Synthesis of (+)-Hinokiol, (+)-Hinokione, (+)-Salviol, and (+)-2-Oxoferruginol

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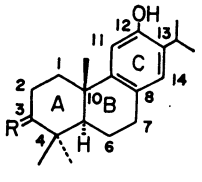
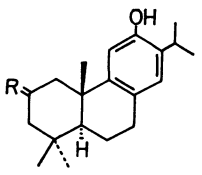
(Received August 11, 1980)

Reduction of abieta-5,8,11,13-tetraen-3-one with lithium aluminium hydride afforded the corresponding alcohol, which was submitted to catalytic hydrogenation to yield abieta-8,11,13-trien-3β-ol (**7**) together with its 5βH-isomer. Acetylation of **7**, followed by the Friedel-Crafts acylation, afforded 3β-acetoxy-12-acetylabieta-8,11,13-triene. This compound was converted into 3β,12-diacetoxyabieta-8,11,13-triene (**11**) by the Baeyer-Villiger oxidation. Treatment of **11** with lithium aluminium hydride yielded hinokiol, which was oxidized to hinokione. Subsequently, hinokiol was methylated and the resulting 12-methyl ether was dehydrated to afford 12-methoxyabieta-2,8,11,13-tetraene. The tetraene was then submitted to hydroboration-oxidation to give 12-methoxyabieta-8,11,13-trien-2α-ol (**15**) which, on demethylation with ethanethiol and anhydrous aluminium chloride, afforded salviol. Oxidation of **15** with pyridinium chlorochromate, followed by demethylation, gave 2-oxoferruginol.

Hinokiol (**1**) and hinokione (**2**) have been isolated from the heartwood of *Chamaecyparis obtusa*, Sieb. et. Zucc.,[1] *Cupressus torulosa* Don,[2] and *Tetraclinis articulata* (Vahl) Masters,[3] and from the leaf of *Torreya nucifera* Sieb. et. Zucc.[4] The similar diterpenes, salviol (**3**) and 2-oxoferruginol (**4**), have also been isolated from the roots of *Salvia miltiorrhiza* Bunge[5] and from the bark of *Podocarpus ferrugineus* D. Don,[6] respectively. All these natural diterpenes possess the oxygen functions in both the rings A and C of the abietane skeleton. As a part of our synthetic studies on the naturally-occurring terpenes, we have attempted the syntheses of these tricyclic diterpenes. This paper will describe the syntheses of (+)-hinokiol (**1**), (+)-hinokione (**2**),[7] (+)-salviol (**3**), and (+)-2-oxoferruginol (**4**), starting from the optically active abieta-5,8,11,13-tetraen-3-one (**5**) which was prepared from (+)-dehydroabietic acid by the known procedure.[8]



