

Synthesis of 3- and 4-(ω -Phenylalkyl)catechols, the Sap Exuded from a Burmese Lac Tree, *Melanorrhoea Usitate*

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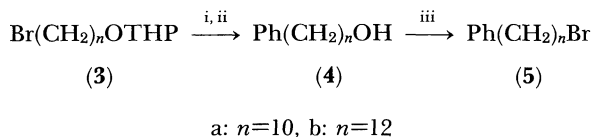
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Synopsis. The presence of 3- and 4-(ω -phenylalkyl)-catechols in Burmese lac has been confirmed by their synthesis. 3-(ω -Phenylalkyl)veratroles were synthesized by alkylation of ω -phenylalkyl bromide with aryl lithium derived from veratrole. 4-(ω -Phenylalkyl)veratroles were similarly obtained from ω -phenylalkyl bromide and 4-bromoveratrole. Demethylation of 3- and 4-(ω -phenylalkyl)-veratroles with boron tribromide gave the corresponding catechols in good yields.

In Asian countries, the exuded fluid sap from several kinds of lac trees is used as a preservative surface coating material for wood, porcelain, and metallic wares.^{1,2)} The sap of a Burmese lac tree, *Melanorrhoea usitate*, has been used as a naturally occurring phenolic coating material. In 1922, Majima reported that 4-substituted catechols having an n -C₁₇ alkyl side chain were the main constituents of the sap of *Melanorrhoea usitate*,³⁾ but little is known about the other compounds of the sap of this plant. We executed an intensive compositional investigation of the sap of the Burmese lac tree by use of liquid chromatography, and isolated 3- (**1**) and 4-(ω -phenylalkyl)catechols (**2**), phenolic lipids with novel structure.^{4–6)} These compounds are included in about 40% in the sap of the Burmese lac tree. Novel structures **1** and **2** and their characteristic properties as phenolic coating materials have prompted us to synthesize **1** and **2**. We describe here the total syntheses of **1** and **2** on the basis of the cross coupling reaction previously developed in our laboratory for the synthesis of terpenoids.⁷⁾

Results and Discussion

ω -Phenyl-1-alkanols (**4**) are useful intermediates in organic synthesis.⁸⁾ ω -Phenyl fatty acids are also important compounds in studies of metabolism.^{8,9)} Generally, **4** were prepared through reduction of ω -phenyl fatty acids¹⁰⁾ starting from the half ester



Scheme 1. Reagents: i, PhMgBr, CuCl, THF; ii, PPTS, MeOH; iii, HBr, H₂SO₄.

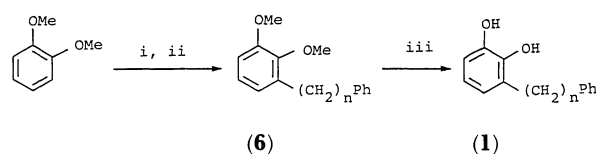
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chloride of aliphatic dicarboxylic acid¹¹⁾ and benzene, or ω -phenylalkyl bromide and diethyl malonate.¹²⁾ In the present case, we needed an efficient and mild procedure for the preparation of **4**. We recently reported a new synthetic method⁷⁾ of terpenoids using the copper(I) salt-catalyzed Grignard cross coupling reaction.¹³⁾ Based on these, we now report here analogous convenient synthesis of **4** as shown in Scheme 1.

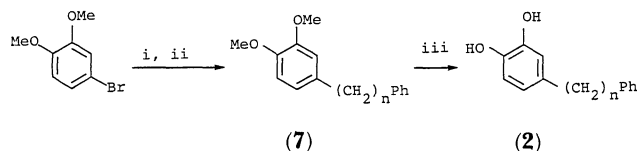
The reaction of ω -bromo-1-(2-tetrahydropyranyloxy)-alkanes (**3**)^{14–16)} with phenylmagnesium bromide in the presence of copper(I) chloride in THF at reflux temperature gave exclusively cross coupling products, which were then hydrolyzed to the desired **4** in 78–80% isolated yields.

The reaction of 2,3-dimethoxyphenyllithium, prepared from veratrole and butyllithium with 1-bromo-10-phenyldecane (**5a**) gave 3-(10-phenyldecyl)veratrole (**6a**) in 74% yield.^{17,18)} 3-(12-Phenyldecyl)veratrole (**6b**) was also prepared in the same manner from veratrole and 1-bromo-12-phenyldecane (**5b**) in 76% yield (see Scheme 2).

