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Structure and Synthesis of (+)-Shonanol

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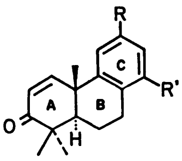
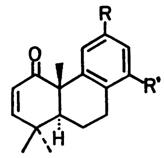
The structure of shonanol was restudied and found to be 12-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**) by the following synthesis. A Grignard reaction of methyl (+)-12-methoxyabieta-8,11,13-trien-18-oate with phenylmagnesium bromide, followed by treatment with lead tetraacetate and calcium carbonate afforded a mixture of Δ^3-, Δ^4-, and $\Delta^{4(18)}$-19-nor compounds. This was oxidized with selenium dioxide to give (+)-12-methoxy-19-norabieta-4(18),8,11,13-tetraen-3α-ol. This alcohol was converted to (+)-12-methoxyabieta-5,8,11,13-tetraen-3-one (**6**) by the known procedure. Reduction of **6** with lithium aluminium hydride, followed by catalytic hydrogenation, yielded (+)-12-methoxyabieta-8,11,13-trien-3β-ol (**8**) and a small amount of its *cis* isomer. The compound (**8**) was then converted to (+)-12-methoxyabieta-1,8,11,13-tetraen-3-one (**12**) by a series of reactions: oxidation with pyridinium chlorochromate, bromination with pyridinium tribromide, and dehydrobromination with lithium carbonate and lithium bromide. Demethylation of **12** with boron tribromide gave (+)-12-hydroxyabieta-1,8,11,13-tetraen-3-one. Oxidation of **12** with alkaline hydrogen peroxide, followed by treatment with hydrazine hydrate, gave (+)-12-methoxyabieta-2,8,11,13-tetraen-1α-ol; this was oxidized with Jones reagent to give the corresponding 1-oxo compound. The 1-oxo compound was finally demethylated with boron tribromide to yield (+)-**1**, whose spectra were identical with those of natural shonanol.

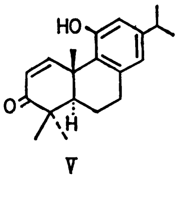
The structure of shonanol, a tricyclic diterpene phenol isolated from the sawdust of *Libocedrus formosana* by Lin and Liu[1] in 1965, has been tentatively assigned as 12-hydroxytotara-1,8,11,13-tetraen-3-one (I) on the basis of spectroscopic studies. To confirm this structure we synthesized (±)-I in our laboratory.[2] However, this synthetic (±)-I was shown to be different from natural shonanol by spectral comparison. Further synthetic studies on the structural isomers[3,4] possessing a hydroxyl group at the position meta to an isopropyl group in the C ring: (±)-12-hydroxytotara-2,8,11,13-tetraen-1-one (II), (±)-14-hydroxy-12-isopropylpodocarpa-1,8,11,13-tetraen-3-one (III), (±)-14-hydroxy-12-isopropylpodocarpa-2,8,11,13-tetraen-1-one (IV), (+)-11-hydroxyabieta-1,8,11,13-tetraen-3-one (V), and (+)-11-hydroxyabieta-2,8,11,13-tetraen-1-one (VI), led to the same result, whereas the spectral analyses of these synthetic materials I—VI and natural shonanol suggested that the structure of shonanol is 12-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**).[4] To confirm the validity of our proposed structure, we now attempted the synthesis of **1**. This paper will describe the structural confirmation of natural shonanol by the synthesis of (+)-**1** starting from methyl (+)-12-methoxyabieta-8,11,13-trien-18-oate (**2**).[5,6]



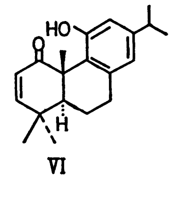
I R=OH, R'=i-Pr
III R=i-Pr, R'=OH



II R=OH, R'=i-Pr
IV R=i-Pr, R'=OH



V



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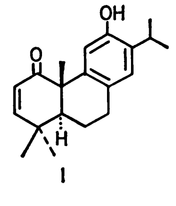
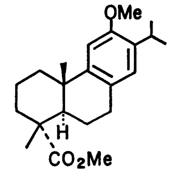


