

Studies on Aromatic Sesquiterpenes. XII.¹⁾ Synthesis of (±)-*cis*-5-Hydroxycalamenene

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Synopsis. Starting from *o*-cresol, (±)-*cis*-5-hydroxycalamenene was synthesized through 4-isopropyl-5-methoxy-6-methyl-1-tetralone as a key intermediate and identified with the natural compound spectroscopically.

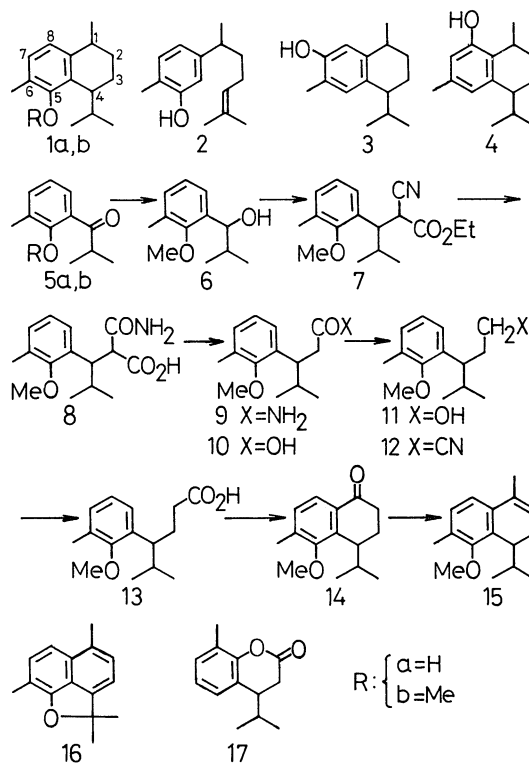
The new phenolic sesquiterpene 5-hydroxycalamenene was isolated, together with some sesquiterpene hydrocarbons and alcohols, from the essential oil of European liverwort *Bazzania tricrenata* and 5-hydroxy-4-isopropyl-1,6-dimethyl-1,2,3,4-tetrahydronaphthalene (5-hydroxycalamenene; 8-isopropyl-2,5-dimethyl-5,6,7,8-tetrahydro-1-naphthol) (**1a**) was proposed as the gross structure of this phenol on the basis of comprehensive spectral studies.²⁾ On the other hand, we reported that the acid-catalyzed cyclization of the phenolic sesquiterpene xanthorrhizol³⁾ (**2**) yields a mixture of the hydroxycalamenenes **1** and **3**, and that each of them is a diastereomer mixture mainly consisting of the trans isomer.⁴⁾ The ¹H NMR spectrum of the resulting trans isomer of **1a** was found to be apparently different from that of the natural product. While on acid-catalyzed cyclization of α -curcumene the resulting calamenene was mainly the trans isomer, catalytic hydrogenation of γ -calacorene (1,2-dihydrocadalene) oppositely gave the *cis* isomer as the major product.⁵⁾ We also reported that the calamenene derivatives and their related compounds having substituents such as methyl⁶⁾ or methoxyl^{7,8)} groups at C₅ and/or C₈ were obtained as homogeneous products from the corresponding 1,2- and 3,4-dihydronaphthalenes by catalytic hydrogenation, respectively. Furthermore, it was found that 8-hydroxycalamenene (**4**) derived from 1,2-dihydro-8-methoxycadalene by catalytic hydrogenation and demethylation has a *cis*-configuration.⁷⁾ Therefore, the synthetic approach using catalytic hydrogenation seems to be useful for the preparation of *cis*-5-hydroxycalamenene (**1a**).

