Practical and Efficient Strategy for Synthesis of Ferruginol, Sugiol, and Sugiol Methyl Ether from Geraniol

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Aromatic abietane diterpenoids are naturally occurring phenolic tricyclic compounds that have a wide range of biological properties, including antitumor, antimicrobial, antiviral, antiulcer, antileishmanial, antiplasmodial, antifungal, cardiovascular, antioxidant, antibacterial as well as anti-inflammatory activity.[1] Among these compounds, C-12 (and C-7) oxidized aromatic abietane compounds: ferruginol (1), sugiol (2), and sugiol methyl ether (3) isolated from *Podocarpus ferrugineus*, *Juniperus communis* L., and *Melia azadirachta* Linn., respectively, have been most widely investigated in the field of natural products synthesis and biological studies. In addition, increased biological activities of these synthetic derivatives possessing an aromatic C-ring have been reported.[2]

Thus, the unique and simple structure of aromatic abietane diterpenoids can be used as a template for lead compounds in the development of new drugs that are derived from natural products. Although several methods have been developed for the synthesis of **1**, **2**, and **3** from, *e.g.,* podocarpic acid,[3] dehydroabietic acid,[4] clareol,[5] dehydroabietylamine,[6] 2,2,6-trimethylcyclohexanone/sodium *p*-methoxyphenylacetylide,[7] and *α*-cyclocitral,[8] some have disadvantages including multiple steps, tedious separation, and expensive starting materials. Herein, we report a practical and efficient strategy for the synthesis of **1**, **2**, and **3** from a simple starting material: geraniol (Scheme 1). The aromatic tricyclic compound **6** is involved as the key intermediate in obtaining the natural products **1**, **2**, and **3**. **6** can be obtained from homogeranyl benzene **5** through the construction of A/B *trans*-fused bicycle by cationic polycyclization. The geranylation of benzyl anion would afford homogeranyl benzene **5** from commercially available monoterpene **4**. On the basis of the strategy mentioned in Scheme 1, 4-(homogeranyl)anisole **8** was synthesized from **4** via geraniol diethyl phosphate **7** using a *p*-methoxybenzyl Grignard reagent having the C-ring of the aromatic tricyclic structure. Next, cationic polycyclization using **5** for the construction of A/B *trans*-fused bicycle was investigated under several well-known conditions in the presence of $SnCl_4$,[9] $RuCl_3{\cdot}xH_2O/AgOTf$,[10] $SbCl_5$,[11] and $BF_3{\cdot}Et_2O$.[12] The best result (76%) was obtained under the $RuCl_3{\cdot}xH_2O/AgOTf$ condition. The desired tricyclic compound **6** was easily purified by column chromatography and assigned by comparing the spectroscopic data with literature.[6] Further, compound **6** was then continuously treated with AcCl in CH_2Cl_2 at −5 °C in the presence of $AlCl_3$ to give the corresponding selectively mono acetylated acetophenone **8** in 90% yield. Thereafter, methylation to the ketone using MeMgBr followed by the Pd-catalyzed hydrogenation under acidic conditions (AcOH/MeOH) gave ferruginol methyl ether **10**[13] in 86% yield over two steps. The intermediate **10** was oxidized with CrO_3 under $AcOH/H_2O$ at the room temperature for 1 h to afford sugiol methyl ether (**3**)[14] in 95% yield (Scheme 2). Finally, deprotection of the methyl ether **12** and **3** were performed with BBr_3 in CH_2Cl_2 at 0 °C overnight to give ferruginol (**1**) and sugiol (**2**) in 97% and 94% yields, respectively (Scheme 3.).

In summary, we have demonstrated a new synthetic approach for the preparation of **1**, **2**, and **3** in 44.2% (seven steps), 40.7% (eight steps), and 43.3% (seven steps) overall yields, respectively, from **4** by cationic polycyclization of **5** followed by the insertion of the isopropyl group. Further investigations of the evaluation of C-ring transformed derivatives of aromatic abietane diterpenoids are currently underway in our laboratory.