1

The Grignard reaction of **2** with phenylmagnesium bromide at 95—100 °C afforded a diphenylmethanol derivative (**3**: 80%). This was treated with lead tetraacetate and calcium carbonate in refluxing benzene to give a mixture (**4**: 78%) of Δ^3-, Δ^4-, and $\Delta^{4(18)}$-19-nor compounds in a ratio of *ca.* 1:2:7. The mixture was then oxidized with selenium dioxide in refluxing aqueous ethanol to yield (+)-12-methoxy-19-norabieta-4(18), 8,11,13-tetraen-3α-ol (**5**: 51%).[7,8] This alcohol (**5**) was subsequently converted to (+)-12-methoxyabieta-5,8,11,13-tetraen-3-one (**6**) by a series of known procedures:[7] isomerization with lithium in ethylenediamine to 12-methoxy-19-norabieta-4,8,11,13-tetraen-3α-ol, Jones oxidation, and methylation with methyl iodide in the presence of potassium *t*-butoxide. Reduction of **6** with lithium aluminium hydride in ether afforded (−)-12-methoxyabieta-5,8,11,13-tetraen-3β-ol (**7**: 90%), which was submitted to catalytic hydrogenation over 5% Pd–C in methanol to yield (+)-12-methoxyabieta-8,11,13-trien-3β-ol (**8**: 68%)[9,10] as a major product and its *cis* isomer (**9**: 11%) as a minor one. The stereochemistry of the hydroxyl group at the C-3 position in **7**, which was expected to be β-configuration from many literature precedents,[2,3,10,11] was confirmed by the conversion to the known compound (**8**).[9,10] The *cis*-configuration of the A/B ring junction in **9** was supported by the appearance of a signal due to one of the *gem*-dimethyl groups at the C-4 position in very high field (δ 0.42 ppm) owing to the shielding effect of the aromatic C ring. The β-configuration of the hydroxyl group at the C-3 position was also supported by a signal at δ 3.22 ppm with half-height width of 9 Hz, suggesting the presence



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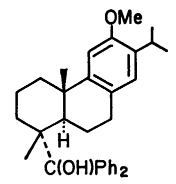

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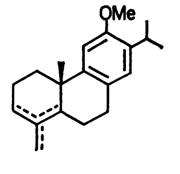

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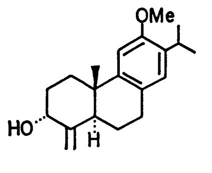

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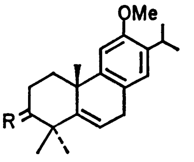
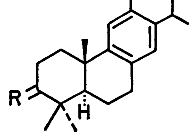
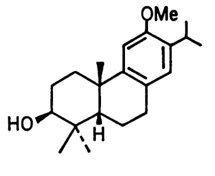


6 R=O
7 R=β-OH,α-H



8 R=β-OH,α-H
10 R=O



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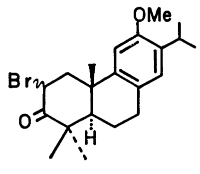

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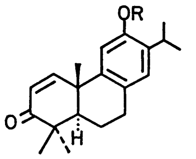
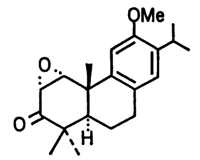


12 R=Me
13 R=H



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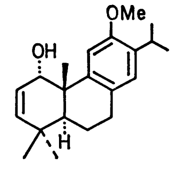

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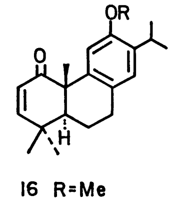

16 R=Me
17 R=Ac

of an equatorial α hydrogen. Oxidation of the *trans*-compound (**8**) with pyridinium chlorochromate in dichloromethane afforded (+)-12-methoxyabieta-8,11,13-trien-3-one (**10**: 73%).[7,9,10] On bromination with pyridinium tribromide in ethanol and chloroform, this was converted to a mixture of the epimeric 2-bromo derivatives (**11**: 69%). The mixture (**11**), without purification, was immediately treated with lithium carbonate and lithium bromide in *N*,*N*-dimethylformamide at 120—125 °C to produce (+)-12-methoxyabieta-1,8,11,13-tetraen-3-one (**12**: 63%), which was demethylated with boron tribromide in dichloromethane to give (+)-12-hydroxyabieta-1,8,11,13-tetraen-3-one (**13**: 82%).[12] The physical and spectral data of **13** were different from those of natural shonanol.