In order to confirm the stereochemistry of the naturally occurring 5-hydroxycalamenene, the synthesis of (±)-*cis*-**1** from *o*-cresol through 3,4-dihydro-4-isopropyl-5-methoxy-6-methyl-1(2*H*)-naphthalenone (**14**) as a key intermediate has been carried out. The resulting product was a mixture of some components, though the synthesis of **1** through another intermediate was reported.⁹⁾

The methyl ether (**5b**) of 2'-hydroxy-3'-methylisobutyrophenone (**5a**) derived from *o*-tolyl isobutyrate¹⁰⁾ by the Fries rearrangement and methylation was reduced with NaBH₄ to alcohol **6**, which was then treated with hydriodic acid to give a thermally unstable iodide. The reaction of the iodide with ethyl cyanoacetate gave cyano ester **7**. Amic acid **8** obtained by alkaline hydrolysis of **7** was decarboxylated by heating to give amide **9**, which was hydrolyzed to 3-(2-

methoxy-3-methylphenyl)-4-methylpentanoic acid (**10**). The reduction of carboxylic acid **10** with LiAlH₄ gave 3-(2-methoxy-3-methylphenyl)-4-methyl-1-pentanol (**11**), from which, through its tosylate, 4-(2-methoxy-3-methylphenyl)-5-methylhexanenitrile (**12**) was prepared. The nitrile (**12**) was hydrolyzed to 4-(2-methoxy-3-methylphenyl)-5-methylhexanoic acid (**13**), which was converted to 3,4-dihydro-4-isopropyl-5-methoxy-6-methyl-1(2*H*)-naphthalenone (**14**) by cyclodehydration with POCl₃. An alcohol obtained from tetralone **14** by the Grignard reaction was dehydrated with formic acid to 3,4-dihydro-5-methoxycadalene (**15**). The catalytic hydrogenation of dihydronaphthalene **15** yielded (±)-5-methoxycalamenene (**1b**), whose NMR spectra (¹H and ¹³C) showed no signals of any known trans isomer.⁴⁾ This result unambiguously showed that the hydrogenation proceeded exclusively to *cis*-**1b**. The demethylation of **1b** with BBr₃ afforded (±)-*cis*-5-hydroxycalamenene (**1a**), whose ¹H NMR data were identical with those of the natural product isolated from the liverwort.²⁾

In order to confirm the gross structure, **1a** thus obtained was dehydrogenated by heating with 5% Pd-C to afford 2,2,5,8-tetramethyl-2*H*-naphtho[1,8-*bc*]furan (**16**), cadalene, and 3,4-dihydro-8-isopropyl-2,5-dimethyl-1(2*H*)-naphthalenone.¹¹⁾



Experimental

All melting and boiling points are uncorrected. IR spectra were measured on a Shimadzu Infrared Spectrometer IR-430, either as neat (liquids) or KBr disk (solids); the absorption is reported in cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a JEOL Spectrometer JNM-FX90Q (90 MHz for ^1H and 22.5 MHz for ^{13}C) for CDCl_3 solutions with tetramethylsilane as an internal standard; signals are reported in δ (ppm). The elemental analyses were carried out by a Yanagimoto CHN Corder MT-2. Gas chromatography was taken on a Shimadzu Gas Chromatograph GC-4C equipped with a stainless steel column (3 mm $\times$ 3 m) packed with Apiezon Grease L of 30% on Cellite 545, at 70 ml min^{-1} He and column temperature 260 $^\circ\text{C}$.

3-(2-Methoxy-3-methylphenyl)-4-methylpentanoic Acid (10). A mixture of *o*-tolyl isobutyrate¹⁰ (0.1 mol) and AlCl_3 (0.12 mol) in carbon disulfide (16 ml) was refluxed for 2 h with stirring. After removing the solvent, the residue was heated at 140 $^\circ\text{C}$ for 4 h and then decomposed with dil. HCl. The crude reaction product was steam-distilled to separate the volatile *o*-hydroxy ketone (**5a**) from its crystalline *p*-isomer.

2'-Hydroxy-3'-methylisobutyrophenone (**5a**): 44.9%, bp 135–137 $^\circ\text{C}/23$ mmHg (1 mmHg=133.322 Pa).

4'-Hydroxy-3'-methylisobutyrophenone: 44.4%, mp 123.0–124.0 $^\circ\text{C}$ (from methanol).

To a mixture of **5a** (0.1 mol) and K_2CO_3 (0.23 mol) in acetone (50 ml) was added dimethyl sulfate (0.2 mol) at room temperature, and the mixture was refluxed for 10 h with stirring. After removing the solvent, the residue was extracted with ether to give 2'-methoxy-3'-methylisobutyrophenone (**5b**) (93.2%), bp 124–125 $^\circ\text{C}/15$ mmHg.

