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

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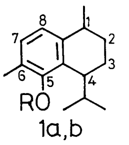
Synopsis. Starting from *o*-cresol, (±)-*cis*-5-hydroxycalamenene was synthesized through 4-isopropyl-5-methoxy-6-methyl-1-tetralone as a key intermediate and identified with the natural compound spectroscopically.

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 xanthorrhizol[3] (**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 ^{1}H 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 methyl[6] or methoxyl[7,8] groups at C$_5$ and/or C$_8$ 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**).

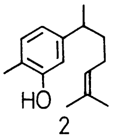
In order to confirm the stereochemistry of the naturally occurring 5-hydroxycalamenene, the synthesis of (±)-*cis*-**1** from *o*-cresol through 3,4-dihydro-4-isopropyl-5-methoxy-6-methyl-1(2*H*)-naphthalenone (**14**) as a key intermediate has been carried out. The resulting product was a mixture of 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 isobutyrate[10] by the Fries rearrangement and methylation was reduced with NaBH$_4$ 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 LiAlH$_4$ 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 POCl$_3$. 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 (^{1}H and ^{13}C) 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 BBr$_3$ afforded (±)-*cis*-5-hydroxycalamenene (**1a**), whose ^{1}H 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]



1a,b



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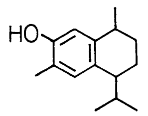

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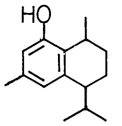

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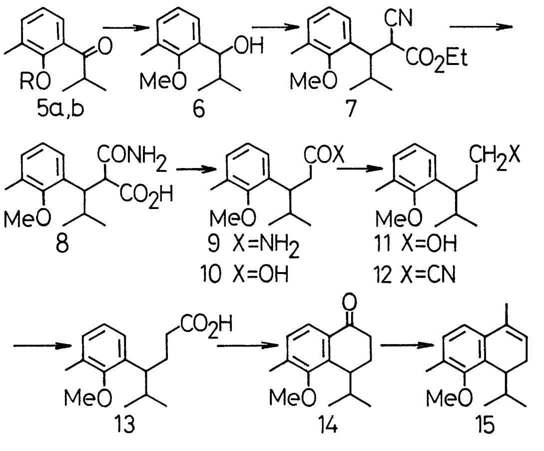
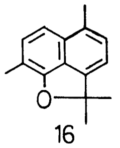


5a,b 6 7
8 9 X=NH$_2$ 11 X=OH
10 X=OH 12 X=CN
13 14 15



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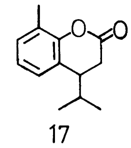

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R: {a=H, b=Me}

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}. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Spectrometer JNM-FX90Q (90 MHz for ^{1}H and 22.5 MHz for ^{13}C) for $\mathrm{CDCl_3}$ 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×3 m) packed with Apiezon Grease L of 30% on Cellite 545, at 70 ml min^{-1} He and column temperature 260 °C.

3-(2-Methoxy-3-methylphenyl)-4-methylpentanoic Acid (10). A mixture of *o*-tolyl isobutyrate[10] (0.1 mol) and $\mathrm{AlCl_3}$ (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 °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 °C/23 mmHg (1 mmHg=133.322 Pa).

4′-Hydroxy-3′-methylisobutyrophenone: 44.4%, mp 123.0—124.0 °C (from methanol).

To a mixture of **5a** (0.1 mol) and $\mathrm{K_2CO_3}$ (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 °C/15 mmHg.

