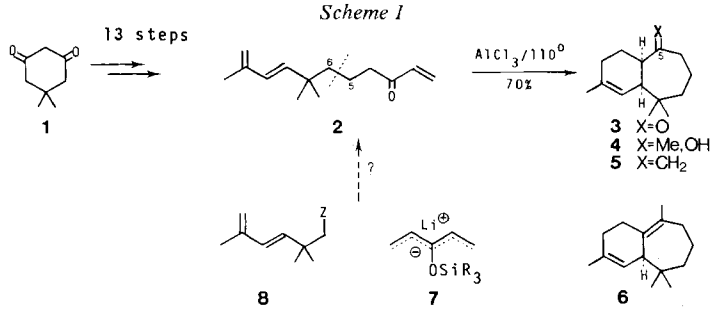
Summary

(±)-α- and β-Himachalene, **5** and **6**, have been synthesized in a convergent manner from 3,3-dimethylacrolein (**9**), the ester enolate **10** and the silyloxypentadienyllithium **7**. The key steps are the regioselective γ-addition of the dienal **13** to **7** and the intramolecular *Diels-Alder* addition **15** → **16**. Hydrogenolysis of the diethylphosphate group and functionalization at C(5) completed the synthesis of **5** and **6**.

Introduction. – The isolation of α- and β-himachalene, **5** and **6**, from the essential oil of Himalayan deodar *Cedrus deodora* was first reported by *Sukh Dev et al.* [1] and their structures have been established on the basis of chemical and spectroscopic evidence [2]. Of the three syntheses so far accomplished [3–5] the approach of *Wenkert & Naemura* [3] appeared particularly interesting *(Scheme 1)*. In the crucial step a *Lewis*-acid mediated intramolecular *Diels-Alder* addition[2]) of the trienone **2** furnished directly the octahydrobenzocycloheptenone **3**, which on successive treatment with methyllithium and $POCl_3$/pyridine was converted to **5** and **6**. However, the elegance of this bisannelation is impaired by the lengthy and low-yielding construction of the cycloaddition precursor **2**. We intended to replace this

Scheme 1



[1]) Presented by one of us *(W.O.)* at the 6th International Symposium on Synthesis in Organic Chemistry, Cambridge (England), July 1979.

[2]) Reviews: [6].

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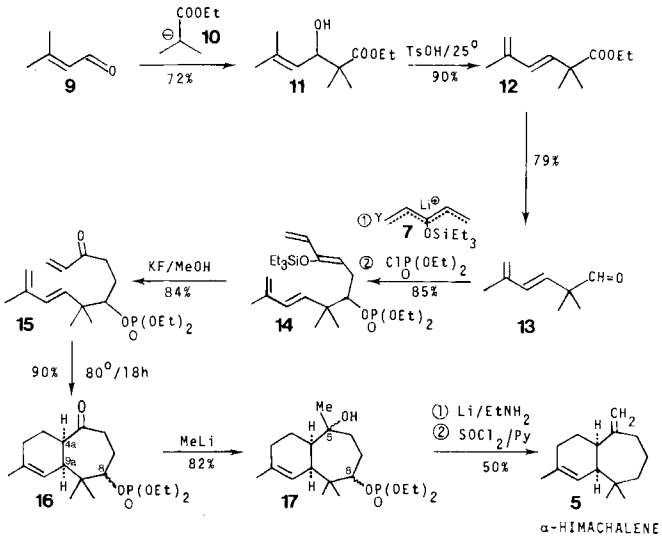
multistep, linear approach to **2** by a short, convergent route utilising the C_5-synthon **7** as an equivalent of the hypothetical homoenolate of ethyl vinyl ketone. According to our previous work [7], regioselective γ-substitution of **7** by an electrophile **8** was envisaged to afford **2** by C(5), C(6)-bond formation.

Preparation of acyclic trienone 15 *(Scheme 2).* – The nine C-atoms of the electrophile **8** were rapidly assembled by 1,2-addition of the ester enolate **10** (ethyl isobutyrate deprotonated with lithium diisopropylamide) to 3,3-dimethylacrolein (**9**) in THF at $-78°$ to give the allylic alcohol **11** (72%). Subsequent acid-catalyzed dehydration smoothly afforded the *trans*-dienyl ester **12** (90%) whose reduction with $LiAlH_4$ furnished alcohol **8**, Z = OH (96%). Despite numerous attempts **8**, Z = OH, could not be converted to the halides **8**, Z = Br, I. This lack of reactivity is probably due to the neopentyl-type steric congestion which even obstructed substitution of the tosylate **8**, Z = OTs, by iodide ion and, less unexpectedly, by the pentadienyllithium **7**.

