Synthesis of (+)-11-Hydroxyabieta-2,8,11,13-tetraen-1-one

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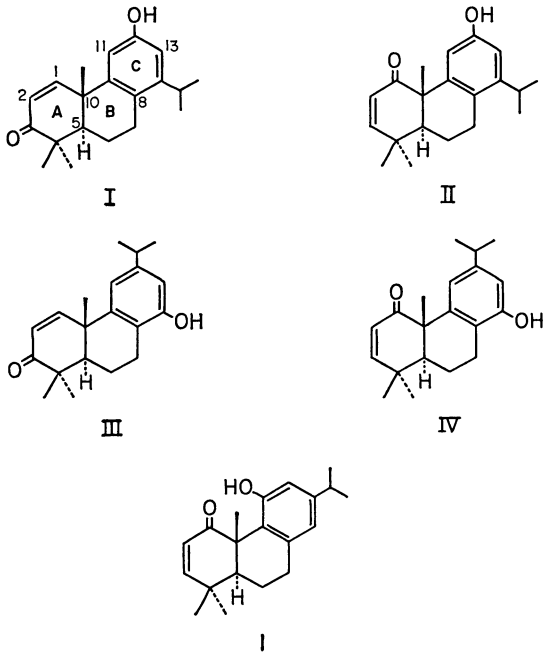
Treatment of methyl (+)-11-oxo-13β-abieta-8-en-18-oate with copper(II) bromide and lithium bromide afforded the corresponding phenol derivative, which was methylated to methyl 11-methoxyabieta-8,11,13-trien-18-oate (**7**). The same compound was also prepared from methyl (+)-7,11-dioxo-13β-abieta-8-en-18-oate *via* methyl 11-hydroxy-7-oxoabieta-8,11,13-trien-18-oate, its methyl ether, and methyl 11-methoxyabieta-6,8,11,13-tetraen-18-oate. The Grignard reaction of **7** with phenylmagnesium bromide followed by treatment with lead tetraacetate and subsequent oxidation with selenium dioxide afforded 11-methoxy-19-norabieta-4(18),8,11,13-tetraen-3α-ol (**12**), which was converted to 11-methoxy-19-norabieta-8,11,13-trien-3-one (**20**) by catalytic hydrogenation, Jones oxidation, and isomerization. The compound **20** was also obtained by Birch reduction of 11-methoxy-19-norabieta-4,8,11,13-tetraen-3-one prepared from **12** *via* 11-methoxy-19-norabieta-4,8,11,13-tetraen-3α-ol. Subsequently, the compound **20** was transformed to 11-methoxyabieta-1,8,11,13-tetraen-3-one (**27**) by a series of reactions: acetalization, demethylation, hydrolysis, acetylation, bromination, dehydrobromination, and methylation. Finally, the compound **27** was converted to the title compound, (+)-11-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**), by oxidation with alkaline hydrogen peroxide, heating with hydrazine hydrate, Jones oxidation, and demethylation. Although the synthetic (+)-**1** was shown to be different from natural shonanol, the spectral analyses of the synthetic structural isomers showed the structure of shonanol to be 12-hydroxyabieta-2,8,11,13-tetraen-1-one.

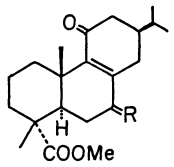
Shonanol is a tricyclic diterpene phenol isolated from *Libocedrus formosana* by Lin and Liu.[1] On the basis of spectroscopic studies, they deduced the structure of shonanol to be 12-hydroxytotara-1,8,11,13-tetraen-3-one (I). This structure is unique among the naturally-occurring tricyclic diterpenes, in that it contains an α,β-unsaturated carbonyl group in the A ring and a hydroxyl group at the position meta to an isopropyl group in the C ring. To make the structural confirmation, (±)-I had been synthesized in our laboratory.[2] However, the synthetic (±)-I had been shown to be different from natural shonanol by spectral comparison. Further studies[3] on the syntheses of (±)-12-hydroxytotara-2,8,11,13-tetraen-1-one (II), (±)-14-hydroxy-12-isopropylpodocarpa-1,8,11,13-tetraen-3-one (III), and (±)-14-hydroxy-12-isopropylpodocarpa-2,8,11,13-tetraen-1-one (IV) led to the same result, whereas the chemical shifts of vinyl protons in the NMR spectra of these synthetic I—IV suggested that shonanol (δ 5.91 and 6.47 ppm) must have a Δ^2-1-oxo moiety (δ 5.95, 5.90 and 6.53, 6.48 ppm in those of II and IV) rather than the proposed Δ^1-3-oxo one (δ 5.99, 5.94, and 7.54, 7.55 ppm in those of I and III) in the A ring of the tricyclic skeleton. In this study, (+)-11-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**) possessing a hydroxyl group at the position meta to an isopropyl group was synthesized starting from methyl (+)-11-oxo-13β-abieta-8-en-18-oate (**2**)[4] and methyl (+)-7,11-dioxo-13β-abieta-8-en-18-oate (**3**),[4] to allow a comparison of the physical and spectral data with those of natural shonanol.