To a solution of **5b** (30.0 g) in methanol (90 ml) was added $\mathrm{NaBH_4}$ (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 °C/11 mmHg. IR: 3450. ^{1}H NMR: 0.77 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.02 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.92 (1H, m, *J*=7 Hz, >CH–), 2.26 (3H, s, $\mathrm{CH_3}$), 2.68 (1H, d, *J*=5 Hz, OH), 3.69 (3H, s, $\mathrm{OCH_3}$), 4.57 (1H, dd, *J*=7, 5 Hz, >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. ^{1}H NMR: 0.80 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.27 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 2.2 (1H, m, >CH–), 2.27 (3H, s, $\mathrm{CH_3}$), 3.79 (3H, s, $\mathrm{OCH_3}$), 5.36 (1H, d, *J*=10 Hz, >CH–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 °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 $\mathrm{SiO_2}$ column to give pure ethyl 2-cyano-3-(2-methoxy-3-methylphenyl)-4-methylpentanoate (**7**) as the sample for analysis, bp 139—141 °C/3 mmHg. IR: 2250, and 1740. ^{1}H NMR: 0.82 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.03 and 1.14 (3H, d each, *J*=7 Hz, $\mathrm{CH_3}$), 1.04 and 1.23 (3H, t each, *J*=7 Hz, $\mathrm{CH_3}$), 2.2 (1H, m, >CH–), 2.28 and 2.31 (3H, s each, $\mathrm{CH_3}$), 3.6 (1H, m, >CH–), 3.7 (1H, m, >CH–), 3.72 and 3.77 (3H, s each, $\mathrm{OCH_3}$), 4.01 and 4.19 (2H, q each, *J*=7 Hz, $\mathrm{CH_2}$), 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 °C (decomp). IR (Nujol): 3400, 3330, and 1710. Found: C, 65.05; H, 7.99; N, 4.27%. Calcd for $\mathrm{C_{15}H_{21}NO_4}$: C, 64.49; H, 7.58; N, 5.01%.

The amic acid **8** (6.6 g) was decarboxylated by heating at 135 °C for 2 h to give 3-(2-methoxy-3-methylphenyl)-4-methylpentanamide (**9**) (5.5 g, 98.2%). IR: 3350, 3200, and 1660. ^{1}H NMR: 0.76 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 0.99 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.82 (1H, m, *J*=7 Hz, >CH–), 2.28 (3H, s, $\mathrm{CH_3}$), 2.6 (2H, m, $\mathrm{CH_2}$), 3.2 (1H, m, >CH–), 3.73 (3H, s, $\mathrm{OCH_3}$), 6.0 (2H, broad, $\mathrm{-NH_2}$), 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 °C. IR: 1705. ^{1}H NMR: 0.78 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 0.90 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.81 (1H, m, *J*=7 Hz, >CH–), 2.28 (3H, s, $\mathrm{CH_3}$), 2.7 (2H, m, $\mathrm{CH_2}$), 3.4 (1H, m, >CH–), 3.70 (3H, s, $\mathrm{OCH_3}$), 6.89—7.03 (3H, m), and 11.04 (1H, broad, $\mathrm{CO_2H}$). Found: C, 71.17; H, 8.80%. Calcd for $\mathrm{C_{14}H_{20}O_3}$: C, 71.16; H, 8.53%.

The acidic hydrolysis of **8** was also investigated. A mixture of **8** (3.0 g), concd $\mathrm{H_2SO_4}$ (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 $\mathrm{NaHCO_3}$ 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-methylcoumarine (**17**) (1.0 g, 40.0%). IR: 1770. ^{1}H NMR: 0.91 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 0.96 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.82 (1H, m, *J*=7 Hz, >CH–), 2.30 (3H, s, $\mathrm{CH_3}$). 2.7 (3H, m, $\mathrm{CH_2}$ and >CH–), and 7.0 (3H, m).

3,4-Dihydro-4-isopropyl-5-methoxy-6-methyl-1(2*H*)-naphthalenone (14). A solution of **10** (3.3 g) in ether (25 ml) was added to a suspension of $\mathrm{LiAlH_4}$ (1.1 g) in ether (25 ml) at room temperature. The mixture was refluxed for 2 h and acidified with 10% $\mathrm{H_2SO_4}$ 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. ^{1}H NMR: 0.78 (3H, d, *J*=6 Hz, $\mathrm{CH_3}$), 1.07 (3H, d, *J*=6 Hz, $\mathrm{CH_3}$), 2.0 (3H, m, $\mathrm{CH_2}$ and >CH–), 2.30 (3H, s, $\mathrm{CH_3}$), 2.43 (1H, broad, OH), 3.0 (2H, m, $\mathrm{CH_2}$), 3.4 (1H, m, >CH–), 3.73 (3H, s, $\mathrm{OCH_3}$), 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. ^{1}H NMR: 0.72 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 0.92 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.9 (3H, m, $\mathrm{CH_2}$ and >CH–), 2.27 (3H, s, $\mathrm{CH_3}$), 2.42 (3H, s, $\mathrm{CH_3}$), 2.9 (1H, m, >CH–), 3.65 (3H, s, $\mathrm{OCH_3}$), 3.84 (2H, t, *J*=7 Hz, $\mathrm{CH_2}$), 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 °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. ^{1}H NMR: 0.78 (3H, d, *J*=7 Hz, $\mathrm{CH_3}$), 1.02 (3H, d, *J*=7 Hz,