Scheme 2



To by-pass this problem, as well as to profit from the known high γ-regioselectivity of the addition of aldehydes to **7** [7] the alcohol **8**, Z = OH was oxidized with pyridinium chlorochromate at 25° [8] to afford the dienal **13** (82%). Indeed, slow addition of **13** into a freshly prepared solution of **7** (1 mol-equiv.) in THF at $-78°$ followed by quenching of the reaction mixture with diethylphosphorochloridate (1.2 mol-equiv.) in hexamethylphosphotriamide selectively furnished the tetraenyl phosphate **14** (85%). This *in situ* trapping of the alkoxide initially formed by the addition of **13** to **7** serves a dual purpose: 1) to block the alcohol function which otherwise interferes with the *Diels-Alder* reaction, and 2) to use a protecting group which ultimately permits a facile hydrogenolysis of the C,O-bond [9]. Finally, cleavage of the silylenol ether with KF in methanol at 0° gave **15** (85%).

Conversion of trienone 15 into α- and β-himachalenes (5 and 6). – The stage was now set for the crucial [4+2]-cycloaddition. Heating a solution of **15** in benzene under reflux for 18 h furnished the expected octahydrobenzocycloheptenone **16** (2:1 mixture of C(8)-epimers) in 90% yield. Thus the non-catalyzed thermal process **15** → **16** compares favourably in terms of efficiency and smoothness with the reported *Lewis*-acid mediated cyclization **2** → **3**. The *cis*-fusion of **16**[3]), established by its ultimate conversion to α-himachalene, indicates a kinetically-controlled *endo*-selectivity for the cycloaddition. Treatment of **16** with methyllithium in ether at −30° gave tertiary alcohol **17** (epimeric mixture at C(5) and C(8), 82%). Reductive removal of the diethylphosphate group[4]) with a solution of lithium (5 mol-equiv.) in THF/ethylamine/*t*-butyl alcohol (1 mol-equiv.) at −10° afforded predominantly a single himachalol stereoisomer (**4**)[5]) which was directly dehydrated with $POCl_3$ in pyridine at reflux to give mainly α-himachalene (**5**, 44% from **17**) together with minor amounts of β-himachalene (**6**, 6% from **17**). The synthetic (±)-**5** was identified by comparison with natural α-himachalene. Since α-himachalene (**5**) is readily isomerized to β-himachalene (**6**) [4] our approach also constitutes a formal synthesis of the latter sesquiterpene. In summary, this work illustrates once more the usefulness of the silyloxydienyllithium **7** for the efficient application of intramolecular *Diels-Alder* reactions in synthesis[6]).

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Experimental Part

General. The normality of the commercially available solutions of *s*-BuLi, *n*-BuLi and MeLi *(Fluka)* was determined immediately prior to use by *Gilman*'s double titration method [11]. Solvents and reagents were dried and purified prior to their use. Work-up refers to the general procedure of washing an organic phase with H_2O, sat. aq. $NaHCO_3$-solution, and then sat. aq. NaCl-solution, followed by drying (Na_2SO_4) filtration, and removal of solvent by distillation *in vacuo*. GC. was carried out on a *Carlo Erba* SS455 with a 1 m column of 5% SE 30 on chromosorb WAW 80/160 at a pressure of 1 kg/cm^2, retention time in min. For TLC. glass plates coated with *Kieselgel* 60F-254 were eluted with the solvent mixtures mentioned in the text and viewed under UV. light and developed with iodine. Column chromatography was carried out using SiO_2 [*Merck* (Art. 7734) *Kieselgel* 60, Korngrösse 0.063 → 0.2 mm, 70–230 mesh ASTM]. Melting points (m.p.) were determined on a *Kofler* hot stage using polarized light and are uncorrected. IR. spectra: in CCl_4 unless otherwise specified, $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H-NMR. spectra: at 100 MHz in $CDCl_3$, standard tetramethylsilane δ(ppm) = 0; abbreviations: *s* singlet, *d* doublet, *t* triplet, *qa* quadruplet, *m* multiplet, *J* spin-spin coupling constant (Hz). Mass spectra (MS.): fragments are given as *m/z* (rel.-%).