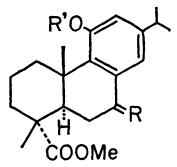
The 11-oxo compound (**2**) was refluxed with copper(II) bromide and lithium bromide in acetonitrile[5] to give methyl 11-hydroxyabieta-8,11,13-trien-18-oate (**4**) and a small amount of methyl 11-hydroxyabieta-6,8,11,13-tetraen-18-oate (**5**), which was also prepared from the 7,11-dioxo compound **3** by the following route. Similar treatment of **3** with copper(II) bromide and lithium bromide, followed by heating at 100 °C with lithium carbonate and lithium chloride in *N,N*-dimethylformamide and then at 45 °C with zinc in acetic acid, produced methyl 11-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**6**). This 7-oxo compound **6** was reduced with sodium borohydride in methanol and the resulting alcohol was immediately dehydrated with *p*-toluenesulfonic acid monohydrate in refluxing benzene to give **5**, which was easily converted to **4** by catalytic hydrogenation over PtO_2. **4** and **6** were each methylated at 35—40 °C with methyl iodide and sodium hydride in *N,N*-dimethylformamide under a stream of nitrogen to give the corresponding methyl ether, **7**[6] and **8**.[6,7] The compound **7** was also obtained by catalytic hydrogenation of methyl 11-methoxyabieta-6,8,11,13-tetraen-18-oate (**9**), which was prepared by reduction of **8** with sodium borohydride, followed by dehydration with *p*-toluenesulfonic acid monohydrate. The Grignard reaction of **7** with phen-

ylmagnesium bromide at 100—110 °C afforded a *gem*-diphenyl alcohol (**10**), which was treated with lead tetraacetate and calcium carbonate in refluxing benzene to give a mixture of Δ^3-, Δ^4-, and $\Delta^{4(18)}$-19-nor compounds (**11**) in a ratio of *ca.* 1:1:8. The mixture was oxidized at room temperature with selenium dioxide and *t*-butyl hydroperoxide in dichloromethane in the presence of salicylic acid[8] or with selenium dioxide in refluxing aqueous ethanol to yield 11-methoxy-19-norabieta-4(18),8,11,13-tetraen-3α-ol (**12**). The α-configuration of the hydroxyl group at the C-3 position in **12** was supported by a signal at δ 4.14 ppm with half-height width of 5 Hz in the NMR spectrum, suggesting the presence of an equatorial β hydrogen. The 3α-ol (**12**) was isomerized at 100 °C with lithium in ethylenediamine under a stream of nitrogen to 11-methoxy-19-norabieta-4,8,11,13-tetraen-3α-ol (**13**), which was immediately oxidized with Jones reagent to 11-methoxy-19-norabieta-4,8,11,13-tetraen-3-one (**14**). Methylation of this conjugated ketone **14** with methyl iodide and potassium *t*-pentyl oxide in refluxing benzene under a stream of nitrogen gave the corresponding 4,4-dimethyl ketone (**15**), which was reduced with lithium aluminium hydride in ether to give 11-methoxyabieta-5,8,11,13-tetraen-3β-ol (**16**). The stereochemistry of the hydroxyl group in **16**, which was expected to be β-configuration from previously published results,[2,3,9,10] was confirmed by conversion to the corresponding acetate (**17**), whose NMR spectrum showed a double doublet signal at δ 4.44 ppm (J=6.5 and 9 Hz), suggesting the presence of an α hydrogen at the C-3 position. The 3β-ol **16** was so unstable that it was gradually transformed to a naphthalene derivative (**18**). The structure of **18** was also supported by its NMR spectrum. Since catalytic hydrogenation of C-5 double bond in **16** proved to be more difficult than expected, this synthetic route was discontinued. Thus, another synthetic route was attempted.

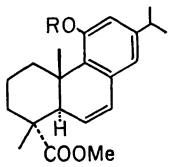
Catalytic hydrogenation of **12** in ethanol over Raney Ni, followed by oxidation with Jones reagent, gave 11-methoxy-18-norabieta-8,11,13-trien-3-one (**19**) and its 19-nor isomer (**20**) in a ratio of 69:2. The former **19** was easily isomerized with sodium methoxide in refluxing methanol to the thermodynamically-stable latter **20** in an almost quantitative yield. The stable



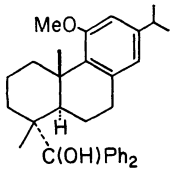
2 R=H_2
3 R=O



4 R=H_2, R'=H 7 R=H_2, R'=Me
6 R=O, R'=H 8 R=O, R'=Me



5 R=H
9 R=Me



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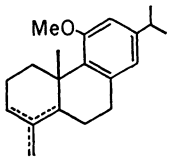

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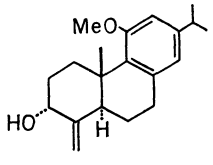

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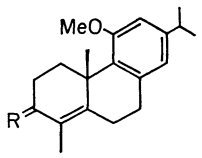
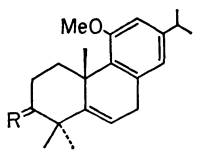
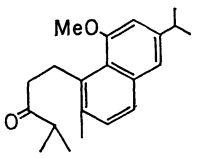


13 R=α-OH, β-H
14 R=O



15 R=O
16 R=α-H, β-OH
17 R=α-H, β-OAc



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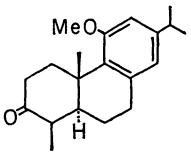

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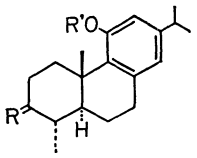
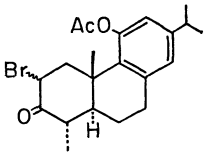


20 R=O, R'=Me
21 R=  , R'=Me
22 R=  , R'=H

23 R=O, R'=H
24 R=O, R'=Ac



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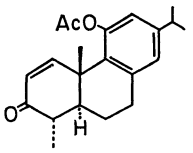

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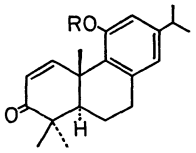
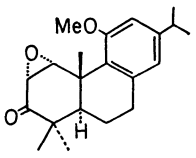


27 R=Me
28 R=H



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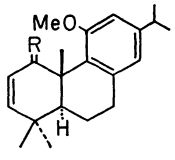
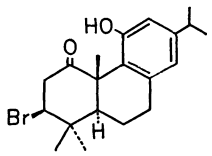