Experimental

General. ^1H NMR spectra were recorded with a Bruker AVANCE 400 spectrometer, and the chemical shifts are reported in parts per million (ppm) relative to $SiMe_4$ as an internal standard (δ = 0 ppm) for $CDCl_3$. The resonance

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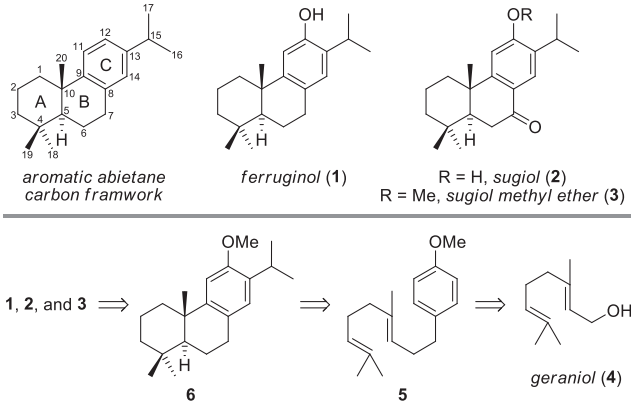
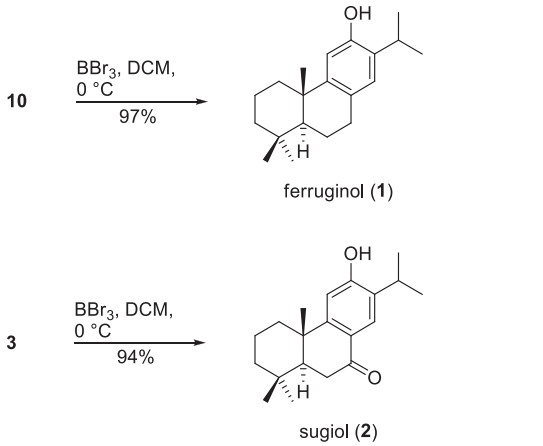


Scheme 1. Structure and retrosynthesis of ferruginol (**1**), sugiol (**2**), and sugiol methyl ether (**3**) from geraniol (**4**).

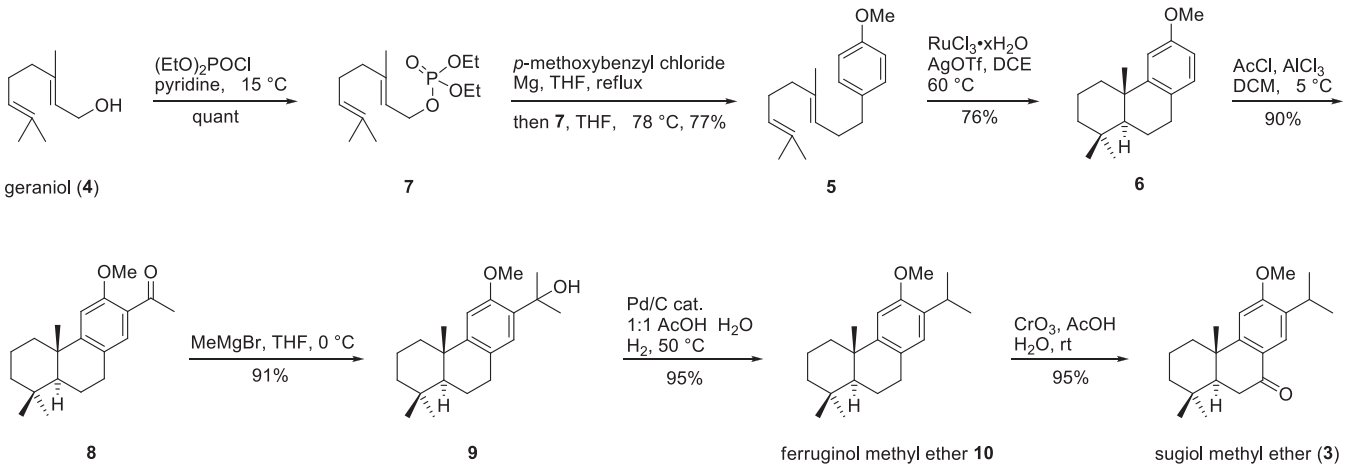


Scheme 3. Total synthesis of ferruginol (**1**) and sugiol (**2**).

patterns are indicated as follows: s, singlet; d, doublet; br. s, broad singlet; dd, doublet of doublets; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained on the same spectrometer and are referenced to the internal solvent signals (central signal δ = 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. Mass spectra were determined with a GC-MS: JMS-700 MStation Mass Spectrometer (Jeol, Tokyo, Japan) for EI-MS. Flash column chromatography was performed over silica gel 200–300. All reagents were weighed and handled in air at room temperature, and all reactions were performed under an air atmosphere. Unless otherwise noted, all reagents were purchased from commercial suppliers and were used without further purification.