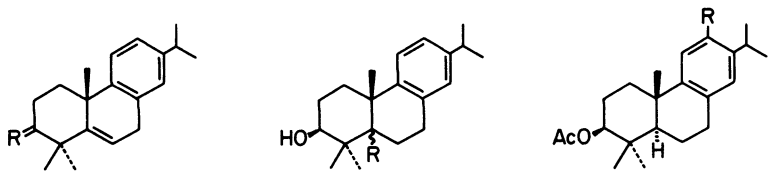
1 R=α-H, β-OH
2 R=O



3 R=α-OH, β-H
4 R=O

Reduction of **5** with lithium aluminium hydride in ether afforded abieta-5,8,11,13-tetraen-3β-ol (**6**). The β-configuration of the hydroxyl group at the C-3 position was supported by its NMR spectrum, which showed a triplet at δ 2.80 ppm with a half-height width of 16 Hz, suggesting the presence of an axial α hydrogen. Catalytic hydrogenation of **6** in methanol over Pd–C, followed by chromatographic purification, gave abieta-8,11,13-trien-3β-ol (**7**) as a major product and its 5βH-isomer (**8**) as a minor one. The NMR spectrum of **7** showed signals at δ 0.89 and 1.06 ppm due to the *gem*-dimethyl groups at the C-4 position, while that of **8** showed the corresponding signals at δ 0.39 and 0.99 ppm. The *cis*-configuration of the A/B ring junction in **8** was supported by the appearance of the signal due to one of the *gem*-dimethyl groups in very high field (δ 0.39 ppm),[9] owing to the shielding effect of the C ring The *trans*-isomer (**7**) was acetylated with acetic anhydride in pyridine to give 3β-acetoxyabieta-8,11,13-triene (**9**). The Friedel-Crafts acylation of **9** with acetyl chloride in dichloromethane in the presence of anhydrous aluminium chloride afforded 3β-acetoxy-12-acetylabieta-8,11,13-triene (**10**), whose IR spectrum showed carbonyl bands at 1725 and 1675 cm^{-1}. The NMR spectrum of **10** showed two singlets at δ 6.98 and 7.32 ppm due to the two aromatic protons. These spectral data of **10** supported the presence of an acetyl group at the C-12 position. The Baeyer-Villiger oxidation of **10** with *m*-chloroperbenzoic acid in dichloromethane afforded 3β,12-diacetoxyabieta-8,11,13-triene (hinokiol diacetate) (**11**).[1,4] Treatment of **11** with lithium aluminium hydride in ether yielded abieta-8,11,13-triene-3β,12-diol (hinokiol) (**1**)[1–4] which, on methylation with methyl iodide and anhydrous potassium carbonate in refluxing ethyl methyl ketone, afforded 12-methoxyabieta-8,11,13-trien-3β-ol (hinokiol 12-methyl ether) (**12**).[1] The synthetic **1** was then oxidized with Jones reagent to give 12-hydroxyabieta-8,11,13-trien-3-one (hinokione) (**2**).[1–3]

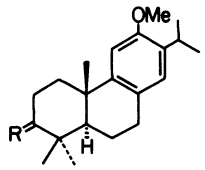
Our next effort was directed toward the syntheses of salviol (**3**) and 2-oxoferruginol (**4**). The methyl ether (**12**) was dehydrated with phosphoryl chloride in refluxing pyridine to yield 12-methoxyabieta-2,8,11,-13-tetraene (**13**). Hydroboration of **13**, followed by oxidation with alkaline hydrogen peroxide, afforded a mixture of alcohols. This was separated by column chromatography on silica gel to give 12-methoxyabieta-8,11,13-trien-3α-ol (**14**), **12**, and 12-methoxyabieta-8,11,13-trien-2α-ol (**15**). Oxidation of **14** with pyridinium chlorochromate[10] in dichloromethane afforded 12-methoxyabieta-8,11,13-trien-3-one(hinokione methyl ether) (**16**).[1,11] The alcohol (**14**) was also converted into **13** by dehydration with phosphoryl chloride in refluxing pyridine. The stereochemistry of the hydroxyl group at the C-2 position in **15** was assigned to be α-configuration by its NMR spectrum, which showed a signal due to the C-2 proton at δ 4.08 ppm with a half-height width of 22 Hz, suggesting the presence of an axial β hydrogen. Demethylation of **15** with anhydrous aluminium chloride and ethanethiol[12] in dichloro-



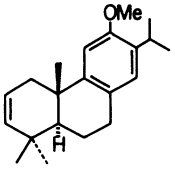
5 R=O
6 R=α-H,β-OH

7 R=α-H
8 R=β-H

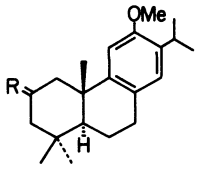
9 R=H
10 R=Ac
11 R=OAc



12 R=α-H,β-OH
14 R=α-OH,β-H
16 R=O



13



15 R=α-OH,β-H
17 R=O

methane afforded abieta-8,11,13-triene-2α,12-diol (salviol) (**3**).[5] Subsequently, the alcohol (**15**) was oxidized with pyridinium chlorochromate in dichloromethane to give 12-methoxyabieta-8,11,13-trien-2-one (**17**) which, on demethylation with boron tribromide in dichloromethane, afforded 12-hydroxyabieta-8,11,13-trien-2-one (2-oxoferruginol) (**4**).[6]

Experimental

All melting points are uncorrected. The IR spectra and optical rotations were measured in chloroform, and the NMR spectra in carbon tetrachloride at 60 MHz, with tetramethylsilane as an internal standard, unless otherwise stated. The chemical shifts are presented in terms of δ values; s: singlet, bs: broad singlet, d: doublet, bd: broad doublet, t: triplet, m: multiplet. Column chromatography was performed using Merck silica gel (0.063 mm).