Subsequently, 1,3-carbonyl transposition[3,4,13] of the α,β-unsaturated carbonyl group in **12** was carried out as follows. Oxidation of **12** with alkaline hydrogen peroxide in methanol and dichloromethane at −10—−5 °C, followed by treatment of the resulting epoxy ketone (**14**)[14] with hydrazine hydrate in refluxing methanol containing a small amount of acetic acid, yielded (+)-12-methoxyabieta-2,8,11,13-tetraen-1α-ol (**15**: 49% from **12**). This alcohol (**15**) was then oxidized with Jones reagent. The resulting (+)-12-methoxyabieta-2,8,11,13-tetraen-1-one (**16**: 78%) was demethylated with boron tribromide to give (+)-12-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**: 74%), whose melting point and spectra (IR and ^{1}H NMR) were identical with those of natural shonanol. The synthetic **1** was further characterized as its acetate (**17**).

From the present study, the structure of shonanol was conclusively assigned as **1**.

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, t: triplet, m: multiplet. Column chromatography was performed using Merck silica gel (0.063 mm).

*Grignard Reaction of Methyl 12-Methoxyabieta-8,11,13-trien-18-oate (**2**) with Phenylmagnesium Bromide.* A solution of **2**[5,6] (43.985 g) in dry ether (90 ml) was added to a refluxing ethereal solution of phenylmagnesium bromide prepared from magnesium turnings (12.4 g) and bromobenzene (80.2 g) in dry ether (180 ml). The mixture was refluxed for 1 h, the ether was removed, and the viscous residue was heated at 95—100 °C for 8 h. After standing overnight at room temperature, the mass was carefully hydrolyzed with a mixture of dilute hydrochloric acid and ice, and then extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated. The residue was recrystallized from acetone–hexane to give a diphenylmethanol derivative (**3**) (34.796 g), mp 205—207.5 °C, $[\alpha]_D$ +97.4° (*c* 2.73), IR: 3591 cm^{-1}; NMR: 1.10 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 1.22 and 1.34 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 2.33 (1H, s, –OH, disappeared on deuteration), 3.14 (1H, m, $-C\underline{H}(CH_3)_2$), 3.69 (3H, s, $-OCH_3$), 6.53 (2H, s, C_{11}–H and C_{14}–H), 7.0—7.9 (10H, m, 2-C_6H_5). Found: C, 84.79; H, 8.86%. Calcd for $C_{33}H_{40}O_2$: C, 84.57; H, 8.60%.

The mother liquor of recrystallization was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (300 g), using hexane–benzene (6:4 and then 4:6) as the eluent, to give an additional alcohol (**3**: 10.047 g).

*Fragmentation of **3** with Lead Tetraacetate.* A solution of **3** (18.383 g) in dry benzene (100 ml) was added to a stirred suspension of 87% lead tetraacetate (24.0 g) and calcium carbonate (23.5 g) in dry benzene (150 ml). The mixture was refluxed for 8 h, cooled, and then filtered. The filtrate was diluted with ether and the solution was washed successively with 10% aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. The dried solution was evaporated *in vacuo* and the residue was purified by column chromatography on silica gel (200 g), using hexane as the eluent, to give a mixture of Δ^3-, Δ^4-, and $\Delta^{4(18)}$-19-nor compounds (**4**) (8.654 g: 77.6%). The NMR spectrum of the mixture indicated that it was composed of approximately 7% of Δ^3- (δ 1.02 ppm, C_{10}–CH_3; 5.38 ppm, C_3–H), 21% of Δ^4- (δ 1.36 ppm, C_{10}–CH_3), and 72% of $\Delta^{4(18)}$-19-nor compound (δ 0.99 ppm, C_{10}–CH_3; 4.57 and 4.81 ppm, $CH_2{=}\overset{|}{C}-$).

12-Methoxy-19-norabieta-4(18),8,11,13-tetraen-3α-ol (5). A solution of selenium dioxide (1.494 g) in ethanol (48 ml) and water (2.0 ml) was added dropwise to a stirred suspension of **4** (7.661 g) in ethanol (50 ml). The mixture was refluxed for 4 h, cooled, and then filtered. The filtrate was diluted with chloroform, evaporated *in vacuo*, and the residue was chromatographed on aluminium oxide (Merck activ. II—III: 150 g), using ether–benzene (1:9 and then 4:6) as the eluent, to give **5**[7,8] (4.097 g: 50.6%) which was recrystallized from hexane, mp 59—61 °C, $[\alpha]_D$ +159° (*c* 5.80); IR: 3610, 3415 cm⁻¹; NMR: 0.91 (3H, s, C_{10}–CH_3), 1.17 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 2.58 (1H, s, -OH, disappeared on deuteration), 3.22 (1H, m, $-C\underline{H}(CH_3)_2$), 3.73 (3H, s, $-OCH_3$), 4.17 (1H, bs, $W_{1/2}$=5 Hz, C_3–H), 4.60 and 4.92 (each 1H and bs, $CH_2{=}\overset{|}{C}-$), 6.63 and 6.77 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.86; H, 9.55%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