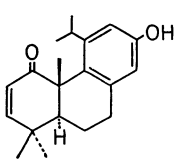
30 R=α-OH, β-H
31 R=O



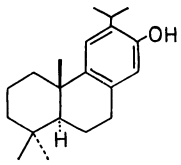
32

isomer **20** was also obtained by Birch reduction of **14** with lithium in liquid ammonia and tetrahydrofuran. Acetalization of **20** with ethylene glycol in the presence of *p*-toluenesulfonic acid monohydrate in refluxing benzene, followed by demethylation of the crude acetal (**21**) with sodium ethanethiolate in refluxing *N,N*-dimethylformamide, yielded a phenol derivative (**22**). This compound, without purification, was converted to 11-acetoxy-19-norabieta-8,11,13-trien-3-one (**24**) by hydrolysis with hydrochloric acid in acetone and subsequent acetylation of the resulting ketone (**23**) with acetic anhydride in pyridine. Bromination[11] of **24** in chloroform with bromine in carbon tetrachloride at 0 °C, followed by dehydrobromination of the crude 2-bromo derivative (**25**) with lithium carbonate and lithium bromide in *N,N*-dimethylformamide at 120—125 °C, afforded an α,β-unsaturated ketone (**26**) which was converted to 11-methoxyabieta-1,8,11,13-tetraen-3-one (**27**) by refluxing with methyl iodide and potassium *t*-pentyl oxide in benzene under a stream of nitrogen. Demethylation of **27** with sodium ethanethiolate in refluxing *N,N*-dimethylformamide produced 11-hydroxyabieta-1,8,11,13-tetraen-3-one (**28**), whose physical and spectral data were different from those of natural shonanol. Subsequently, 1,3-carbonyl transposition[3,12] of the α,β-unsaturated carbonyl group in **27** was carried out as follows. Oxidation of **27** with alkaline hydrogen peroxide in methanol at −10 °C, followed by treatment of the resulting epoxy ketone (**29**)[13] with hydrazine hydrate in refluxing methanol containing a small amount of acetic acid, led to 11-methoxyabieta-2,8,11,13-tetraen-1α-ol (**30**), which was immediately oxidized at 0 °C with Jones reagent to afford 11-methoxyabieta-2,8,11,13-tetraen-1-one (**31**). The 1-oxo compound **31** was finally demethylated at 0 °C with boron tribromide in dichloromethane to give the title compound, 11-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**), and 3β-bromo-11-hydroxyabieta-8,11,13-trien-1-one (**32**) in a ratio of *ca.* 1:1. Dehydrobromination of **32** with lithium carbonate and lithium bromide in *N,N*-dimethylformamide at 120—125 °C produced **1** in an almost quantitative yield. The structure of **32** was supported by the NMR spectrum, which showed signals at δ 2.91 (1H, dd, J=12 and 4.5 Hz) and 3.60 ppm (1H, dd, J=13 and 12 Hz) due to the methylene protons at the C-2 position, and at δ 4.04 ppm (1H, dd, J=13 and 4.5 Hz) due to the methine proton at the C-3 position. The physical and spectral data of the synthetic **1** were also different from those of natural shonanol.

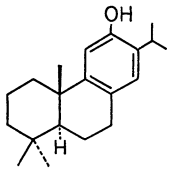
Another structural isomer possessing a hydroxyl group at the position meta to an isopropyl group is 13-hydroxy-11-isopropylpodocarpa-2,8,11,13-tetraen-1-one (V), whose isopropyl group should be sterically hindered by a methyl group at the C-10 position and a carbonyl group at the C-1 position. Therefore, the chemical shifts and coupling pattern of the isopropyl group in V might be expected to be different from those of sempervirol (VI) or ferruginol (VII), which possess an isopropyl group at the less hindered C-12 or C-13 position. However, since the reported chemical shifts of two methyl groups (6H, d, δ 1.15—1.20 ppm) and a methine proton (1H, hept, δ 3.03—3.30 ppm) of the isopropyl group in shonanol were very similar to those[14] in VI (δ 1.19 and 3.10 ppm) or VII (δ 1.19 and 3.09 ppm), the possibility of V could also be ruled out. In the NMR spectrum of natural shonanol, Lin and Liu[1] assigned two singlet signals at δ 6.67 (2H) and 7.30 ppm (1H) to two aromatic protons and a hydroxyl proton, respectively. However, we favored an alternative assignment, in which the signal at δ 6.67 ppm was due to an aromatic proton and a hydroxyl proton and that at δ 7.30 ppm was due to another aromatic proton, because II and IV showed a signal at δ 7.21 ppm[3] corresponding to an aromatic proton at the C-11 position. Consideration of these NMR spectral data suggested that shonanol is either 13-hydroxy-12-isopropyl or a 12-hydroxy-13-isopropyl derivative. Moreover, it is known[14] that VI shows a singlet signal at δ 6.18 ppm due to an aromatic proton at the C-14 position, while VII shows the corresponding signal at δ 6.68 ppm.



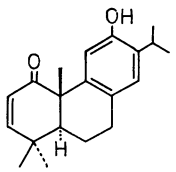
V



VI



VII



VIII

From these NMR analyses we now propose the structure of shonanol to be 12-hydroxyabieta-2,8,11,13-tetraen-1-one (VIII).

Experimental

All melting points are uncorrected. The IR and optical rotations were measured in chloroform. The NMR spectra (90 MHz) were taken in carbon tetrachloride on a Hitachi Model R-22 NMR spectrometer using 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, dd: double doublet, t: triplet, m: multiplet. Column chromatography was performed using Merck silica gel (0.063 mm).

*Methyl 11-Hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**6**).* A mixture of methyl 7,11-dioxo-13β-abieta-8-en-18-oate (**3**: 3.46 g)[4] (mp 87—89.5 °C, $[\alpha]_D$ +78°), copper(II) bromide (4.24 g), and lithium bromide (0.82 g) in freshly distilled acetonitrile (170 ml) was refluxed for 5 h and then evaporated *in vacuo*. After the addition of a mixture of ether and brine, the reaction mixture was extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated to give a brown oil (4.00 g).