Demethylation of **6a** using boron tribromide¹⁹⁾ yielded 3-(10-phenyldecyl)catechol (**1a**) in 86% yield.



Scheme 2. Reagents: i, BuLi, THF; ii, Ph(CH₂)_nBr, THF; iii, BBr₃, CH₂Cl₂.



Scheme 3. Reagents: i, BuLi, THF; ii, Ph(CH₂)_nBr, THF; iii, BBr₃, CH₂Cl₂.

Similarly, 3-(12-phenyldodecyl)catechol (**1b**) was prepared in 87% yield. The IR, ^1H NMR, and EI-MS spectra of these products were in good agreement with those of the reported data.⁴

In a next stage, 4-(10-phenyldecyl)- (**7a**) and 4-(12-phenyldodecyl)veratrole (**7b**) were obtained by the coupling reaction of 3,4-dimethoxyphenyllithium²⁰ with 1-bromo-10-phenyldecane (**5a**) and 1-bromo-12-phenyldecane (**5b**), respectively (see Scheme 3).

Demethylation of **7a** and **7b** using BBr_3 yielded 4-(10-phenyldecyl)- (**2a**) and 4-(12-phenyldodecyl)catechol (**2b**) in 83 and 85% yield, respectively. The IR, NMR, and EI-MS spectra of **2** were in agreement with those of authentic sample. The ^1H NMR spectrum of **2** in CDCl_3 showed two triplets at $\delta=2.47$ (2H, α -methylene protons of catechol group) and $\delta=2.57$ (2H, α -methylene protons of phenyl group). On the other hand, the ^1H NMR spectrum of **1a** and **1b** in CDCl_3 each showed a triplet at $\delta=2.51$ (4H, α -methylene protons of catechol and phenyl group).

The presence of **1** and **2** in the Burmese lac was confirmed using GLC by separate co-injection of their synthetic compounds with the natural products.

Experimental

Melting points were determined with a Yanagimoto micromelting point apparatus and were not corrected. IR spectra were measured on a Shimadzu IR-435 spectrometer in a liquid film or in KBr disc. All ^1H NMR spectra were taken in deuteriochloroform or carbon tetrachloride with tetramethylsilane as internal standard on a Varian EM 390 spectrometer (90 MHz) or JEOL GSX-270 spectrometer (270 MHz). Low resolution mass spectra were taken on a JEOL DX-300 mass spectrometer at 70 eV or with an emission current of 100 μA . High-performance liquid chromatography (HPLC) was performed on a Gilson liquid chromatograph with a Unisil ODS reverse phase column (4.6 mm $\times$ 2.5 cm, 5 μm) or Develosil silica gel (4.6 mm $\times$ 25 cm, 5 μm). Thin-layer chromatography (TLC) was run with precoated silica-gel plates (Merck, Art 5554). Spot detection was carried out with visualization by UV light and/or iodine vapor. Flash column chromatography was performed with glass column packed with Merck silica gel 60 (230–400 mesh). Capillary gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph using a DB-1 column (25 mm $\times$ 0.25 mm).

Materials. ω -Bromo-1-(2-tetrahydropyranyloxy)alkane (**3**) were obtained from α,ω -alkanediol in good yields via ω -bromoalkyl alcohols.^{14–16}

10-Phenyl-1-decanol (4a). A Grignard reagent was prepared from bromobenzene (7.07 mg, 45 mmol) and magnesium turning (0.96 g, 40 mmol) in dry THF (20 mL) with a small amount of I_2 as starter at 20–25 $^\circ\text{C}$ under dry nitrogen. To this Grignard solution, a solution of a mixture of 1-bromo-10-(2-tetrahydropyranyloxy)decane (**3a**) (9.63 g, 30 mmol) and CuCl (20 mg, 0.2 mmol) in dry THF (10 mL) was added at 0 $^\circ\text{C}$ for 10 min. The mixture was stirred for 5 h at reflux temperature. Then the ice-cooled reaction mixture was carefully added dropwise to a cold saturated NH_4Cl aq solution. The THF layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layer was washed with brine, dried (K_2CO_3) and concentrated in vacuo to give 9.8 g of crude cross-coupling product. This was employed in the next step without further purification.