(*E*)-3,7-Dimethylocta-2,6-dienyl diethyl phosphate (7). To a stirred solution of geraniol (5.7 mL, 32.4 mmol) and pyridine (7.8 mL, 97.2 mmol) in Et_2O (30 mL) at −15 °C was added diethyl chlorophosphate (7.0 mL, 48.6 mmol) and the mixture was allowed to slowly warm to room temperature. The resulting reaction mixture was stirred at room temperature for 12 h by which time TLC analysis indicated that the reaction was completed. The reaction mixture was quenched with 1.0 M aq HCl solution, extracted with EtOAc, washed with saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated *in vacuo* to give **7** (9.4 g, quant) as a colorless oil which was used directly without purification. The spectroscopic data are in accordance with the literature values reported.[15]

(*E*)-1-(4,8-Dimethylnona-3,7-dienyl)-4-methoxybenzene (5). The Grignard reagent was prepared as followed: To magnesium turnings (2.2 g, 92.0 mmol) stirred in dry THF (50 mL) was added a portion of 4-methoxybenzyl chloride (0.23 mL, 1.69 mmol), where the reaction could be started by gentle heating. Subsequently, a solution of 4-methoxybenzyl chloride (5.97 mL, 43.8 mmol) in THF (20 mL) was added dropwise over 30 min to maintain reflux. After complete addition, reflux was continued for another 2 h. The Grignard reagent was cooled to −78 °C and a solution of **7** (6.6 g, 23.0 mmol) in THF (20 mL) was added dropwise via *cannula* at the same temperature. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. When no starting material could be detected by TLC, the reaction was quenched with saturated NH_4Cl solution, extracted with Et_2O, washed with saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated *in*



Scheme 2. Total synthesis of sugiol methyl ether (**3**) from geraniol (**4**).

vacuo. The residue was purified by silica gel chromatography (4:1 hexane–CH_2Cl_2) to afford **5** (4.54 g, 77%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (d, 2H, *J* = 11.6 Hz), 6.80 (d, 2H, *J* = 11.6 Hz), 5.18 (d, 1H, *J* = 7.2 Hz), 5.10 (d, 1H, *J* = 8.0 Hz), 3.80 (s, 3H), 2.59 (t, 2H, *J* = 8.0 Hz), 2.28 (q, 2H, *J* = 8.0 Hz), 2.06 (t, 2H, *J* = 7.6 Hz), 1.98 (t, 2H, *J* = 8.0 Hz), 1.69 (s, 3H), 1.61 (s, 3H), 1.56 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 135.8, 131.7, 131.2, 129.5, 124.5, 123.8, 113.8, 55.4, 39.9, 35.3, 30.3, 26.9, 25.8, 17.8, 16.1. HR-MS (EI) calcd. For $C_{18}H_{26}O$ $[M]^+$ 258.1984; found 258.1985.

6-Methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydr-ophenanthrene (6)**.** A mixture of $RuCl_3{\cdot}xH_2O$ (11.0 mg, 0.05 mmol) and AgOTf (27.0 mg, 0.11 mmol) in $ClCH_2CH_2Cl$ (10 mL) was stirred vigorously for 30 min. Then the compound **5** (1.38 g, 5.34 mmol) in $ClCH_2CH_2Cl$ (10 mL) was added at room temperature. The resulting solution was heated to 60 °C and stirred for 4 h. TLC analysis indicated that the reaction was completed, and the crude was filtered through a short pad silica with the aid of CH_2Cl_2. The filterate was concentrated *in vacuo* and purified by silica gel chromatography (2:1 hexane–CH_2Cl_2) to afford **6** (1.05 g, 76%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.99 (d, 1H, *J* = 8.4 Hz), 6.85 (s, 1H), 6.69 (dd, 1H, *J* = 2.8 and 8.4 Hz), 3.80 (s, 3H), 2.91–2.82 (m, 2H), 2.28 (d, 1H, *J* = 12.8 Hz), 1.88 (d, 1H, *J* = 7.6 Hz), 1.89–1.72 (m, 3H), 1.53 (d, 1H, *J* = 1.2 Hz), 1.44 (d, 1H, *J* = 3.6 Hz), 1.36 (dd, 1H, *J* = 2.4 and 12.6 Hz), 1.29 (dt, 1H, *J* = 2.8 and 4.0 Hz), 1.23 (s, 3H), 0.99 (s, 3H), 0.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.8, 151.6, 129.9, 127.6, 110.8, 110.3, 55.4, 50.4, 41.8, 39.0, 38.1, 33.5, 29.7, 24.9, 21.8, 19.4, 19.3. HR-MS (EI) calcd. For $C_{18}H_{26}O$ $[M]^+$ 258.1984; found 258.1982.