CH_3), 2.0 (5H, m, two CH_2 and >CH–), 2.31 (3H, s, CH_3), 2.8 (1H, m, >CH–), 3.72 (3H, s, OCH_3), 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. ^{1}H NMR: 0.76 (3H, d, J=7 Hz, CH_3), 1.00 (3H, d, J=7 Hz, CH_3), 1.8 (2H, m, CH_2), 2.1 (3H, m, CH_2 and >CH–), 2.29 (3H, s, CH_3), 2.80 (1H, m, >CH–), 3.68 (3H, s, OCH_3), 6.98 (3H, m), and 10.61 (1H, broad, CO_2H).

A solution of **13** (1.4 g) and $POCl_3$ (0.6 g) in 1,1,2,2-tetrachloroethane (20 ml) was refluxed for 2 h. The reaction mixture was washed with water, aqueous Na_2CO_3 solution, and water, successively. After removing the solvent, the residue was chromatographed on silica gel and eluted with CH_2Cl_2 to give **14** (1.1 g, 84.6%). IR: 1675. ^{1}H NMR: 0.82 (3H, d, J=7 Hz, CH_3), 1.06 (3H, d, J=7 Hz, CH_3), 1.77 (1H, m, >CH–), 2.2 (2H, m, CH_2), 2.35 (3H, s, CH_3), 2.6 (2H, m, CH_2), 2.9 (1H, m, >CH–), 3.71 (3H, s, OCH_3), 7.13 (1H, d, J=8 Hz), and 7.70 (1H, d, J=8 Hz). 2,4-Dinitrophenylhydrazone; brown microcrystals (from xylene), mp 275.0 °C (decomp). Found: C, 61.38; H, 5.92; N, 13.34%. Calcd for $C_{21}H_{24}N_4O_5$: 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 NH_4Cl 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 CCl_4 to give (±)-*cis*-5-methoxycalamenene (**1b**) (0.8 g, 88.9%), bp 121—122 °C/8 mmHg, whose ^{1}H and ^{13}C NMR spectra showed no signals due to the trans isomer.[4] IR: 1480, 1455, 1400, 1250, 1110, 1085, 1040, 1010, and 810. ^{1}H NMR: 0.86 (3H, d, J=7 Hz, CH_3), 0.90 (3H, d, J=7 Hz, CH_3), 1.29 (3H, d, J=7 Hz, CH_3), 1.7 (4H, m, two CH_2), 2.10 (1H, m, J=7 Hz, >CH–), 2.25 (3H, s, CH_3), 2.82 (2H, m, two >CH–), 3.64 (3H, s, OCH_3), 6.87 (1H, d, J=8 Hz), and 6.98 (1H, d, J=8 Hz). ^{13}C 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 CH_2Cl_2 (5 ml) was added a solution of BBr_3 (0.7 g) in CH_2Cl_2 (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-hydroxycalamenene (**1a**) (250 mg, 89.0%). ^{1}H 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. ^{1}H NMR: 0.91 (3H, d, J=7 Hz, CH_3), 0.94 (3H, d, J=7 Hz, CH_3), 1.29 (3H, d, J=7 Hz, CH_3), 1.6 (2H, m, CH_2), 1.8 (2H, m, CH_2), 1.97 (1H, m, J=7 Hz, >CH–), 2.18 (3H, s, CH_3), 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). ^{13}C 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 (SiO_2, CH_2Cl_2) provided three compounds, which were identified with cadalene (0.05 g), 2,2,5,8-tetramethyl-2*H*-naphtho[1,8-*bc*]-furan (**16**) (0.07 g), and 3,4-dihydro-8-isopropyl-2,5,-dimethyl-1(2*H*)-naphthalenone (0.05 g).[11]

16: oil. IR: 1350, 1220, 1085, 820, and 810. ^{1}H NMR: 1.68 (6H, s, two CH_3), 2.36 (3H, s, 8-CH_3), 2.58 (3H, s, 5-CH_3), 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 $C_{21}H_{19}N_3O_8$: C, 57.14; H, 4.34; N, 9.52%.

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