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[3]) Obtained as a 1:2-mixture of C(8)-epimers. Previous work implies the *cis*-octahydrobenzocycloheptenone **3** to be less stable than its *trans*-fused epimer [2c, d].

[4]) Treatment of the separated major and minor cycloadducts **16** with methyllithium gave in each case a different tertiary alcohol **17** (epimeric at C(8)), in yields of 83 and 92% respectively. Whereas hydrogenolysis of the former epimer afforded **4** in 78% yield, under identical conditions the latter epimer gave only a complex mixture of unidentified polar products.

[5]) According to IR. evidence **4** derived from **17B** is the C(5)-epimer of natural himachalol [10].

[6]) For other examples see [7], ref. [19] [25–27].

Preparation of the acyclic trienone 15 *(Scheme 2). – Ethyl 3-hydroxy-2,2,5-trimethyl-4-hexenoate* (**11**). A solution of ethyl isobutyrate (6.96 g, 60 mmol) in THF (10 ml) was added dropwise to a stirred solution of lithium diisopropylamide (60 mmol, freshly prepared from BuLi and diisopropylamine) in THF (200 ml) at −78°. After 1 h at −78° 3-methyl-2-butenal [12] (5.04 g, 60 mmol) was added dropwise and, after a further 1 h at −78° the reaction mixture was poured into sat. aq. NH_4Cl-solution. Extraction (ether), work-up and distillation gave the hydroxyester **11** (8.68 g, 72%) as a colourless oil, b.p. 117–118°/12 Torr; Rf 0.40 (toluene/EtOAc 3:1). – IR.: 3600, 3510 (br.), 2980, 1710, 1132, 1027. – ^{1}H-NMR.: 1.16 (*s*, 6 H); 1.28 (*t*, *J* = 7, 3 H); 1.72 (*d*, *J* = 1.5, 3 H); 1.76 (*d*, *J* = 1.5, 3 H); 2.80 (br. *s*, disappears after exchange with D_2O, 1 H); 4.18 (*qa*, *J* = 7, 2 H); 4.45 (br. *d*, *J* = 7, 1 H); 5.22 (*d*×*m*, *J* = 7, 1 H). – MS.: (M^+ not observed), 182 (13), 109 (82), 84 (100), 83 (50), 70 (62), 69 (42).

*Ethyl (*E*)-2,2,5-trimethyl-3,5-hexadienoate* (**12**). A mixture of the hydroxyester **11** (2.0 g, 10 mmol), *p*-toluenesulfonic acid (150 mg) and molecular sieves (type 3 Å) in dry CH_2Cl_2 (200 ml) was stirred at 25° under Ar for 1 h. Work-up and distillation gave the dienoate **12** as a colourless oil (1.64 g, 90%), b.p. 85–86°/12 Torr; Rf 0.42 (toluene); GC. (132°): 5.41. – IR.: 2975, 1730, 1472, 1390, 1253, 1142, 972, 892. – ^{1}H-NMR.: 1.27 (*t*, *J* = 7, 3 H); 1.36 (*s*, 6 H); 1.87 (*s*, 3 H); 4.17 (*qa*, *J* = 7, 2 H); 4.99 (*s*, 2 H); 5.88 (*d*, *J* = 16, 1 H); 6.23 (*d*, *J* = 16, 1 H). – MS.: 182 ($C_{11}H_{18}O_2^+$, 11), 167 (4), 109 (100), 81 (14), 67 (43), 55 (16).

*(*E*)-2,2,5-Trimethyl-3,5-hexadienol* (**8**, Z = OH, *Scheme 1*). A solution of the ester **12** (4.2 g, 23 mmol) in ether (20 ml) was added dropwise to a stirred slurry of $LiAlH_4$ (874 mg, 23 mmol) in ether (80 ml) at 0°. After 2 h acidification with 1N aq. HCl, work-up and distillation afforded the dienol **8**, Z = OH (oil, 3.1 g, 96%), b.p. 82–83°/12 Torr; Rf 0.27 (toluene/EtOAc 9:1). – IR.: 3630, 2960, 1610, 1053, 980, 892. – ^{1}H-NMR.: 1.05 (*s*, 6 H); 1.83 (br. *s*, disappears after exchange with D_2O, 1 H); 1.84 (*s*, 3 H); 3.36 (*s*, 2 H); 4.94 (*s*, 2 H); 5.62 (*d*, *J* = 16, 1 H); 6.18 (*d*, *J* = 16, 1 H). – MS.: 140 ($C_9H_{16}O^+$, 18), 110 (12), 109 (100), 84 (14), 81 (17), 67 (57).