1-(3-Methoxy-4b,8,8-trimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)ethanone (8)**.** Aluminum chloride (1.08 g, 8.1 mmol) and acetyl chloride (0.58 mL, 8.1 mmol) were added to a solution of **6** (1.05 g, 4.1 mmol) in CH_2Cl_2 at −10 °C, and the reaction mixture was stirred for 1 h at −5 °C. After the reaction, the reaction mixture was poured into ice water and extracted with EtOAc. The organic layer was successively washed with saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (6:1 hexane–EtOAc) to afford **8** (1.11 g, 90%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (s, 1H), 6.83 (s, 1H), 3.87 (s, 3H), 2.90 (dd, 1H, *J* = 6.4 and 17.2 Hz), 2.80 (dd, 1H, *J* = 7.6 and 11.2 Hz), 2.58 (s, 3H), 1.88 (t, 1H, *J* = 11.6 Hz), 1.91–1.18 (m, 11H), 0.95 (s, 3H), 0.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.6, 157.4, 156.5, 131.0, 127.7, 125.6, 107.6, 55.6, 50.1, 41.6, 38.9, 38.6, 33.4, 31.9, 29.3, 21.8, 19.3, 19.1. HR-MS (EI) calcd. For $C_{20}H_{28}O_2$ $[M]^+$ 300.2089; found 300.2086.

2-(3-Methoxy-4b,8,8-trimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)propan-2-ol (9)**.** Methyl magnesium bromide (3.0 M in diethyl ether, 1.8 mL, 5.49 mmol) was added to a solution of **8** (1.11 g, 3.66 mmol) in THF (20 mL) at 0 °C and the reaction mixture was stirred for 30 min. After the reaction, the reaction mixture was poured into saturated NH_4Cl and extracted with EtOAc. The organic layer was washed with brine, dried over anhydr. $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (6:1 hexane–EtOAc) to afford **9** (1.06 g, 91%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.94 (s, 1H), 6.87 (s, 1H), 3.90 (s, 3H), 2.86–2.81 (m, 2H), 2.12 (s, 1H), 1.87 (d, 1H, *J* = 7.2 Hz), 1.76–1.20 (m, 7H), 1.60 (s, 3H), 1.58 (s, 3H), 1.87 (d, 1H, *J* = 7.2 Hz), 1.23 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 149.8, 133.0, 127.3, 126.3, 107.4, 72.4, 50.5, 55.4, 41.8, 39.0, 38.0, 33.6, 33.4, 30.0, 29.9, 24.9, 21.7, 19.2. HR-MS (EI) calcd. For $C_{21}H_{32}O_2$ $[M]^+$ 316.2402; found 316.2398.

Ferruginol methyl ether (10)**.** 10% Pd/C (ca.76 mg) was added to a solution of compound **9** (0.76 g, 2.4 mmol) in methanol (10 mL) and acetic acid (10 mL), and the mixture was stirred at 50 °C for 3 h under H_2. After the reaction, the mixture was filtered through celite which was washed with EtOAc, and the filtrate was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (10:1 hexane–EtOAc) to afford **10** (0.68 g, 95%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.9 (s, 1H), 6.77 (s, 1H), 3.83 (s, 3H), 3.27 (t, 1H, *J* = 6.8 Hz), 2.90–2.83 (m, 2H), 1.94–1.38 (m, 9H), 1.25 (s, 3H), 1.24 (s, 3H), 1.22 (s, 3H), 0.99 (s, 3H), 0.96 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 155.1, 148.2, 134.3, 127.0, 126.5, 106.7, 55.7, 50.6, 41.9, 39.1, 38.0, 33.6, 33.5, 30.0, 26.6, 25.0, 23.1, 21.8, 19.5. HR-MS (EI) calcd. For $C_{21}H_{32}O$ $[M]^+$ 300.2453; found 300.2455.