A mixture of the brown oil (4.00 g), lithium carbonate (3.70 g), and lithium chloride (3.40 g) in *N,N*-dimethyl-

formamide (200 ml) was heated at 100 °C for 8 h in a stream of nitrogen. After cooling, the mixture was diluted with ether, acidified with dilute sulfuric acid, and then extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated to give a dark brown oil (3.81 g).

A mixture of the dark brown oil (3.81 g) and zinc dust (15.2 g) in acetic acid (95 ml) was stirred at 45 °C for 4 h. The reaction mixture was filtered and the filtrate was diluted with water, neutralized with sodium hydrogencarbonate, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue (3.58 g) was purified by column chromatography on silica gel (380 g), using ether–benzene (5:95) as the eluent, to give **6** (2.50 g: 73%), which was recrystallized from ethanol; mp 154—155 °C, mp 180—181 °C after drying at 140—145 °C; $[\alpha]_D$ +38° (*c* 1.17); IR: 3600, 3330br, 1725, 1680, 1610, 1577 cm^{-1}; NMR (DMSO-d_6); 1.17 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.27 and 1.37 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 3.61 (3H, s, $-CO_2CH_3$), 6.92 (1H, d, J=2 Hz, C_{12}–H), 7.28 (1H, d, J=2 Hz, C_{14}–H). Found: C, 72.93; H, 8.20%. Calcd for $C_{21}H_{28}O_4$: C, 73.22; H, 8.19%.

Methyl 11-Hydroxyabieta-6,8,11,13-tetraen-18-oate (5). A mixture of **6** (1.03 g) and sodium borohydride (170 mg) in methanol (25 ml) was allowed to stand overnight at room temperature. After the addition of acetone (1.0 ml), the solvent was removed *in vacuo* and the residue was acidified with dilute hydrochloric acid. The mixture was then extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated to give a curde alcohol (1.07 g) as a pale brown solid.

A mixture of the crude alcohol (1.07 g) and *p*-toluenesulfonic acid monohydrate (20 mg) in benzene (100 ml) was refluxed for 2 h. After cooling, the mixture was diluted with ether, washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and then evaporated *in vacuo*. The residue was recrystallized from methanol to afford **5** (0.87 g: 89%); mp 173.5—175 °C; $[\alpha]_D$ −35° (*c* 1.93); IR: 3600, 3400br, 1720 cm^{-1}; NMR ($CDCl_3$): 1.18 and 1.39 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.03 (1H, t, J=3 Hz, C_5–H), 3.65 (3H, s, $-CO_2CH_3$), 4.86 (1H, bs, –OH, disappeared on deutration), 5.64 and 6.43 (each 1H, dd, and J=10 and 3 Hz, C_6–H and C_7–H), 6.40 and 6.49 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 76.78; H, 8.80%. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%. The mother liquor of recrystallization was evaporated *in vacuo* and the residue was chromatographed on silica gel (15 g), using benzene as the eluent, to give some additional **5** (0.11 g: 11%).

Methyl 11-Hydroxyabieta-8,11,13-trien-18-oate (4). a): A mixture of methyl 11-oxo-13β-abieta-8-en-18-oate (**2**: 9.49 g)[4] (mp 108—110 °C, $[\alpha]_D$ +104° (EtOH)), copper(II) bromide (11.50 g), and lithium bromide (2.23 g) in freshly distilled acetonitrile (470 ml) was refluxed for 5 h and then evaporated *in vacuo*. After the addition of a mixture of ether and brine, the mixture was extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residual solid (10.37 g) was recrystallized from ethanol to give **4** (5.30 g: mp 201—203 °C). A pure sample for analysis was obtained by repeated crystallization; mp 203—205 °C; $[\alpha]_D$ +77° (*c* 1.22); IR: 3600, 3370br, 1720, 1617, 1575 cm^{-1}; NMR ($CDCl_3$): 1.19 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.29 and 1.35 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 3.14 (1H, bd, J=12.5 Hz, $C_{1\beta}$–H), 3.68 (3H, s, $-CO_2CH_3$), 4.82 (1H, s, –OH, disappeared on deutration), 6.32 and 6.51 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 76.20; H, 9.16%. Calcd for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15%. The mother liquor of recrystallization was evaporated *in vacuo* and the residue was chromatographed on silica gel (300 g), using benzene as the eluent, to give a colorless solid (**4**: 1.85 g) containing a small amount of **5**. Further elution with ether–benzene (1:99) afforded the recovered **2** (1.73 g: 18%).

b): A mixture of **5** (651 mg) and PtO_2 (100 mg) in ethanol (30 ml) was subjected to catalytic hydrogenation at room temperature. After the usual work-up, the crude product was recrystallized from ethanol to give **4** (600 mg: 90%), mp 201—203.5 °C, whose IR and NMR spectra were identical with those of the sample prepared in *a)*. The mother liquor of recrystallization was evaporated *in vacuo* and the residue was chromatographed on silica gel to give some additional **4** (61 mg: 9%).

Methyl 11-Methoxy-7-oxoabieta-8,11,13-trien-18-oate (8). A mixture of **6** (344 mg) and 50% sodium hydride (72 mg) in *N*,*N*-dimethylformamide (6.5 ml) was stirred at room temperature for 45 min under a stream of nitrogen. After the addition of methyl iodide (0.06 ml), the mixture was stirred at 35—40 °C for 3 h, cooled, and some additional methyl iodide (0.02 ml) was added. The mixture was further stirred at 35—40 °C for 5 h, 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 *in vacuo*. The residue was purified by column chromatography on silica gel (40 g), using ether–benzene (1:99) as the eluent, to give **8** (309 mg: 86%), which was recrystallized from hexane; mp 113—114 °C; $[\alpha]_D$ +60° (*c* 1.15); IR: 1727, 1680 cm^{-1}; NMR: ($CDCl_3$): 1.25 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.30 and 1.38 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 3.64 (3H, s, $-CO_2CH_3$), 3.82 (3H, s, C_{11}–OCH_3), 6.94 (1H, d, J=2 Hz, C_{12}–H), 7.59 (1H, d, J=2 Hz, C_{14}–H). Found: C, 73.44; H, 8.39%. Calcd for $C_{22}H_{30}O_4$: C, 73.71; H, 8.44%. The IR and NMR spectra of **8** were identical with those of an authentic sample.[7]