*Preparation and attempted substitution of (*E*)-2,2,5-trimethyl-3,5-hexadienyl* p-*toluenesulfonate* (**8**, Z = OTs). A solution of the dienol **8**, Z = OH (140 mg, 1 mmol) in pyridine (1 ml) was added dropwise to a stirred solution of *p*-toluenesulfonyl chloride (228 mg, 1.2 mmol) in pyridine (2 ml) at 0°. The reaction mixture was stirred at 0° for 1 h, then at +25° during 2 days and finally was poured into cold water. Work-up gave the tosylate **8**, Z = OTs (viscous oil, 252 mg, 80%); Rf 0.39 (toluene). – IR.: 2970, 1380, 1182, 1102, 970, 672. – ^{1}H-NMR.: 1.05 (*s*, 6 H); 1.77 (*s*, 3 H); 2.44 (*s*, 3 H); 3.77 (*s*, 2 H); 4.92 (*s*, 2 H); 5.50 (*d*, *J* = 16, 1 H); 6.09 (*d*, *J* = 16, 1 H); 7.34 (*d*, *J* = 8.5, 2 H); 7.79 (*d*, *J* = 8.5, 2 H). – MS.: (M^+ not observed), 244 (36), 229 (38), 201 (48), 197 (55), 173 (100), 159 (52). The tosylate **8**, Z = OTs was heated with 3 to 7 mol-equiv. of NaI in DMSO at 70° for 1 h or in acetone under reflux for 4.5 h to give an intractable mixture. Under the same condition the analogous mesylate **8**, Z = OMs remained unchanged. Stirring the tosylate **8**, Z = OTs with 3 mol-equiv. of NaI in acetone at 25° for 2 days or with 1 mol-equiv. of the pentadienyllithium **7** [7] in THF at −78° for 30 min gave after work-up the unchanged tosylate **8** and no isolable substitution product.

*(*E*)-2,2,5-Trimethyl-3,5-hexadienal* (**13**). A solution of the dienol **8**, Z = OH (3.1 g, 22.1 mmol) in dry CH_2Cl_2 (10 ml) was added quickly to a mechanically-stirred slurry of pyridinium chlorochromate (9.1 g, 45 mmol) in dry CH_2Cl_2 (500 ml) at +25°. The mixture was stirred at 25° for 2.5 h, then diluted with ether (1 l) and filtered through *Celite*. Washing of the filtrate successively with aq. 1N NaOH, H_2O, aq. 1N HCl, H_2O, sat. aq. $NaHCO_3$- and sat. aq. NaCl-solution followed by work-up and distillation gave the dienal **13** as a light-yellow oil (2.5 g, 82%); b.p. 68–71°/12 Torr; Rf 0.67 (toluene/EtOAc 3:1). – IR.: 2970, 2800, 1730, 972, 900. – ^{1}H-NMR.: 1.24 (*s*, 6 H); 1.85 (*s*, 3 H); 5.01 (*s*, 2 H); 5.60 (*d*, *J* = 16, 1 H); 6.24 (*d*, *J* = 16, 1 H); 9.40 (*s*, 1 H). – MS.: 138 ($C_9H_{14}O^+$, 17), 109 (100), 97 (17), 81 (20), 67 (66), 55 (31).

*Diethyl (3*Z*,8*E*)-6-(3-triethylsilyloxy-7,7,10-trimethyl-1,3,8,10-undecatetraenyl)phosphate* (**14**). A solution of the dienal **13** (138 mg, 1 mmol) in THF (0.5 ml) was added dropwise to a freshly prepared solution of **7** [7] (1 mmol) in THF (4 ml) at −78°. After 5 min a solution of diethylphosphorochloridate (207 mg, 1.2 mmol) in HMPA (1 ml) was added slowly at −78°. The reaction mixture was kept at −78° for 1 h and then was poured into sat. aq. NH_4Cl-solution. Work-up and rapid chromatography (CH_2Cl_2/EtOAc 4:1) afforded the tetraene **14** (406 mg, 85%) as a colourless viscous oil, Rf 0.10 (CH_2Cl_2). – IR.: 2960, 2880, 1646, 1606, 1370, 1262, 1000, 908, 890. – ^{1}H-NMR.: 0.5–1.2 (15 H); 1.11 (*s*, 6 H); 1.29 (*t*×*m*, *J* = 7, 6 H); 1.83 (*m*, 3 H); 2.44 (*m*, 2 H); 3.9–4.4 (5 H); 4.80–5.12 (4 H);