12-Methoxyabieta-5,8,11,13-tetraen-3-one (6). The 3α-ol (**5**) was converted to **6** by the known procedure.[7] The crude product was purified by column chromatography on silica gel, using ether–benzene (1.5:98.5) as the eluent, to give **6** which was recrystallized from hexane, mp 92.5—93.5 °C, $[\alpha]_D$ +41.3° (*c* 3.25), IR: 1705 cm⁻¹; NMR: 1.18 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 1.18, 1.24, and 1.32 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 3.32 (2H, d, *J*=4 Hz, $=CHC\underline{H}_2-$), 3.78 (3H, s, $-OCH_3$), 5.90 (1H, t, *J*=4 Hz, C_6–H), 6.72 and 6.85 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 80.77; H, 9.14%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

12-Methoxyabieta-5,8,11,13-tetraen-3β-ol (7). A mixture of **6** (502 mg) and lithium aluminium hydride (61 mg) in dry ether (15 ml) was stirred at room temperature for 80 min, poured into a mixture of ice and 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 (15 g), using ether–benzene (2:98) as the eluent, to give **7** (457 mg: 90.5%), which was recrystallized from hexane, mp 69—71 °C, $[\alpha]_D$ −53.5° (*c* 3.10); IR: 3616, 3454 cm⁻¹, NMR: 1.13, 1.21, and 1.28 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.17 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 2.17 (1H, s, -OH, disappeared on deuteration), 3.26 (2H, d, *J*=4 Hz, $=CHC\underline{H}_2-$), 3.75 (3H, s, $-OCH_3$), 5.97 (1H, t, *J*=4 Hz, C_6–H), 6.68 and 6.80 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.92; H, 9.91%. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%.

Catalytic Hydrogenation of 7. A mixture of **7** (456 mg) and 5% Pd-C (450 mg) in methanol (10 ml) was subjected to catalytic hydrogenation at room temperature for *ca.* 24 h. After the usual work-up, the crude product was purified by column chromatography on silica gel (40 g), using ether–benzene (1:99) as the eluent, to give 12-methoxy-5βH-abieta-8,11,13-trien-3β-ol (**9**) (51 mg: 11.1%) $[\alpha]_D$ +41.2° (*c* 1.68); IR: 3630, 3455 cm⁻¹; NMR: 0.42, 0.99, and 1.18 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.15 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 1.60 (1H, s, -OH, disappeared on deuteration), 3.22 (1H, m, $W_{1/2}$=9 Hz, C_3–H), 3.75 (3H, s, $-OCH_3$), 6.67 and 6.70 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.42; H, 10.33%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

Further elution with ether–benzene (5:95) afforded 12-methoxyabieta-8,11,13-trien-3β-ol (**8**)[9,10] (314 mg: 68.4%) which was recrystallized from hexane, mp 104—105 °C (softened at *ca.* 95 °C), $[\alpha]_D$ +60.7° (*c* 2.39); IR: 3625, 3455 cm⁻¹; NMR: 0.85, 1.04, and 1.19 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.16 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 1.95 (1H, s, -OH, disappeared on deuteration), 3.20 (1H, m, $W_{1/2}$=15 Hz, C_3–H), 3.74 (3H, s, $-OCH_3$), 6.58 and 6.72 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 79.94; H, 10.30%. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19%.

12-Methoxyabieta-8,11,13-trien-3-one (10). Pyridinium chlorochromate (2.74 g) was added at 0—5 °C to a stirred solution of **8** (2.649 g) in dry dichloromethane (30 ml) over a 5 min period. The mixture was stirred at room temperature for 2 more hours and then diluted with ether. After the addition of 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 chromatographed on silica gel (80 g), using ether–benzene (1:99) as the eluent, to give **10** (1.911 g: 72.6%), whose IR and NMR spectra were identical with those of authentic hinokione methyl ether.[10]

12-Methoxyabieta-1,8,11,13-tetraen-3-one (12). A mixture of **10** (1.295 g) and 80% pyridinium tribromide (1.482 g) in ethanol (13.3 ml) and chloroform (26.6 ml) was stirred at room temperature for 30 min. After the addition of aqueous sodium thiosulfate, the mixture was extracted with ether. The ether extract was washed with dilute hydrochloric acid and brine, dried over sodium sulfate, and then evaporated *in vacuo*. The residue was chromatographed on silica gel (100 g), using hexane–benzene (1:1) as the eluent, to give a mixture of epimeric 2-bromo derivatives (**11**) (1.115 g: 68.9%), which was immediately submitted to dehydrobromination.