Methyl 11-Methoxyabieta-6,8,11,13-tetraen-18-oate (9). A solution of **8** (270 mg) and sodium borohydride (43 mg) in methanol (7.0 ml) was allowed to stand overnight at room temperature. The crude alcohol was then dehydrated with *p*-toluenesulfonic acid monohydrate in refluxing benzene, as described for the preparation of **5**. The crude product was chromatographed on silica gel (25 g), using hexane–benzene (1:1) as the eluent, to give **9** (244 mg: 95%); $[\alpha]_D$ −15° (*c* 1.45); IR: 1717 cm^{-1}; NMR: 1.10 and 1.33 (each 3H and s, C_4–$C\underline{H}_3$ and C_{10}–CH_3), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 2.89 (1H, t, J=3 Hz, C_5–H), 3.58 (3H, s, $-CO_2CH_3$), 3.73 (3H, s, C_{11}–OCH_3), 5.55 and 6.32 (each 1H, dd, J=10 and 3 Hz, C_6–H and C_7–H), 6.42 and 6.48 (each 1H, d, and J=2 Hz, C_{12}–H and C_{14}–H). Found: C, 77.45; H, 9.02%. Calcd for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83%.

Methyl 11-Methoxyabieta-8,11,13-trien-18-oate (7). a): A mixture of **9** (190 mg) and PtO_2 (19 mg) in ethanol (20 ml) was submitted to catalytic hydrogenation at room temperature. After the usual work-up, the crude product was purified by column chromatography on silica gel (20 g), using hexane–benzene (1:1) as the eluent, to give **7**[6] (181 mg: 95%); $[\alpha]_D$ +89° (*c* 1.35); IR: 1718, 1610, 1568 cm^{-1}; NMR ($CDCl_3$): 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.27 and 1.31 (each 3H and s, C_4–CH_3 and C_{10}–CH_3), 3.65 (3H, s, $-CO_2CH_3$), 3.77 (3H, s, C_{11}–OCH_3), 6.50 (2H, bs, C_{12}–H and C_{14}–H). Found: C, 76.84; H, 9.50%. Calcd for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36%.

b): A mixture of **4** (7.15 g) containing a small amount

of **5**, 50% sodium hydride (5.20 g), and *N,N*-dimethylformamide (200 ml) was methylated with methyl iodide (4.0 ml) as described for the preparation of **8**. The crude product was purified by column chromatography on silica gel (350 g), using hexane–benzene (1:1) as the eluent, to give **7** (3.98 g) and a mixture (2.42 g) of **7** and a small amount of **9**.

The above mixture (2.42 g) in ethanol (14 ml) was hydrogenated over PtO_2 and then purified by column chromatography to give **7** (2.14 g), whose IR and NMR spectra were identical with those of the sample prepared in *a)*.

*Grignard Reaction of **7** with Phenylmagnesium Bromide.* A solution of **7** (344 mg) in dry ether (3.4 ml) was added dropwise to a refluxing ethereal solution of phenylmagnesium bromide prepared from magnesium turnings (194 mg) and bromobenzene (1.26 g) in dry ether (3.4 ml). The mixture was further refluxed for 2 h and the ether was removed in a stream of nitrogen. The viscous residue was heated at 100—110 °C for 5 h, allowed to stand overnight at room temperature, carefully hydrolyzed with a mixture of ice and dilute sulfuric acid, and then extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (65 g), using hexane–benzene (1:1) as the eluent, to give a *gem*-diphenyl alcohol (**10**) (373 mg: 80%) as a colorless solid, which was recrystallized from methanol; mp 191.5—193 °C; $[\alpha]_D$ +101° (*c* 1.65); IR: 3580, 1610, 1568, 700 cm^{-1}; NMR: 1.15 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.28 and 1.30 (each 3H and s, C_4-CH_3 and $C_{10}-CH_3$), 2.34 (1H, s, –OH, disappeared on deutration), 3.69 (3H, s, $C_{11}-OCH_3$), 6.17 and 6.31 (each 1H and bs, C_{12}–H and C_{14}–H), 6.9—7.9 (10H, m, 2-C_6H_5). Found: C, 84.84; H, 8.68%. Calcd for $C_{33}H_{40}O_2$: C, 84.57; H, 8.60%.

*Fragmentation of **10** with Lead Tetraacetate.* A mixture of lead tetraacetate (1.06 g) and calcium carbonate (1.20 g) in dry benzene (60 ml) was refluxed for 5 min. To this mixture was added a solution of **10** (937 mg) in dry benzene (30 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 aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine. After drying over sodium sulfate, the solution was evaporated *in vacuo* and the residue was chromatographed on silica gel (100 g), using hexane–benzene (95:5) as the eluent, to give a mixture of Δ^3-, Δ^4-, and $\Delta^{4(18)}$-19-nor isomers (**11**) (508 mg: 89%). The NMR spectrum of the mixture indicated that it was composed of approximately 10% of Δ^3- (δ 5.34 ppm, C_3–H), 10% of Δ^4- (δ 1.42 ppm, $C_{10}-CH_3$), and 80% of $\Delta^{4(18)}$-19-nor compound (δ 4.48 and 4.74 ppm, $CH_2=\overset{|}{C}-$). Found: C, 84.74; H, 10.18%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%. The above olefinic mixture (**11**) was recrystallized from methanol to afford the pure $\Delta^{4(18)}$-19-nor compound; mp 81—82 °C; $[\alpha]_D$ +242° (*c* 1.23); NMR: 1.17 (3H, s, $C_{10}-CH_3$), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.01 (1H, bd, J=12 Hz, $C_{1\beta}$–H), 3.75 (3H, s, $C_{11}-OCH_3$), 4.48 and 4.74 (each 1H, bs, and $W_{1/2}$=4 Hz, $CH_2=\overset{|}{C}-$), 6.39 (2H, bs, C_{12}–H and C_{14}–H). Found: C, 84.32; H, 10.15%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%.