5.27 (*d*×*m*, *J*=17, 1H); 5.70 (*d*, *J*=16, 1H); 6.13 (*d*, *J*=16, 1H); 6.24 (*d*×*d*, *J*=17 and 10, 1H).– MS.: (M^+ not observed), 318 (1), 249 (9), 183 (6), 155 (12), 103 (100), 75 (91).

(E)-6-Diethoxyphosphoryloxy-7,7,10-trimethyl-1,8,10-undecatrien-3-one (**15**). KF (29 mg, 0.5 mmol) was added portionwise to a stirred solution of the silyl ether **14** (118 mg, 0.25 mmol) in methanol (4 ml) at 0°. The reaction mixture was kept at 0–5° for 1 h and then was poured into water. Work-up and fast chromatography (EtOAc) gave the trienone **15** (75 mg, 84%) as an oil, Rf 0.58 (EtOAc). – IR.: 2970, 1700, 1685, 1270, 1000, 885. – ^{1}H-NMR.: 1.10 (*s*, 3H); 1.12 (*s*, 3H); 1.31 (*t*, *J*=7, 6H); 1.5–2.1 (2H); 1.84 (*s*, 3H); 2.87 (*m*, 2H); 4.06 (*qa*, *J*=7, 4H); 4.21 (*m*, 1H); 4.93 (*s*, 2H); 5.72 (*d*, *J*=16, 1H); 5.73–6.40 (3H); 6.15 (*d*, *J*=16, 1H). – MS.: (M^+ not observed), 204 (20), 189 (9), 155 (100), 127 (54), 99 (49), 94 (31).

Conversion of the trienone 15 into α- and β-himachalenes *(Scheme 2).* – *(4aR*,9aS*)-8-Diethoxyphosphoryloxy-4,4a,5,6,7,8,9,9a-octahydro-2,9,9-trimethyl-3H-benzocyclohepten-5-ones* (**16**). A solution of the trienone **15** (35.8 mg, 0.1 mmol) in benzene (5 ml) was heated under reflux for 18 h. Chromatography of the evaporated solution (EtOAc) gave the less polar C(8)-isomer of **16** (isomer A, 10 mg, 28%), Rf 0.51 (EtOAc). – IR.: 2960, 2920, 1700, 1450, 1395, 1370, 1260, 1000. – ^{1}H-NMR.: 0.97 (*s*, 3H); 1.20 (*s*, 3H); 1.37 (*t*×*m*, *J*=7, 6H); 1.72 (br. *s*, 3H); 1.60–2.9 (10H); 3.90–4.35 (4H); 4.53 (*m*, 1H); 5.65 (br. *s*, 1H). – MS.: 358 ($C_{18}H_{31}O_5P^+$, 4), 279 (1), 204 (27), 189 (8), 155 (100), 127 (15). Further elution furnished the more polar C(8)-isomer of **16** (isomer B, 22 mg, 62%), Rf 0.40 (EtOAc). – IR.: 2975, 2925, 2910, 1700, 1452, 1400, 1370, 1260, 1000. – ^{1}H-NMR.: 1.00 (*s*, 3H); 1.20 (*s*, 3H); 1.34 (*m*, 6H); 1.6–3.1 (10H); 1.70 (br. *s*, 3H); 3.9–4.5 (4H); 4.30 (*m*, 1H); 5.81 (br. *s*, 1H). – MS.: 358 ($C_{18}H_{31}O_5P^+$, 0.5), 204 (19), 189 (8), 155 (100), 147 (10), 127 (22).