A solution of the cross coupling product 9.8 g and *p*-

toluenesulfonic acid (0.5 g, 2.4 mmol) in methanol (50 mL) were stirred for 8 h at room temperature. The mixture was neutralized with potassium carbonate and filtered through Celite. After removal of methanol in vacuo from the filtrate, the residual oil was purified by silica-gel column chromatography. Biphenyl as a by-product was obtained from the eluate with hexane–benzene (1:1) in 18% yield. The pure **4a** was obtained by chromatography over silica gel eluting with benzene–ethyl acetate (9:1) to give a compound (**4a**) (5.62 g) as oil. Yield: 80% from **3a** by 135–138 $^\circ\text{C}/2$ Torr (1 Torr=133.322 Pa), $R_f=0.38$ (hexane–diethyl ether=1:1); IR (neat) 3300, 1600, 1500, and 700 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=0.9$ –1.8 (br. s, 16H, CH_2), 2.54 (t, $J=7$ Hz, 2H, CH_2Ar), 2.91 (br. s, 1H, OH, D_2O exchangeable), 3.51 (t, $J=6$ Hz, 2H, CH_2O), and 6.9–7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 234 (M^+ , 9), 216 (5), 117 (19), 104 (90), and 91 (100). Found: C, 81.87; H, 11.25%. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}$: C, 81.99; H, 11.18%.

12-Phenyl-1-dodecanol (4b): In the same manner as described for compound (**4a**), 1-bromo-12-(2-tetrahydropyranyloxy)alkane (**3**) was converted to compound (**4b**). Yield: 80%, mp 37–38 $^\circ\text{C}$ (Lit.⁹ mp 38–40 $^\circ\text{C}$).

ω -Phenylalkyl Bromide (5). Compounds (**5**) were prepared from the ω -phenylalkyl alcohols (**4**) and hydrobromic acid in the presence of sulfuric acid by mechanical stirring for 4 h at reflux temperature according to the general procedure reported in the literature.²¹

10-Phenyldecyl Bromide (5a). Yield: 81%, bp 145–146 $^\circ\text{C}/3$ Torr, $R_f=0.53$ (hexane); IR (neat) 1600, 1500, 700, and 640 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.15$ –2.0 (m, 16H, CH_2), 2.58 (t, $J=7$ Hz, 2H, CH_2Ar), 3.35 (t, $J=7$ Hz, 2H, CH_2Br), and 7.0–7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 298 (M^+ , 17), 296 (M^+ , 16), 133 (8), 105 (9), 92 (100), and 91 (74). Found: C, 64.54; H, 8.40%. Calcd for $\text{C}_{16}\text{H}_{25}\text{Br}$: C, 64.64; H, 8.48%.

12-Phenyldodecyl Bromide (5b). Yield: 83%, bp 155 $^\circ\text{C}/3$ Torr, $R_f=0.54$ (hexane); IR (neat) 1600, 1500, 700, and 640 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.13$ –2.0 (br. s, 20H, CH_2), 2.58 (t, $J=7$ Hz, 2H, CH_2Ar), 3.35 (t, $J=7$ Hz, 2H, CH_2Br), and 7.0–7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 326 (M^+ , 13), 324 (M^+ , 12), 133 (11), 104 (13), 92 (99), and 91 (100). Found: C, 66.48; H, 8.87%. Calcd for $\text{C}_{18}\text{H}_{29}\text{Br}$: C, 66.45; H, 8.99%.