*11-Methoxy-19-norabieta-4(18),8,11,13-tetraen-3α-ol (**12**).*

a): The olefinic mixture (**11**: 142 mg) was added to a stirred mixture of 70% *t*-butyl hydroperoxide (0.26 ml), selenium dioxide (1 mg), and salicylic acid (7 mg) in dichloromethane (0.3 ml). The mixture was further stirred at room temperature for 28 h, diluted with benzene (5.0 ml), and then evaporated. The residue was dissolved in ether and the ether solution was washed successively with aqueous potassium hydroxide and brine. After the solution had been evaporated *in vacuo*, the residue was dissolved in cold acetic acid (1.0 ml) and dimethyl sulfide (0.25 ml) was added slowly with stirring and cooling in a water bath. The mixture was then stirred at room temperature for 3 h, neutralized with aqueous potassium carbonate at 0—5 °C, and 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 (17 g), using ether–benzene (1:99) as the eluent, to give **12** (95 mg: 63%), which was recrystallized from hexane; mp 68—69.5 °C; $[\alpha]_D$ +186° (*c* 2.59); IR: 3600, 3420br, 1648, 1610, 1568 cm^{-1}; NMR: 1.01 (3H, s, $C_{10}-CH_3$), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.92 (1H, bs, –OH, disappeared on deutration), 3.73 (3H, s, $C_{11}-OCH_3$), 4.14 (1H, bs, $W_{1/2}$=5 Hz, C_3–H), 4.55 and 4.90 (each 1H and bs, $CH_2=\overset{|}{C}-$), 6.39 (2H, bs, C_{12}–H and C_{14}–H). Found: C, 80.20; H, 9.56%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

b): A solution of selenium dioxide (566 mg) in ethanol (29 ml) and water (0.08 ml) was added dropwise to a stirred solution of the olefinic mixture (**11**: 2.88 g) in ethanol (29 ml) at room temperature over a 20 min period. The mixture was further stirred at room temperature for 30 min, refluxed for 8 h, cooled, and then filtered. The filtrate was diluted with ether and the ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (320 g), using ether–benzene (1:99) as the eluent, to give **12** (1.68 g: 55%) as a pale brown solid, whose IR and NMR spectra were identical with those of the sample prepared in *a)*.

*11-Methoxy-19-norabieta-4,8,11,13-tetraen-3-one (**14**).* A solution of **12** (1.01 g) in ethylenediamine (70 ml) was added to lithium (1.18 g) in ethylenediamine (70 ml). The mixture was heated at 100 °C for 1 h under a stream of nitrogen, poured into brine, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated to give a crude 11-methoxy-19-norabieta-4,8,11,13-tetraen-3α-ol (**13**) as an oil (1.00 g); NMR (60 MHz): 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.38 (3H, s, $C_{10}-CH_3$), 1.74 (3H, s, C_4-CH_3), 3.65 (1H, bs, $W_{1/2}$=6 Hz, C_3–H), 3.76 (3H, s, $C_{11}-OCH_3$), 6.42 (2H, bs, C_{12}–H and C_{14}–H).

A solution of the crude **13** (1.00 g) in acetone (60 ml) was oxidized with Jones reagent (2.5 M: 3.37 ml) at 0 °C for 30 min. After the usual work-up, the crude product was purified by column chromatography on silica gel (50 g), using ether–benzene (1:99) as the eluent, to give **14** (830 mg: 83%) as an oil; $[\alpha]_D$ +362° (*c* 1.71); IR: 1650, 1613, 1570 cm^{-1}; NMR: 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.61 (3H, s, $C_{10}-CH_3$), 1.78 (3H, s, C_4-CH_3), 3.80 (3H, s, $C_{11}-OCH_3$), 6.44 and 6.48 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 80.25; H, 8.96%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

*11-Methoxyabieta-5,8,11,13-tetraen-3-one (**15**).* A solution of potassium *t*-pentyl oxide in *t*-pentyl alcohol prepared from potassium (141 mg) and *t*-pentyl alcohol (7.8 ml) was evaporated to dryness and the residual potassium *t*-pentyl oxide was suspended in dry benzene (7.0 ml). After a solution of **14** (596 mg) in dry benzene (18 ml) had been added over a 10 min period under a stream of nitrogen, the stirred mixture was refluxed for 30 min, cooled, and a solution of methyl iodide (0.37 ml) in dry benzene (5.0

ml) was added. The stirred mixture was further refluxed for 2 h, poured into dilute hydrochloric acid, and extracted with ether. The ether extract was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (60 g), using benzene as the eluent, to give **15** (447 mg: 72%) as a colorless solid; IR: 1700, 1612, 1573 cm^{-1}; NMR: 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.25 (6H, s) and 1.28 (3H, s) ($-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 3.36 (2H, bd, J=4 Hz, $=CHC\underline{H}_2-$), 3.80 (3H, s, $C_{11}-OCH_3$), 5.67 (1H, t, J=4 Hz, C_6–H), 6.46 (2H, bs, C_{12}–H and C_{14}–H). The compound (**15**) was labile and it was immediately subjected to the next reaction.

*11-Methoxyabieta-5,8,11,13-tetraen-3β-ol (**16**).* A solution of **15** (99 mg) in dry ether (4.0 ml) was added to a stirred suspension of lithium aluminium hydride (24.3 mg) in dry ether (1.5 ml). The mixture was refluxed for 1.5 h, 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 *in vacuo*. The residue was chromatographed on silica gel (10 g), using ether–benzene (1:99) as the eluent, to give **16** (70 mg: 70%) as an oil; IR: 3610, 3400br, 1610, 1572 cm^{-1}; NMR: 1.13, 1.18, and 1.41 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), *ca.* 3.1 (2H, m, $C_{1\beta}$–H and C_3–H), 3.28 (2H, bd, J=4 Hz, $=CHC\underline{H}_2-$), 3.75 (3H, s, $C_{11}-OCH_3$), 5.78 (1H, t, J=4 Hz, C_6–H), 6.42 (2H, bs, C_{12}–H and C_{14}–H).