Sugiol methyl ether (3)**.** A solution of CrO_3 (0.27 g, 2.70 mmol) in AcOH (15 mL) and H_2O (0.3 mL) was added to a solution of **10** (0.65 g, 2.16 mmol) in AcOH (15 mL), and the mixture was stirred for 1 h at room temperature. After the reaction, the mixture was poured into ice water. The aqueous solution was neutralized with 1.0 M NaOH solution and extracted with EtOAc. The organic layer was successively washed with saturated $NaHCO_3$ solution, brine, dried over anhyd. $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (1:2 hexane–CH_2Cl_2) to afford **3** (0.65 g, 95%) as white solids. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (s, 1H), 6.74 (s, 1H), 3.87 (s, 3H), 3.22 (t, 1H, *J* = 6.8 Hz), 2.69–2.53 (m, 2H), 1.85 (dd, 1H, *J* = 4.4 and 13.6 Hz), 1.76 (tt, 1H, *J* = 3.2 and 13.6 Hz), 1.69–1.50 (m, 3H), 1.27 (d, 1H, *J* = 4.5 Hz), 1.23 (s, 3H), 1.19 (t, 3H, *J* = 2.8 Hz), 1.17 (s, 3H), 0.98 (s, 3H), 0.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) *δ* 198.5, 161.7, 156.4, 135.2, 125.6, 124.1, 104.5, 55.4, 49.7, 41.4, 38.3, 38.0, 36.1, 33.3, 32.6, 26.5, 23.2, 22.4, 21.4, 18.9. HR-MS (EI) calcd. For $C_{21}H_{30}O_2$ $[M]^+$ 314.2246; found 314.2247.

Ferruginol (1)**.** To a solution of **10** (0.2 g, 0.67 mmol) in CH_2Cl_2 (6.7 mL) was added BBr_3 (1.0 M in CH_2Cl_2, 2.0 mL, 2.01 mmol) dropwise at 0 °C, and stirring was

continued for 12 h. The reaction was quenched by H_2O and allowed to warm to room temperature gradually. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic extracts were combined, washed with saturated $NaHCO_3$ solution, brine, dried over anhyd. $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (5:1 hexane–EtOAc) to afford **1** (185.2 mg, 97%) as white solids. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (s, 1H), 6.63 (s, 1H), 4.54 (brs, 1H), 3.12 (sept, 1H, J = 6.8 Hz), 2.90–2.73 (m, 2H), 2.17 (d, 1H, J = 12.4 Hz), 1.89–1.56 (m, 5H), 1.50–1.30 (m, 3H), 1.25 (d, 3H, J = 6.8 Hz), 1.23 (d, 3H, J = 6.8 Hz), 1.17 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 150.7, 148.7, 131.4, 127.3, 126.6, 111.0, 50.3, 41.7, 38.9, 37.5, 33.5, 33.3, 29.8, 26.8, 24.8, 22.8, 22.6, 21.6, 19.3, 19.2. HR-MS (EI) calcd. For $C_{20}H_{30}O$ $[M]^+$ 286.2297; found 286.2261.

Sugiol (2). To a solution of **3** (0.5 g, 1.59 mmol) in CH_2Cl_2 (10 mL) was added BBr_3 (1.0 M in CH_2Cl_2, 4.8 mL, 4.77 mmol) dropwise at 0 °C, and stirring was continued for 12 h. The reaction was quenched by H_2O and allowed to warm to room temperature gradually. The phases were separated, and the aqueous layer was extracted with CH_2Cl_2. The organic extracts were combined, washed with saturated $NaHCO_3$ solution, brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (1:1 hexane–EtOAc) to afford **2** (0.45 g, 94%) as white solids. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (s, 1H), 6.76 (s, 1H), 1.86–1.81 (m, 2H), 1.67 (dq, 1H, J = 6.8 and 14.0 Hz), 1.56–1.51 (m, 2H), 1.31 (dt, 1H, J = 3.6 and 13.6 Hz), δ1.23 (s, 3H), 1.21 (d, 3H, J = 6.8 Hz), 1.20 (d, 3H, J = 7.2 Hz), 1.02 (s, 3H), 0.94 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 158.4, 156.6, 132.8, 126.7, 124.8, 110.1, 49.6, 41.5, 38.0, 36.2, 33.4, 32.7, 26.9, 23.4, 22.6, 21.5, 19.0. HR-MS (EI) calcd. For $C_{20}H_{28}O_2$ $[M]^+$ 300.2089; found 300.2090.

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