3-(10-Phenyldecyl)veratrole (6a). Ten milliliters of butyllithium (1.6 M in hexane) was added to a stirred solution veratrole (6.62 g, 48 mmol) in dry THF (20 mL) at 0 $^\circ\text{C}$ under a nitrogen atmosphere ($\text{M}=\text{mol dm}^{-3}$). After stirring for 1 h at room temperature, a solution of 1-bromo-10-phenyldecane (**5a**) (4.75 g, 16 mmol) in dry THF (20 mL) was added and the mixture was refluxed for 4 h. The mixture was then poured into a saturated NH_4Cl aq solution and extracted with ethyl acetate. The ethyl acetate solution was washed with brine, dried (K_2CO_3), and concentrated in vacuo to give crude compound (**6a**). The residual oil was chromatographed over silica gel eluting with hexane to give tetradecylbenzene (15% yield). Compound (**6a**) was obtained from chromatography over silica gel eluting with hexane–benzene (5:95) to give 4.19 g (74% yield) of compound (**6a**) as a colorless liquid. IR (neat) 1600, 1585, 1500, 1080, 740, and 700 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.1$ –1.6 (m, 16H, CH_2), 2.50 (t, $J=7$ Hz, 4H, CH_2Ar , CH_2Ph), 3.70 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 6.6–6.9 (m, 3H, ArH), and 7.1 (br. s, 5H, ArH). EI-MS m/z (rel intensity) 354 (M^+ , 60), 151 (95), 120 (55), 91 (80), and 73 (100). Found: C, 81.22; H, 9.50%. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2$: C, 81.31; H, 9.67%.

3-(12-Phenyldodecyl)veratrole (6b) was obtained by the reaction of compound (**5b**) (3.12 g, 9.6 mmol) with veratrole (3.97 g, 28.8 mmol) and butyllithium (6 mL, 9.6 mmol) in THF (20 mL). Yield 2.79 g (76%), IR (neat) 1600, 1585, 1500,

1080, 740, and 700 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.1\text{--}1.6$ (m, 20H, CH_2), 2.50 (t, $J=7$ Hz, 4H, CH_2Ar , CH_2Ph), 3.70 (s, 3H, CH_3O), 3.75 (s, 3H, CH_3O), 6.6—6.9 (m, 3H, ArH), and 7.1 (br. s, 5H, ArH). EI-MS m/z (rel intensity, %) 382 (M^+ , 50), 152 (48), 124 (30), and 91 (100). Found: C, 81.55; H, 9.95%. Calcd for $\text{C}_{26}\text{H}_{38}\text{O}_2$: C, 81.62; H, 10.01%.

4-(10-Phenyldodecyl)veratrole (7a). To a solution of butyllithium (2.5 ml, 4 mmol) in dry THF (10 ml) was added 4-bromoveratrole (0.44 g, 2 mmol) in dry THF (10 mL) under nitrogen atmosphere. The mixture is stirred for 1 h at room temperature and then compound (5a) (0.60 g, 2 mmol) in dry THF (5 mL) was added under vigorous stirring. The reaction mixture was refluxed for 3 h. Then the mixture was allowed to cool to room temperature, and immediately hydrolyzed by pouring onto an iced NH_4Cl aq solution. The aqueous solution was acidified with hydrochloric acid. The mixture was then extracted with 50 mL of ethyl acetate. The ethyl acetate layer was separated, dried and evaporated. The residue was chromatographed over silica gel eluting with hexane-benzene (5:95) to give 0.43 g (61% yield) of compound (7a) as a colorless liquid. $R_f=0.61$ (hexane-benzene=5:95); IR (neat) 1600, 1520, 1260, 1230, 1140, 1020, 810, and 710 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.3\text{--}1.8$ (m, 16H, CH_2), 2.50 (t, $J=7$ Hz, 2H, CH_2Ar), 2.53 (t, $J=7$ Hz, 2H, CH_2Ar), 3.70 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), and 6.6—7.3 (m, 8H, ArH). EI-MS m/z (rel intensity, %) 354 (M^+ , 80), 151 (100), and 91 (90). Found: C, 81.19; H, 9.58%. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2$: C, 81.31; H, 9.67%.

4-(12-Phenyldodecyl)veratrole (7b) was obtained by the reaction of compound (5b) with 4-bromoveratrole and butyllithium in dry THF. Yield 65%, $R_f=0.65$ (hexane-benzene=5:95); IR (neat) 1600, 1520, 1260, 1230, 1140, 1020, 810, and 710 cm^{-1} ; ^1H NMR (CCl_4/TMS) $\delta=1.3\text{--}1.8$ (m, 20H, CH_2), 3.73 (t, $J=7$ Hz, 2H, CH_2Ar), 2.53 (t, $J=7$ Hz, 2H, CH_2Ar), 3.70 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), and 6.6—7.3 (m, 8H, ArH). EI-MS m/z (rel intensity, %) 382 (M^+ , 45), 151 (56), and 91 (100). Found: C, 81.49; H, 10.12%. Calcd for $\text{C}_{26}\text{H}_{38}\text{O}_2$: C, 81.62; H, 10.01%.