A mixture of **11** (1.009 g), lithium carbonate (570 mg), and lithium bromide (446 mg) in *N*,*N*-dimethylformamide (16 ml) was stirred at 120—125 °C for 3 h in a stream of nitrogen. The reaction mixture was cooled, poured into dilute sulfuric acid, and extracted with ether. The ether extract was washed with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and then evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (30 g), using benzene as the eluent, to give **12** (505 mg: 62.9%), which was recrystallized from hexane, mp 145.5—146.5 °C, $[\alpha]_D$ +158° (*c* 0.505), IR: 1665 cm⁻¹; NMR: 1.14, 1.17, and 1.39 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.15 (6H, d, *J*=7 Hz, $-CH(C\underline{H}_3)_2$), 3.19 (1H, m, $-C\underline{H}(CH_3)_2$), 3.73 (3H, s, $-OCH_3$), 5.89 (1H, d, *J*=10 Hz, C_2–H), 6.72 and 6.77 (each 1H and s, C_{11}–H and C_{14}–H), 7.46 (1H, d, *J*=10 Hz, C_1–H). Found: C, 80.70; H, 9.16%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

12-Hydroxyabieta-1,8,11,13-tetraen-3-one (13). A solution of **12** (58.4 mg) and boron tribromide (0.05 ml) in dichloromethane (1.5 ml) was allowed to stand at 0—5 °C for 30 min, poured into a mixture of ice and water, and extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and water, dried over sodium sulfate, and then evaporated *in vacuo*. The crude product was chromatographed on silica gel (3.0 g), using ether–benzene (3:97) as the eluent, to give **13** (45.9 mg: 82.3%), which was recrystallized from acetone–hexane, mp 175.5—176.5 °C, $[\alpha]_D$ +162° (*c* 0.500, EtOH) (lit,[12] mp 175—178 °C, $[\alpha]_D$ +163° (EtOH)); IR: 3607, 3357, 1665 cm^{-1}; NMR (90 MHz): 1.16, 1.18, and 1.36 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.22 (6H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 3.15 (1H, m, $-C\underline{H}(CH_3)_2$), 5.73 (1H, s, -OH), 5.94 (1H, d, $J=10$ Hz, C_2–H), 6.69 and 6.78 (each 1H and s, C_{11}–H and C_{14}–H), 7.43 (1H, d, $J=10$ Hz, C_1–H). Found: C, 80.21; H, 8.92%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

*12-Methoxyabieta-2,8,11,13-tetraen-1α-ol (**15**).* A solution of **12** (500 mg) in methanol (75 ml) and dichloromethane (25 ml) was cooled to −15 °C and over *ca.* 6 min was added dropwise 30% hydrogen peroxide (0.92 ml), followed by 10% aqueous sodium hydroxide (3.24 ml), in a stream of nitrogen. The solution was stirred at −10—−5 °C for 2 h, poured into water (50 ml), and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and then evaporated to give the corresponding epoxy ketone (**14**) (525 mg).

A solution of the crude epoxy ketone (**14**: 140 mg) in methanol (10 ml) was cooled to 0 °C in a stream of nitrogen and a mixture of hydrazine hydrate (0.65 ml) and acetic acid (0.13 ml) was added dropwise over a 3 min period. The reaction mixture was stirred at 0—5 °C for an additional 15 min, at room temperature for 15 min, and then refluxed for 13.5 h. After the methanol had been evaporated *in vacuo*, the residue was extracted with ether. The ether extract was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and then evaporated *in vacuo*. The crude product was chromatographed on silica gel (10 g), using ether–benzene (1:99) as the eluent, to give **15** (65.6 mg: 48.9% from **12**) as an oil, $[\alpha]_D$ +251° (*c* 3.49), IR: 3550 cm^{-1}; NMR: 0.98, 1.08, and 1.17 (each 3H and s, $-\overset{|}{C}(CH_3)_2$ and C_{10}–CH_3), 1.19) (6H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 1.41 (1H, s, -OH, disappeared on deuteration), 3.21 (1H, m, $-C\underline{H}(CH_3)_2$), 3.78 (3H, s, $-OCH_3$), 4.23 (1H, d, $J=5$ Hz, C_1–H), 5.64 (2H, m, C_2–H and C_3–H), 6.59 and 6.77 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 80.16; H, 9.90%. Calcd for $C_{21}H_{30}O_2$: C, 80.21; H, 9.62%.