(4aR,9aS*)-8-Diethoxyphosphoryloxy-4,4a,5,6,7,8,9,9a-octahydro-2,5,9,9-tetramethyl-3H-benzocyclohepten-5-ols* (**17**). – a) *Isomer* **17A** *from the minor isomer* **16A**. A solution of MeLi in ether (0.3 mmol) was added slowly to a stirred solution of **16A** (89.5 mg, 0.25 mmol) in ether (5 ml) at −30°. After 1 h at −30° the reaction mixture was poured into sat. aq. NaCl-solution. Work-up and chromatography (EtOAc) gave the crystalline alcohol **17A** (78 mg, 83%), m.p. 120–122° (hexane); Rf 0.36 (EtOAc). – IR.: 3420, 2960, 2920, 2870, 1445, 1392, 1370, 1260, 1000. – ^{1}H-NMR.: 1.08 (*s*, 6H); 1.28 (*s*, 3H); 1.36 (*t*, *J*=7, 6H); 1.5–2.4 (9H); 1.60 (br. *s*, disappears after exchange with D_2O, 1H); 1.71 (*s*, 3H); 2.61 (br. *s*, 1H); 3.95–4.45 (5H); 5.43 (*m*, 1H). – MS.: (M^+ not observed), 218 (47), 200 (42), 185 (16), 163 (18), 159 (25), 155 (100).

b) *Isomer* **17B** *from the major isomer* **16B**. Isomer **16B** (89.5 mg, 0.25 mmol) was treated with MeLi as its isomer A to give **17B** (oil, 86 mg, 92%), Rf 0.36 (EtOAc). – IR.: 3420, 2970, 2925, 2910, 1392, 1370, 1260, 1165, 1000. – ^{1}H-NMR.: 1.04 (*s*, 6H); 1.24 (*s*, 3H); 1.32 (*t*, *J*=7, 6H); 1.5–2.5 (11H); 1.68 (*s*, 3H); 3.9–4.4 (5H); 5.50 (*m*, 1H). – MS.: 374 ($C_{19}H_{35}O_5P^+$, 4), 358 (2.5), 281 (2.5), 220 (9), 202 (17), 155 (100).

(4aR,9aS*)-4,4a,5,6,7,8,9,9a-Octahydro-2,9,9-trimethyl-3H-benzocyclohepten-5-ol* (**18**). A solution of the major isomer **17B** (93.5 mg, 0.25 mmol) and *t*-butyl alcohol (74 mg, 1.0 mmol) in dry THF (3 ml) was added dropwise with stirring to a freshly prepared, deep-blue solution of lithium (35 mg, 5 mmol) in ethylamine (4 ml) at −10° under Ar. After 15 min at −10° the reaction mixture was poured into water. Work-up and rapid chromatography (CH_2Cl_2) gave the crystalline alcohol **4**[3]) (43 mg, 78%), m.p. 65–66°; Rf 0.32 (CH_2Cl_2); GC. (180°): 10.06. – IR.: 3615, 2960, 1450, 1375, 920. – ^{1}H-NMR.: 0.94 (*s*, 3H); 0.96 (*s*, 3H); 1.26 (*s*, 3H); 1.30–2.20 (13H); 1.68 (*s*, 3H); 5.54 (*m*, 1H). – MS.: (M^+ not observed), 204 (43), 189 (11), 161 (18), 121 (35), 119 (100), 109 (41). Under identical reaction conditions the minor isomer **17A** gave an intractable mixture.

(±)-α-Himachalene (**5**) *and (±)-β-himachalene* (**6**). $POCl_3$ (0.25 ml) was added dropwise to a stirred solution of the alcohol **18** (4.4 mg, 0.02 mmol) in pyridine (1 ml) at +25°. The mixture was heated under reflux for 2 h and then was poured into ice-water. Work-up and rapid chromatography (hexane) gave (±)-α-himachalene (**5**) together with a small amount of (±)-β-himachalene (**6**, 13% by GC.) (oil, 3.8 mg, 93%), Rf 0.74 (hexane); GC. (160°): 8.33 (82.5%), 9.86 (11%). – IR.: 2910, 2840, 1625, 1450, 885, 865. – ^{1}H-NMR.: 0.96 (*s*, 3H); 0.99 (*s*, 3H); 1.1–2.3 (11H); 1.68 (*m*, 3H); 2.83 (*m*, 1H); 4.75 (*m*, 2H); 5.50 (br. *s*, 1H). – MS.: 204 ($C_{15}H_{24}^+$, 100), 189 (71), 175 (14), 161 (71), 147 (28), 135 (50), 134 (70), 133 (65). The synthetic product **5** showed IR., ^{1}H-NMR., mass spectra and GC. behaviour (coinjection) identical to those of natural α-himachalene.

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