3-(10-Phenyldodecyl)catechol (1a). To a stirred solution of boron tribromide 0.7 g (2.8 mmol) in dichloromethane 5 mL was added dropwise a solution of compound (6a) (0.39 g, 1.1 mmol) in dichloromethane (20 mL) for 1 h at -10°C . The mixture was allowed to warm up to room temperature slowly over 12 h. The mixture was hydrolyzed with water, diluted with dichloromethane. The dichloromethane layer was separated, washed with brine, dried (MgSO_4), and concentrated in vacuo below 30°C . The residual oil was chromatographed on silica gel eluting with hexane-diethyl ether to give 0.31 g of compound (1a). Yield 86%, bp $185^\circ\text{C}/3$ Torr, $R_f=0.46$ (hexane-diethyl ether=1:1); IR (neat) 3400, 1600, 1500, 780, and 730 cm^{-1} ; ^1H NMR (CDCl_3/TMS) $\delta=1.1\text{--}1.8$ (m, 16H, CH_2), 2.51 (t, $J=7$ Hz, 4H, CH_2Ar , CH_2Ph), 5.05, 5.18 (br. s, 1H, OH, D_2O exchangeable), 6.4—6.7 (m, 3H, ArH), and 6.9—7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 326 (M^+ , 48), 124 (100), 123 (96), and 91 (47). Found: C, 80.89; H, 9.20%. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2$: C, 80.93; H, 9.26%.

3-(12-Phenyldodecyl)catechol (1b) was obtained by the reaction of compound (6b) with boron tribromide. Yield 87%, $R_f=0.58$ (hexane-diethyl ether=1:1), mp 36.5°C ; IR (KBr) 3400, 1600, 1500, 780, and 730 cm^{-1} ; IR (neat) 3400, 1600, 1500, 780, and 730 cm^{-1} ; ^1H NMR (CDCl_3/TMS) $\delta=1.10\text{--}1.82$ (m, 20H, CH_2), 2.51 (t, $J=7$ Hz, 4H, CH_2Ar , CH_2Ph), 5.15, 5.71 (br. s, 1H, OH, D_2O exchangeable), 6.44—6.68 (m, 3H, ArH), and 6.93—7.30 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 354 (M^+ , 97), 124 (100), 123 (100), and 91 (87). Found: C, 81.25; H, 9.59%. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2$: C, 81.31; H, 9.67%.

4-(10-Phenyldodecyl)catechol (2a) was obtained by the

reaction of compound (7a) with boron tribromide. Yield 83%, mp $56\text{--}57^\circ\text{C}$, $R_f=0.51$ (benzene-ethyl acetate=1:1), IR (KBr) 3300, 1600, 1500, 1100, 800, and 700 cm^{-1} ; ^1H NMR (CDCl_3/TMS) $\delta=1.2\text{--}1.8$ (m, 16H, CH_2), 2.47 (t, $J=7$ Hz, 2H, CH_2), 2.57 (t, $J=7$ Hz, 2H, CH_2), 5.52 (br. s, 2H, OH, D_2O exchangeable), 6.5—6.8 (m, 3H, ArH), and 7.1—7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 326 (M^+ , 55), 123 (100), and 91 (65). Found: C, 80.98; H, 9.19%. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_2$: C, 80.93; H, 9.26%.

4-(12-Phenyldodecyl)catechol (2b) was obtained by the reaction of compound (7b) with boron tribromide. Yield 85%, mp 62°C , $R_f=0.58$ (benzene-ethyl acetate=1:1), IR (KBr) 3300, 1600, 1500, 1100, 800, and 700 cm^{-1} ; ^1H NMR (CDCl_3/TMS) $\delta=1.2\text{--}1.8$ (m, 20H, CH_2), 2.47 (t, $J=7$ Hz, 2H, CH_2Ar), 2.57 (t, $J=7$ Hz, 2H, CH_2Ar), 5.68 (br. s, 2H, OH, D_2O exchangeable), 6.5—6.8 (m, 3H, ArH), and 7.1—7.3 (m, 5H, ArH). EI-MS m/z (rel intensity, %) 354 (M^+ , 55), 123 (100), and 91 (72). Found: C, 81.30; H, 9.75%. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2$: C, 81.31; H, 9.67%.

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