The compound (**16**) was labile and it gradually transformed into a naphthalene derivative (**18**); IR: 1705, 1627, 1572 cm^{-1}; NMR: 1.06 and 1.30 (each 6H, d, and J=7 Hz, 2-$CH(C\underline{H}_3)_2$), 2.38 (3H, s, $-CH_3$), 3.82 (3H, s, $-OCH_3$), 6.57 (1H, d, J=2 Hz), 7.01 (1H, d, J=2 Hz,) 7.05 (1H, d, J=8 Hz), and 7.30 (1H, d, J=8 Hz) (aromatic protons). Found: C, 80.76; H, 9.24%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

*3β-Acetoxy-11-methoxyabieta-5,8,11,13-tetraene (**17**).* A mixture of **16** (107 mg) and acetic anhydride (0.5 ml) in pyridine (0.5 ml) was allowed to stand overnight at room temperature. After the usual work-up, the crude product was chromatographed on silica gel (10 g). Elution with benzene gave **17** (77 mg), which was recrystallized from hexane; mp 122—122.5 °C; $[\alpha]_D$ +24° (*c* 0.37); IR: 1725, 1614, 1577 cm^{-1}; NMR: 1.11, 1.22, and 1.44 (each 3H and s, $-\dot{C}(CH_3)_2$ and $C_{10}-CH_3$), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.98 (3H, s, $-OCOCH_3$), 3.30 (2H, bd, J=4 Hz, $=CHC\underline{H}_2-$), 3.78 (3H, s, $C_{11}-OCH_3$), 4.44 (1H, dd, J=9 and 6.5 Hz, C_3–H), 5.84 (1H, t, J=4 Hz, C_6–H), 6.42 and 6.44 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 77.30; H, 9.19%. Calcd for $C_{23}H_{32}O_3$: C, 77.49; H, 9.05%.

*11-Methoxy-18-norabieta-8,11,13-trien-3-one (**19**) and 11-Methoxy-19-norabieta-8,11,13-trien-3-one (**20**).* *a)*: A solution of **12** (365 mg) in ethanol (8.0 ml) was hydrogenated using Raney Ni (W-2: 750 mg) at room temperature in an atmosphere of hydrogen. The crude dihydro compound, without purification, was oxidized with Jones reagent (2.5 M: 1.2 ml) in acetone (20 ml) at 0 °C for 30 min. After the usual work-up, the crude product was purified by column chromatography on silica gel (40 g), using ether–benzene (0.5:99.5) as the eluent, to give **20** (9 mg: 2%) as an oil. Further elution gave **19** (250 mg: 69%) as an oil; $[\alpha]_D$ +188° (*c* 2.07); IR: 1700, 1610, 1570 cm^{-1}; NMR: 1.16 (3H, d, J=7.5 Hz, C_4-CH_3), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.24 (3H, s, $C_{10}-CH_3$), 3.77 (3H, s, $C_{11}-OCH_3$), 6.42 (2H, bs, C_{12}–H and C_{14}–H). Found: C, 80.05; H, 9.65%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

b): A mixture of **19** (172 mg) and sodium methoxide (154 mg) in methanol (10 ml) was refluxed 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 residue was chromatographed on silica gel (15 g), using ether–benzene (1:99) as the eluent, to give **20** (168 mg: 98%) as an oil; $[\alpha]_D$ +138° (*c* 0.665); IR: 1698, 1610, 1570 cm^{-1}; NMR: 1.05 (3H, d, J=7 Hz, C_4-CH_3), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.36 (3H, s, $C_{10}-CH_3$), 3.77 (3H, s, $C_{11}-OCH_3$), 6.42 (2H, bs, C_{12}–H and C_{14}–H). Found: C, 80.09; H, 9.39%. Calcd for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39%.

c): A solution of **14** (121 mg) in tetrahydrofuran (2.5 ml) was added to a solution of lithium (28 mg) in liquid ammonia (12 ml) at −33 °C. The mixture was stirred at this temperature for 1 h, and ammonium chloride (321 mg) was added. After removal of the ammonia, the residue was diluted with water and 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 (12 g), using ether–benzene (0.5: 99.5) as the eluent, to give **20** (60 mg: 48%) as an oil; its IR and NMR spectra were identical with those of the sample prepared in *a)* and *b)*.

*11-Acetoxy-19-norabieta-8,11,13-trien-3-one (**24**).* A mixture of **20** (170 mg), ethylene glycol (0.32 ml), and *p*-toluenesulfonic acid monohydrate (17 mg) in benzene (15 ml) was refluxed for 4 h. The mixture was cooled, diluted with ether, and then washed successively with aqueous sodium hydrogencarbonate and brine. After drying over sodium sulfate, the solution was evaporated *in vacuo* to give a crude acetal (**21**) as an oil.

A solution of the above crude acetal (**21**) in *N*,*N*-dimethylformamide (10 ml) was added to sodium ethanethiolate prepared from sodium (92 mg) and ethanethiol (2.0 ml). The stirred mixture was refluxed for 2.5 h under a stream of nitrogen, cooled, poured into dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated to give a crude phenol (**22**) as an oil.