Abieta-5,8,11,13-tetraen-3-one (5). According to the known procedure,[8] (+)-dehydroabietic acid was converted into **5**, $[\alpha]_D$ +32.9°, IR: 1705 cm^{-1}, NMR: 1.17, 1.23, and 1.32 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.37 (2H, d, J=4 Hz, =CH–$C\underline{H}_2$–), 5.90 (1H, t, J=4 Hz, C_6–H). Found: C, 84.76; H, 9.38%. Calcd for $C_{20}H_{26}O$: C, 85.05; H, 9.28%.

Abieta-5,8,11,13-tetraen-3β-ol (6). A mixture of **5** (1.159 g) and lithium aluminium hydride (156 mg) in dry ether (25 ml) was stirred at room temperature for 90 min. The mixture was poured into ice-dilute hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified by column chromatography on silica gel (30 g), using ether–benzene (2 : 98) as the eluent, to give **6** (1.107 g: 94.8%), $[\alpha]_D$ −69.7°; IR: 3615, 3450 cm^{-1}; NMR: 1.15, 1.20, and 1.27 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.21 (6H, d, J=6.5 Hz, $-CH(C\underline{H}_3)_2$), 2.80 (1H, t, J=7 Hz, $W_{1/2}$= 16 Hz, C_3–H), 3.31 (2H, bd, J=4 Hz, =CH–$C\underline{H}_2$–), 5.95 (1H, t, J=4 Hz, C_6–H). Found: C, 84.36; H, 10.04%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%.

Catalytic Hydrogenation of 6. A mixture of **6** (1.007 g) and 5% Pd–C (500 mg) in methanol (15 ml) was subjected to catalytic hydrogenation at room temperature for *ca.* 20 h. After the usual work-up, the crude product was purified by column chromatography on silica gel (60 g), using ether-benzene (0.5 : 99.5) as the eluent, to give 5βH-abieta-8,11,13-trien-3β-ol (**8**) (104 mg: 10.3%), $[\alpha]_D$ +22.4°; IR: 3628, 3463 cm^{-1}; NMR: 0.39, 0.99, and 1.18 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.22 (6H, d, J=6.5 Hz, $-CH(C\underline{H}_3)_2$), 1.87 (1H, s, –OH), 3.25 (1H, m, $W_{1/2}$=7 Hz, C_3–H). Found: C, 83.76; H, 10.73%. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%.

Further elution with ether-benzene (5 : 95) afforded abieta-8,11,13-trien-3β-ol (**7**) (683 mg: 67.3%), which was recrystallized from hexane; mp 136.5—138 °C; $[\alpha]_D$ +50.4°; IR: 3617, 3453 cm^{-1}; NMR ($CDCl_3$): 0.89, 1.06, and 1.18 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.22 (6H, d, J=6.5 Hz, $-CH(C\underline{H}_3)_2$), 1.68 (1H, s, –OH), 3.30 (1H, m, $W_{1/2}$=17 Hz, C_3–H). Found: C, 84.03; H, 10.75%. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56%.

3β-Acetoxyabieta-8,11,13-triene (9). A solution of **7** (679 mg) and acetic anhydride (2.5 ml) in pyridine (7.0 ml) was heated at 74—77 °C for 1.5 h. After the usual work-up, the crude product was purified by column chromatography on silica gel (30 g), using hexane–benzene (35 : 65) as the eluent, to give **9** (750 mg: 96.3%), which was recrystallized from hexane; mp 112—114 °C; $[\alpha]_D$ +58.9°; IR: 1720 cm^{-1}; NMR: 0.94 (6H, s, $-\dot{C}(CH_3)_2$), 1.19 (3H, s, C_{10}–CH_3), 1.20 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 2.00 (3H, s, $-OCOCH_3$), 4.5 (1H, m, C_3–H), 6.79 (bs), 6.87 (bd, J=8 Hz), and 7.07 (bd, J=8 Hz) (each 1H, aromatic protons). Found: C, 80.71; H, 9.99%. Calcd for $C_{22}H_{32}O_2$: C,80.44; H, 9.83%.