To a solution of **5b** (30.0 g) in methanol (90 ml) was added NaBH_4 (4.4 g) at room temperature, and the mixture was refluxed for 2 h with stirring. After removing the solvent, the residue was extracted with benzene to give 1-(2-methoxy-3-methylphenyl)-2-methyl-1-propanol (**6**) (29.8 g, 98.3%), bp 132–133 $^\circ\text{C}/11$ mmHg. IR: 3450. ^1H NMR: 0.77 (3H, d, $J=7$ Hz, CH_3), 1.02 (3H, d, $J=7$ Hz, CH_3), 1.92 (1H, m, $J=7$ Hz, $>\text{CH}-$), 2.26 (3H, s, CH_3), 2.68 (1H, d, $J=5$ Hz, OH), 3.69 (3H, s, OCH_3), 4.57 (1H, dd, $J=7, 5$ Hz, $>\text{CH}-$), and 6.95–7.22 (3H, m).

A mixture of **6** (10.0 g) and 58% hydriodic acid (100 ml, $d=1.7$) was stirred for 1 h at room temperature. The reaction mixture was extracted with benzene to give 1-iodo-1-(2-methoxy-3-methylphenyl)-2-methylpropane (15.6 g, 99.4%), which was decomposed by distillation under reduced pressure. IR: 1460, 1250, 1205, and 1000. ^1H NMR: 0.80 (3H, d, $J=7$ Hz, CH_3), 1.27 (3H, d, $J=7$ Hz, CH_3), 2.2 (1H, m, $>\text{CH}-$), 2.27 (3H, s, CH_3), 3.79 (3H, s, OCH_3), 5.36 (1H, d, $J=10$ Hz, $>\text{CH}-\text{I}$), and 7.0–7.4 (3H, m).

A solution of the iodide (15.6 g) in *N,N*-dimethylformamide (50 ml) was added to a mixture of Na (1.4 g), ethyl cyanoacetate (8.7 g), and toluene (70 ml) at room temperature, and the mixture was stirred at 70 $^\circ\text{C}$ for 3 h. After being neutralized with acetic acid, the organic layer of the mixture gave an oily product (13.5 g) by removing the solvent. A portion of the resulting product was purified by passing through a SiO_2 column to give pure ethyl 2-cyano-3-(2-methoxy-3-methylphenyl)-4-methylpentanoate (**7**) as the sample for analysis, bp 139–141 $^\circ\text{C}/3$ mmHg. IR: 2250, and 1740. ^1H NMR: 0.82 (3H, d, $J=7$ Hz, CH_3), 1.03 and 1.14 (3H, d each, $J=7$ Hz, CH_3), 1.04 and 1.23 (3H, t each, $J=7$ Hz, CH_3), 2.2 (1H, m, $>\text{CH}-$), 2.28 and 2.31 (3H, s each, CH_3), 3.6 (1H, m, $>\text{CH}-$), 3.7 (1H, m, $>\text{CH}-$), 3.72 and 3.77 (3H, s each, OCH_3), 4.01 and 4.19 (2H, q each, $J=7$ Hz, CH_2), 7.1

(2H, m), and 7.3 (1H, m).

A mixture of crude **7** and 5% NaOH (240 g) was refluxed for 5 h with stirring. The mixture was washed with benzene to leave out oily impurity. The aqueous alkaline solution was acidified with HCl and extracted with benzene to give 2-carbamoyl-3-(2-methoxy-3-methylphenyl)-4-methylpentanoic acid (**8**) (5.4 g, 37.8%), microcrystals (from benzene), mp 121.0–123.5 $^\circ\text{C}$ (decomp). IR (Nujol): 3400, 3330, and 1710. Found: C, 65.05; H, 7.99; N, 4.27%. Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_4$: C, 64.49; H, 7.58; N, 5.01%.

The amic acid **8** (6.6 g) was decarboxylated by heating at 135 $^\circ\text{C}$ for 2 h to give 3-(2-methoxy-3-methylphenyl)-4-methylpentanamide (**9**) (5.5 g, 98.2%). IR: 3350, 3200, and 1660. ^1H NMR: 0.76 (3H, d, $J=7$ Hz, CH_3), 0.99 (3H, d, $J=7$ Hz, CH_3), 1.82 (1H, m, $J=7$ Hz, $>\text{CH}-$), 2.28 (3H, s, CH_3), 2.6 (2H, m, CH_2), 3.2 (1H, m, $>\text{CH}-$), 3.73 (3H, s, OCH_3), 6.0 (2H, broad, $-\text{NH}_2$), and 7.0 (3H, broad).