*12-Methoxyabieta-2,8,11,13-tetraen-1-one (**16**).* A solution of **15** (170 mg) in acetone (3.0 ml) was oxidized at −12—−6 °C for 5 min with Jones reagent (2.5 M: 0.2 ml) and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was purified by column chromatography on silica gel (10 g), using benzene as the eluent, to give **16** (133 mg: 78.2%), which was recrystallized from hexane, mp 106.5—107 °C, $[\alpha]_D$ +333° (*c* 4.60), IR: 1677 cm^{-1}; NMR: 1.17 (6H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 1.19 (6H, s, $-\overset{|}{C}(CH_3)_2$), 1.47 (3H, s, C_{10}–CH_3), 3.21 (1H, m, $-C\underline{H}(CH_3)_2$), 3.74 (3H, s, $-OCH_3$), 5.78 (1H, d, $J=10$ Hz, C_3–H), 6.38 (1H, d, $J=10$ Hz, C_2–H), 6.66 and 7.22 (each 1H and s, C_{11}–H and C_{14}–H). Found: C, 80.77; H, 9.13%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

*12-Hydroxyabieta-2,8,11,13-tetraen-1-one (Shonanol) (**1**).* A solution of **16** (108.2 mg) and boron tribromide (0.10 ml) in dichloromethane (3.0 ml) was allowed to stand at 0—5 °C for 1 h. After the same work-up as described for the preparation of **13**, the crude product was chromatographed on silica gel (10 g), using ether–benzene (1:99 and then 3:97) as the eluent, to give **1** (76.9 mg: 74.4%) which was recrystallized from ether–hexane, mp 188—189 °C, $[\alpha]_D$ +326° (*c* 0.500, EtOH) (natural shonanol,[1] mp 187—188 °C, $[\alpha]_D$ +3.01 (EtOH)[15]); IR (KBr): 3375, 2960, 1670, 1618, 1515, 1470, 1425, 1376, 1362, 1265, 1205, 1177, 1053, 1020, 947, 883, 825, 816, 750, 715 cm^{-1}; NMR (90 MHz): 1.16 and 1.18 (each 3H, d, and $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 1.19 (6H, s, $-\overset{|}{C}(CH_3)_2$), 1.49 (3H, s, C_{10}–CH_3), 3.18 (1H, m, $-C\underline{H}(CH_3)_2$), 5.95 (1H, d, $J=10$ Hz, C_3–H), 6.50 (1H, d, $J=10$ Hz, C_2–H), 6.67 (1H, s, C_{14}–H), 6.74 (1H, s, C_{12}–OH, disappeared on deuteration), 7.33 (1H, s, C_{11}–H). Found: C, 80.42; H, 8.91%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%. The IR and NMR spectra of the synthetic **1** were identical with those of natural shonanol.

*12-Acetoxyabieta-2,8,11,13-tetraen-1-one (**17**).* A solution of **1** (39.4 mg) and acetic anhydride (0.3 ml) in pyridine (1.0 ml) was heated at 80—85 °C for 1.5 h. After the usual work-up, the crude product was chromatographed on silica gel (5.0 g), using ether–benzene (1:99) as the eluent, to give **17** (37.0 mg: 82.3%) as an oil, $[\alpha]_D$ +295° (*c* 0.285); IR: 1752, 1678 cm^{-1}; NMR (90 MHz): 1.17 (6H, s, $-\overset{|}{C}(CH_3)_2$), 1.18 (6H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 1.47 (3H, s, C_{10}–CH_3), 2.25 (3H, s, $-OCOCH_3$), 5.80 (1H, d, $J=10$ Hz, C_3–H), 6.40 (1H, d, $J=10$ Hz, C_2–H), 6.82 (1H, s, C_{14}–H), 7.31 (1H, s, C_{11}–H). Found: C, 77.71; H, 8.48%. Calcd for $C_{22}H_{28}O_3$: C, 77.61; H, 8.29%.

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14) It is well known that epoxidation occurs preferentially from the less hindered α face of the molecule.[3,4,13]

15) It seems that the low specific rotation value for natural shonanol was obtained by a miscalculation.