3β-Acetoxy-12-acetylabieta-8,11,13-triene (10). Anhydrous aluminium chloride (850 mg) was added at 0—5 °C to a stirred solution of **9** (696 mg) and acetyl chloride (500 mg) in dichloromethane (10 ml). The mixture was stirred at this temperature for 30 min and then at room temperature for 24 h, poured into ice-dilute hydrochloric acid, and extracted with ether. The ether extract was washed successively with water, aqueous sodium hydrogencarbonate, and water. The dried extract was evaporated *in vacuo* to give a crude product, which was purified by column chromatography on silica gel (15 g), using ether–benzene (1 : 99) as the eluent, to afford **10** (748 mg: 95.3%). This was recrystallized from a mixture of acetone and hexane; mp 163.5—165.5 °C; $[\alpha]_D$ +62.6°; IR: 1725, 1675 cm^{-1}; NMR: 0.95 (6H, s, $-\dot{C}(C\underline{H}_3)_2$), 1.16 and 1.20 (each 3H, d, and J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.21 (3H, s, C_{10}–CH_3), 2.00 (3H, s, $-OCOCH_3$), 2.46 (3H, s, $-COCH_3$), 3.46 (1H, m, $-C\underline{H}(CH_3)_2$), 4.45 (1H, m, C_3–H), 6.98 (1H, s, C_{14}–H), 7.32 (1H, s, C_{11}–H). Found: C, 77.85; H, 9.48%. Calcd for $C_{24}H_{34}O_3$: C, 77.80; H, 9.25%.

3β,12-Diacetoxyabieta-8,11,13-triene (Hinokiol Diacetate) (11). A mixture of **10** (739 mg), *m*-chloroperbenzoic acid (85%: 610 mg), and *p*-toluenesulfonic acid (40 mg) in 1,2-dichloroethane (10 ml) was refluxed for 3.5 h. The mixture was then cooled, diluted with ether, and washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and water. The dried ether solution was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (25 g), using ether–benzene (1 : 99) as the eluent, to give **11** (647 mg: 83.9%), which was recrystallized from ethanol; mp 145—146 °C; $[\alpha]_D$ +69.8° (EtOH) (lit,[1] mp 143 °C, $[\alpha]_D$ +70.39° (EtOH)); IR: 1750, 1725 cm^{-1}; NMR: 0.94 (6H, s, $-\dot{C}(CH_3)_2$), 1.16 (6H, d, J=6.5 Hz, $-CH(C\underline{H}_3)_2$), 1.22 (3H, s, $C_{10}-CH_3$), 2.00 (3H, s, $C_3-OCOCH_3$), 2.22 (3H, s, $C_{12}-OCOCH_3$), 4.48 (1H, m, C_3–H), 6.76 and 6.89 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 74.27; H, 8.92%. Calcd for $C_{24}H_{34}O_4$: C, 74.57; H, 8.87%.

Further elution gave the recovered **10** (58 mg: 7.9%).

Abieta-8,11,13-triene-3β,12-diol (Hinokiol) (1). A mixture of **11** (575 mg) and lithium aluminium hydride (140 mg) in dry ether (10 ml) was stirred at 0—5 °C for 45 min and then at room temperature for 30 min. The mixture was poured into ice-dilute hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was purified by column chromatography on silica gel (30 g), using acetone–benzene (3 : 7) as the eluent, to give hinokiol (**1**) (401 mg: 89.1%), which was recrystallized from ethanol; mp 240—242 °C; $[\alpha]_D$ +66.2° (EtOH) (lit, mp 240—242 °C,[3] $[\alpha]_D$ +67.3° (EtOH)[4]); IR (KBr): 3540, 3280 cm^{-1}; NMR (pyridine-d_5): 1.09, 1.23, and 1.25 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.39 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 7.15 and 7.18 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.19; H, 10.11%. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00%. The identity of the synthetic **1** with natural hinokiol provided by Professor T. Hirose was confirmed by mixed melting point determination and by IR spectral comparison.

12-Hydroxyabieta-8,11,13-trien-3-one (Hinokione) (2). A solution of **1** (69 mg) in acetone (6.0 ml) was oxidized with Jones reagent (1 M†: 0.2 ml) at 5 °C for 3 min. The mixture was diluted with ether, washed with water, and dried over sodium sulfate. The ether solution was evaporated and the residue was purified by column chromatography on silica gel (10 g), using ether–benzene (3 : 97) as the eluent, to give **2** (49.2 mg: 71.8%), which was recrystallized from a mixture of ether and hexane; mp 192—193 °C; $[\alpha]_D$ +115.6° (EtOH) (lit,[3] mp 191—192 °C, $[\alpha]_D$ +111.9° (EtOH)); IR: 3605, 3380, 1696 cm^{-1}; NMR ($CDCl_3$): 1.14, 1.18, and 1.30 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 6.66 and 6.89 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.71; H, 9.53%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