A solution of **9** (5.5 g) and 85% KOH (4.6 g) in ethanol (20 ml) was refluxed for 28 h. After removing the solvent from the reaction mixture, the residue was diluted with water and then washed with benzene. An alkaline solution was acidified with HCl and extracted with benzene to give 3-(2-methoxy-3-methylphenyl)-4-methylpentanoic acid (**10**) (5.0 g, 90.9%), prisms (from petroleum ether), mp 93.0–94.0 $^\circ\text{C}$. IR: 1705. ^1H NMR: 0.78 (3H, d, $J=7$ Hz, CH_3), 0.90 (3H, d, $J=7$ Hz, CH_3), 1.81 (1H, m, $J=7$ Hz, $>\text{CH}-$), 2.28 (3H, s, CH_3), 2.7 (2H, m, CH_2), 3.4 (1H, m, $>\text{CH}-$), 3.70 (3H, s, OCH_3), 6.89–7.03 (3H, m), and 11.04 (1H, broad, CO_2H). Found: C, 71.17; H, 8.80%. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$: C, 71.16; H, 8.53%.

The acidic hydrolysis of **8** was also investigated. A mixture of **8** (3.0 g), concd H_2SO_4 (6 ml), acetic acid (6 ml), and water (6 ml) was refluxed for 4 h with stirring. The reaction mixture was extracted with benzene. The extract was shaken with aqueous NaHCO_3 solution. The aqueous layer was acidified with HCl and extracted with benzene to give carboxylic acid **10** (0.6 g, 27.3%). The organic layer freed from **10** was evaporated to give 3,4-dihydro-4-isopropyl-8-methylcoumarin (**17**) (1.0 g, 40.0%). IR: 1770. ^1H NMR: 0.91 (3H, d, $J=7$ Hz, CH_3), 0.96 (3H, d, $J=7$ Hz, CH_3), 1.82 (1H, m, $J=7$ Hz, $>\text{CH}-$), 2.30 (3H, s, CH_3), 2.7 (3H, m, CH_2 and $>\text{CH}-$), and 7.0 (3H, m).

3,4-Dihydro-4-isopropyl-5-methoxy-6-methyl-1(2H)-naphthalenone (14). A solution of **10** (3.3 g) in ether (25 ml) was added to a suspension of LiAlH_4 (1.1 g) in ether (25 ml) at room temperature. The mixture was refluxed for 2 h and acidified with 10% H_2SO_4 under cooling. Removal of the solvent from the organic layer gave 3-(2-methoxy-3-methylphenyl)-4-methyl-1-pentanol (**11**) (2.9 g, 93.5%). IR: 3350. ^1H NMR: 0.78 (3H, d, $J=6$ Hz, CH_3), 1.07 (3H, d, $J=6$ Hz, CH_3), 2.0 (3H, m, CH_2 and $>\text{CH}-$), 2.30 (3H, s, CH_3), 2.43 (1H, broad, OH), 3.0 (2H, m, CH_2), 3.4 (1H, m, $>\text{CH}-$), 3.73 (3H, s, OCH_3), and 7.00 (3H, s).

A mixture of **11** (1.2 g), *p*-toluenesulfonyl chloride (1.6 g), and pyridine (5 ml) was stirred for 5 h under cooling in an ice bath. The reaction mixture was diluted with water and extracted with benzene to give the tosylate (1.9 g, 95.0%). IR: 1360, 1190, and 1175. ^1H NMR: 0.72 (3H, d, $J=7$ Hz, CH_3), 0.92 (3H, d, $J=7$ Hz, CH_3), 1.9 (3H, m, CH_2 and $>\text{CH}-$), 2.27 (3H, s, CH_3), 2.42 (3H, s, CH_3), 2.9 (1H, m, $>\text{CH}-$), 3.65 (3H, s, OCH_3), 3.84 (2H, t, $J=7$ Hz, CH_2), 6.92 (3H, m), 7.27 (2H, broad d, $J=8$ Hz), and 7.69 (2H, broad d, $J=8$ Hz).

A mixture of the tosylate (4.4 g), KCN (1.5 g), and KI (1.0 g) in *N,N*-dimethylformamide (30 ml) was stirred at 60 $^\circ\text{C}$ for 10 h. The reaction mixture was diluted with water and extracted with benzene to give 4-(2-methoxy-3-methylphenyl)-5-methylhexanenitrile (**12**) (2.6 g, 96.3%). IR: 2250. ^1H NMR: 0.78 (3H, d, $J=7$ Hz, CH_3), 1.02 (3H, d, $J=7$ Hz,

CH₃), 2.0 (5H, m, two CH₂ and >CH-), 2.31 (3H, s, CH₃), 2.8 (1H, m, >CH-), 3.72 (3H, s, OCH₃), and 7.0 (3H, m).

A solution of **12** (2.9 g) and 85% KOH (2.1 g) in ethanol (20 ml) was refluxed for 10 h. After removing the solvent, the residue was diluted with water and washed with benzene. The aqueous alkaline solution was acidified with HCl and then extracted with benzene to give 4-(2-methoxy-3-methylphenyl)-5-methylhexanoic acid (**13**) (2.6 g, 83.9%). IR: 1705. ¹H NMR: 0.76 (3H, d, *J*=7 Hz, CH₃), 1.00 (3H, d, *J*=7 Hz, CH₃), 1.8 (2H, m, CH₂), 2.1 (3H, m, CH₂ and >CH-), 2.29 (3H, s, CH₃), 2.80 (1H, m, >CH-), 3.68 (3H, s, OCH₃), 6.98 (3H, m), and 10.61 (1H, broad, CO₂H).

A solution of **13** (1.4 g) and POCl₃ (0.6 g) in 1,1,2,2-tetrachloroethane (20 ml) was refluxed for 2 h. The reaction mixture was washed with water, aqueous Na₂CO₃ solution, and water, successively. After removing the solvent, the residue was chromatographed on silica gel and eluted with CH₂Cl₂ to give **14** (1.1 g, 84.6%). IR: 1675. ¹H NMR: 0.82 (3H, d, *J*=7 Hz, CH₃), 1.06 (3H, d, *J*=7 Hz, CH₃), 1.77 (1H, m, >CH-), 2.2 (2H, m, CH₂), 2.35 (3H, s, CH₃), 2.6 (2H, m, CH₂), 2.9 (1H, m, >CH-), 3.71 (3H, s, OCH₃), 7.13 (1H, d, *J*=8 Hz), and 7.70 (1H, d, *J*=8 Hz). 2,4-Dinitrophenylhydrazones; brown microcrystals (from xylene), mp 275.0 °C (decomp). Found: C, 61.38; H, 5.92; N, 13.34%. Calcd for C₂₁H₂₄N₄O₅: C, 61.15; H, 5.87; N, 13.59%.

(±)-**cis-5-Hydroxycalamenene (1a)**. A solution of **14** (1.1 g) in ether (15 ml) was added to methylmagnesium iodide, prepared from methyl iodide (1.8 g) and Mg (0.3 g) in ether (20 ml), under cooling in an ice bath, and the mixture was stirred at the same temperature for 7 h and then at 35 °C for 8 h. The reaction mixture was decomposed by adding NH₄Cl under cooling. The oily product (1.0 g, IR: 3400 cm⁻¹) obtained from the ether layer was stirred with 98% formic acid (2 ml) at 80 °C for 2 h to afford dihydronaphthalene **15** (0.9 g, 81.8%), which was hydrogenated over 10% Pd-C (0.3 g) in ethanol (20 ml). The oily product (0.9 g) obtained from the ethanol solution was chromatographed on silica gel and eluted with CCl₄ to give (±)-**cis-5-methoxycalamenene (1b)** (0.8 g, 88.9%), bp 121–122 °C/8 mmHg, whose ¹H and ¹³C NMR spectra showed no signals due to the trans isomer.⁴⁾ IR: 1480, 1455, 1400, 1250, 1110, 1085, 1040, 1010, and 810. ¹H NMR: 0.86 (3H, d, *J*=7 Hz, CH₃), 0.90 (3H, d, *J*=7 Hz, CH₃), 1.29 (3H, d, *J*=7 Hz, CH₃), 1.7 (4H, m, two CH₂), 2.10 (1H, m, *J*=7 Hz, >CH-), 2.25 (3H, s, CH₃), 2.82 (2H, m, two >CH-), 3.64 (3H, s, OCH₃), 6.87 (1H, d, *J*=8 Hz), and 6.98 (1H, d, *J*=8 Hz). ¹³C NMR: 16.1 (q, 6-Me), 20.1 (q, *i*-Pr), 21.5 (q, *i*-Pr), 23.4 (q, 1-Me), 23.6 (t, C3), 27.6 (t, C2), 31.8 (d, C1), 32.6 (d, *i*-Pr), 38.8 (d, C4), 59.6 (q, OMe), 123.8 (d, C8), 127.2 (s, C6), 128.4 (d, C7), 134.0 (s, C4a), 141.5 (s, C8a), and 156.9 (s, C5).