12-Methoxyabieta-8,11,13-trien-3β-ol (12). A mixture of **1** (99 mg), methyl iodide (0.5 ml), anhydrous potassium carbonate (1.0 g), and ethyl methyl ketone (5.0 ml) was stirred and refluxed for 8 h. The mixture was cooled, diluted with ether, and water was added. The organic layer was separated, washed first with aqueous sodium thiosulfate and then with water, and then dried over sodium sulfate. After the solvent had been evaporated *in vacuo*, the residue was purified by column chromatography on silica gel (10 g), using ether–benzene (1 : 99) as the eluent, to give **12** (75.8 mg: 72.8%), which was recrystallized from hexane; mp 105.5—107.5 °C (softened at *ca.* 94 °C); $[\alpha]_D$ +61.0° (EtOH) (lit,[1] mp 95—96 °C, $[\alpha]_D$ +59.46° (EtOH)); IR: 3625, 3455 cm^{-1}; NMR: 0.86, 1.04, and 1.19 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.15 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.61 (1H, s, –OH), 3.75 (3H, s, $-OCH_3$), 6.58 and 6.72 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.46; H, 10.35%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

12-Methoxyabieta-2,8,11,13-tetraene (13). a): A mixture of **12** (938 mg), phosphoryl chloride (1.4 ml), and pyridine (10 ml) was refluxed for 1 h, cooled, and then poured into ice-dilute hydrochloric acid. The mixture was extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (40 g), using hexane–benzene (7 : 3) as the eluent, to give **13** as an oil (764 mg: 86.3%); $[\alpha]_D$ +163°; IR: 1655 cm^{-1}; NMR: 0.98, 1.03, and 1.23 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.17 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.21 (1H, m, $-C\underline{H}(CH_3)_2$), 3.75 (3H, s, $-OCH_3$), 5.49 (2H, s, C_2–H and C_3–H), 6.58 and 6.71 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 84.49; H, 10.32%. Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13%.

b): A mixture of 12-methoxyabieta-8,11,13-trien-3α-ol (**14**) (56.4 mg), phosphoryl chloride (0.09 ml), and pyridine (2.0 ml) was refluxed for 1 h. After the work-up described in *a*), the crude product was chromatographed on silica gel (5 g) to give the tetraene derivative (46.2 mg: 86.9%), whose IR and NMR spectra were identical with those of **13**.

Hydroboration-oxidation of 13. Boron trifluoride etherate (1.16 ml) was added dropwise at 0—5 °C to a stirred mixture of **13** (759 mg) and sodium borohydride (260 mg) in dry tetrahydrofuran (12 ml) in a stream of nitrogen. After the mixture had been stirred at this temperature for 2 h, there was added successively aqueous tetrahydrofuran (50%: 1.0 ml), aqueous sodium hydroxide (12%: 3.0 ml), and hydrogen peroxide (30%: 3.0 ml) at −5—0 °C. The mixture was stirred at −5—0 °C for 30 min and then at room temperature for 1 h, poured into dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (70 g), using ether–benzene (2 : 98) as the eluent, to give 12-methoxyabieta-8,11,13-trien-3α-ol (**14**) (305 mg: 37.9%), which was recrystallized from hexane; mp 114—114.5 °C; $[\alpha]_D$ +49.1° (EtOH) (lit,[1] mp 117—118 °C, $[\alpha]_D$ +45.25° (EtOH)); IR: 3630, 3455 cm^{-1}; NMR: 0.90, 0.96, and 1.16 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.15 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.72 (1H, s, –OH), 3.20 (1H, m, $-C\underline{H}(CH_3)_2$), 3.36 (1H, m, $W_{1/2}$=7 Hz, C_3–H), 3.75 (3H, s, $-OCH_3$), 6.59 and 6.71 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.70; H, 10.48%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

Further elution gave **12** (102 mg: 12.7%). Elution with ether–benzene (5 : 95) gave 12-methoxyabieta-8,11,13-trien-2α-ol (**15**) (141 mg: 17%), which was recrystallized from hexane; mp 130—131.5 °C; $[\alpha]_D$ +64.3°; IR 3611, 3430 cm^{-1}; NMR ($CDCl_3$): 0.98, 1.01, and 1.24 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.19 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.25 (1H, m, $-C\underline{H}(CH_3)_2$), 3.80 (3H, s, $-OCH_3$), 4.08 (1H, m, $W_{1/2}$= 22 Hz, C_2–H), 6.76 and 6.88 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.99; H, 10.40%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