To a solution of (±)-**cis-1b** (300 mg) in CH₂Cl₂ (5 ml) was added a solution of BBr₃ (0.7 g) in CH₂Cl₂ (5 ml) at -10 °C and stirred at the same temperature for 5 h, and then the reaction mixture was poured into ice water. By removing the solvent from the organic layer was given (±)-**cis-5-hydro-**

xycalamenene (1a) (250 mg, 89.0%). ¹H NMR spectral data are identical with those of the natural product.²⁾ IR: 3550, 1485, 1460, 1415, 1380, 1310, 1225, 1205, 1165, 910, and 805. ¹H NMR: 0.91 (3H, d, *J*=7 Hz, CH₃), 0.94 (3H, d, *J*=7 Hz, CH₃), 1.29 (3H, d, *J*=7 Hz, CH₃), 1.6 (2H, m, CH₂), 1.8 (2H, m, CH₂), 1.97 (1H, m, *J*=7 Hz, >CH-), 2.18 (3H, s, CH₃), 2.8 (m, 2H, two >CH-), 4.59 (1H, s, OH), 6.72 (1H, d, *J*=8 Hz), and 6.92 (1H, d, *J*=8 Hz). ¹³C NMR: 15.8 (q, 6-Me), 20.3 (q, *i*-Pr), 21.4 (q, *i*-Pr), 23.5 (q, 1-Me), 23.9 (t, C3), 27.4 (t, C2), 31.4 (d, C1), 32.5 (d, *i*-Pr), 38.5 (d, C4), 119.4 (s, C6), 120.3 (d, C8), 127.1 (s, C4a), 127.8 (d, C7), 141.4 (s, C8a), and 151.4 (s, C5).

Dehydrogenation of (±)-cis-5-Hydroxycalamenene (1a) with Pd-C: A mixture of (±)-**cis-1a** (0.22 g) and 5% Pd-C (0.04 g) was heated at 250 °C for 5 h. While the crude dehydrogenation product (0.2 g) showed two main components on GC (51.4%, 34.2%), column chromatography (SiO₂, CH₂Cl₂) provided three compounds, which were identified with cadalene (0.05 g), 2,2,5,8-tetramethyl-2H-naphtho[1,8-*bc*]-furan (**16**) (0.07 g), and 3,4-dihydro-8-isopropyl-2,5-dimethyl-1(2H)-naphthalenone (0.05 g).¹¹⁾

16: oil. IR: 1350, 1220, 1085, 820, and 810. ¹H NMR: 1.68 (6H, s, two CH₃), 2.36 (3H, s, 8-CH₃), 2.58 (3H, s, 5-CH₃), 6.93 (1H, d, *J*=7 Hz), 7.18 (1H, d, *J*=8.5 Hz), 7.22 (1H, d, *J*=7 Hz), and 7.29 (1H, d, *J*=8.5 Hz). Picrate; dark brown needles (from ethanol), mp 129.0–130.0 °C. Found: C, 57.17; H, 4.14; N, 9.50%. Calcd for C₂₁H₁₉N₃O₈: C, 57.14; H, 4.34; N, 9.52%.

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