12-Methoxyabieta-8,11,13-trien-3-one (16). Pyridinium chlorochromate (220 mg) was added at 0—5 °C to a stirred solution of **14** (193 mg) in dichloromethane (4.5 ml). The mixture was stirred at room temperature for an additional 1.5 h and then diluted with ether. After the addition of

† 1M = 1 mol dm^{-3}.

water, the mixture was extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (10 g), using ether–benzene (1 : 99) as the eluent, to give **16** (132 mg: 68.4%), which was recrystallized from ethanol; mp 123.5—124.5 °C; $[\alpha]_D$ +132° (EtOH) (lit,[1] mp 126 °C, $[\alpha]_D$ +122.2° (EtOH)); IR: 1700 cm^{-1}; NMR: 1.10 (6H, s, $-\dot{C}(CH_3)_2$), 1.16 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.28 (3H, s, $C_{10}-CH_3$), 3.20 (1H, m, $-C\underline{H}-(CH_3)_2$), 3.77 (3H, s, $-OCH_3$), 6.58 and 6.75 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 80.03; H, 9.86%. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%.

Abieta-8,11,13-triene-2α,12-diol (Salviol) (3). A mixture of **15** (51.5 mg), ethanethiol (0.5 ml), anhydrous aluminium chloride (150 mg), and dichloromethane (1.5 ml) was stirred at room temperature for 1 h, poured into ice-dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and then evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (5 g), using ether–benzene (4 : 6) as the eluent, to give salviol (**3**) (47.3 mg: 96.1%), which was recrystallized from benzene; mp 106—107 °C (softened at *ca.* 103 °C); $[\alpha]_D$ +55.7° (EtOH) (lit,[5] mp 108 °C); IR (KBr): 3395 cm^{-1}; NMR ($CDCl_3$, 90 MHz): 0.96, 1.00, and 1.23 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.23 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$). 3.15 (1H, m, $-C\underline{H}(CH_3)_2$) 4.09 (1H, m, $W_{1/2}$=22 Hz, C_2–H), 6.06 (1H, s, $=\dot{C}-OH$), 6.68 and 6.83 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.15; H, 10.13%. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00%. The IR and NMR spectra of the synthetic **3** were identical with those of natural salviol provided by Professor H. Kakisawa.

12-Methoxyabieta-8,11,13-trien-2-one (17). Pyridinium chlorochromate (148 mg) was added at 0—5 °C to a stirred solution of **15** (140 mg) in dichloromethane (2.5 ml) and the mixture was stirred at room temperature for 1.5 h. After the work-up described for the preparation of **16**, the crude product was purified by column chromatography on silica gel (10 g), using ether–benzene (3 : 97) as the eluent, to give **17** (109 mg: 78.1%). This was recrystallized from ethanol; mp 152.5—153.5 °C; $[\alpha]_D$ +48.6°; IR: 1703 cm^{-1}; NMR: 0.98, 1.13, and 1.21 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.15 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.20 (1H, m, $-C\underline{H}-(CH_3)_2$), 3.77 (3H, s, $-OCH_3$), 6.51 and 6.76 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.93; H, 9.83%. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%.

12-Hydroxyabieta-8,11,13-trien-2-one (2-Oxoferruginol) (4). A mixture of **17** (76.9 mg) and boron tribromide (0.07 ml) in dichloromethane (1.5 ml) was stirred at 0—5 °C for 30 min. The reaction mixture was poured into ice–water and extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and then evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (7 g) using chloroform as the eluent, to give 2-oxoferruginol (**4**) (61.8 mg: 84.1%), which was recrystallized from methanol; mp 237—239 °C; $[\alpha]_D$ +48.3° (MeOH) (lit,[6] mp 232—234 °C, $[\alpha]_D$ +50° (MeOH)); IR (KBr): 3450, 1706 cm^{-1}; NMR ($CDCl_3$, 90 MHz): 0.99, 1.15, and 1.21 (each 3H and s, $-\dot{C}-(CH_3)_2$ and $C_{10}-CH_3$), 1.23 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.14 (1H, m, $-C\underline{H}(CH_3)_2$), 5.48 (1H, s, –OH), 6.55 and 6.85 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 80.08; H, 9.56%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

The authors are grateful to Arakawa Chemical Co. Ltd. for a generous gift of rosin. Thanks are also due to Professor H. Kakisawa, Tsukuba University, and to Professor T. Hirose, Science University of Tokyo, for kindly supplying the spectral data and natural hinokiol.

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