A solution of the above crude phenol (**22**) in acetone (15 ml) was stirred with dilute hydrochloric acid (6 M: 2.0 ml) at room temperature for 1 h. The mixture was diluted with ether, washed with brine, and dried over sodium sulfate. Evaporation of the solution gave a crude keto phenol (**23**) as an oil, which was then acetylated with acetic anhydride (1.0 ml) in pyridine (1.0 ml) at room temperature for *ca.* 15 h. After the usual work-up, the crude product was purified by column chromatography on silica gel (20 g). Elution with ether–benzene (3:97) afforded **24** (173 mg: 92%), which was recrystallized from hexane; mp 105—106 °C; $[\alpha]_D$ +141° (*c* 1.37); IR: 1750, 1705, 1620, 1567 cm^{-1}; NMR: 1.07 (3H, d, J=6.5 Hz, C_4-CH_3), 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.31 (3H, s, $C_{10}-CH_3$), 2.23 (3H, s, $-OCOCH_3$), 6.53 and 6.71 (each 1H, d, and J=2 Hz, C_{12}–H and C_{14}–H). Found: C, 76.65; H, 8.70%. Calcd for $C_{21}H_{28}O_3$: C, 76.79; H, 8.59%.

*11-Acetoxy-19-norabieta-1,8,11,13-tetraen-3-one (**26**).* A solution of bromine (1 M: 1.25 ml) in carbon tetrachloride was added at 0 °C to a stirred solution of **24** (373 mg) in chloroform (13 ml). The mixture was further stirred at this temperature for 45 min, diluted with ether, and the ether solution was washed successively with aqueous sodium thiosulfate and brine. Evaporation of the dried solution gave a crude 2-bromo derivative (**25**) as an oil.

A stirred mixture of the crude 2-bromo compound (**25**), lithium carbonate (211 mg), and lithium bromide (158 mg)

in *N,N*-dimethylformamide (15 ml) was heated at 120—125 °C for 75 min under a stream of nitrogen. The mixture was cooled, poured into dilute sulfuric acid, and 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 (40 g). Elution with ether–benzene (2:98) afforded **26** (205 mg: 55%) as an oil; $[\alpha]_D$ +199° (*c* 2.05); IR: 1760, 1670, 1620, 1570 cm^{-1}; NMR: 1.19 (3H, d, J=6.5 Hz, C_4–CH_3), 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.34 (3H, s, C_{10}–CH_3), 2.27 (3H, s, $-OCOCH_3$), 5.77 (1H, d, J=10 Hz, C_2–H), 6.65 and 6.76 (each 1H, bd, and J=2 Hz, C_{12}–H and C_{14}–H), 7.78 (1H, d, J=10 Hz, C_1–H). Found: C, 77.07; H, 8.01%. Calcd for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03%.

11-Methoxyabieta-1,8,11,13-tetraen-3-one (27). A solution of **26** (129 mg) in dry benzene (5.0 ml) was added to a stirred suspension of potassium *t*-pentyl oxide (prepared from potassium (139 mg) and *t*-pentyl alcohol (3.0 ml) in dry benzene (3.0 ml) over a 5 min period under a stream of nitrogen. The mixture was gently refluxed for 30 min, cooled, and a solution of methyl iodide (0.15 ml) in dry benzene (1.0 ml) was added. The mixture was refluxed for 2 h, cooled, and some additional solution of methyl iodide (0.15 ml) in dry benzene (1.0 ml) was added. The mixture was further refluxed for 2 h, cooled, poured into water, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The crude product was chromatographed on silica gel (20 g). Elution with ether–benzene (1:99) gave **27** (84 mg: 68%), which was recrystallized from methanol; mp 84.5—85 °C; $[\alpha]_D$ +206° (*c* 0.670); IR: 1660, 1612, 1577 cm^{-1}; NMR: 1.11, 1.16, and 1.43 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.86 (3H, s, C_{11}–OCH_3), 5.77 (1H, d, J=10 Hz, C_2–H), 6.49 (2H, bs, C_{12}–H and C_{14}–H), 7.96 (1H, d, J=10 Hz, C_1–H). Found: C, 80.71; H, 9.18%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

11-Hydroxyabieta-1,8,11,13-tetraen-3-one (28). A stirred mixture of **27** (28 mg) and sodium ethanethiolate (prepared from sodium (21 mg) and ethanethiol (1.5 ml)) in *N,N*-dimethylformamide (3.0 ml) was refluxed for 3 h under a stream of nitrogen. The mixture was cooled, 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 residue was purified by column chromatography on silica gel (5.0 g), using ether–benzene (3:97) as the eluent, to give **28** (16 mg: 60%), which was recrystallized from methanol; mp 199—200 °C; $[\alpha]_D$ +190° (*c* 0.075); IR: 3580, 3280br, 1655, 1610, 1572 cm^{-1}; UV (λ_{max}^{EtOH}): 225 nm (ε 18900), 283 (2490); NMR ($CDCl_3$): 1.22 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.22, 1.25, and 1.53 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 5.53 (1H, bs, –OH, disappeared on deutration), 5.96 (1H, d, J=10.5 Hz, C_2–H), 6.45 (1H, bd, J=2 Hz) and 6.59 (1H, bs) (C_{12}–H and C_{14}–H), 8.34 (1H, d, J=10.5 Hz, C_1–H). Found: C, 80.26; H, 8.98%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

11-Methoxyabieta-2,8,11,13-tetraen-1-one (31). A solution of **27** (35 mg) in methanol (10.5 ml) was cooled to −10 °C under a stream of nitrogen; then 30% hydrogen peroxide (0.064 ml) was added, followed by 5% aqueous sodium hydroxide (0.5 ml). The mixture was stirred at −12—−8 °C for 4.5 h, poured into dilute hydrochloric acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated to give an epoxy ketone (**29**) as an oil (37 mg). Without purification, this was immediately submitted to the next reaction.

A mixture of the crude **29** (37 mg), hydrazine hydrate (0.17 ml), acetic acid (0.04 ml), and methanol (3.7 ml) was refluxed for 13.5 h under a stream of nitrogen. 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 to give a crude 1α-ol (**30**: 37 mg). The crude **30** (37 mg) was oxidized with Jones reagent (2.5 M: 0.112 ml) at 0 °C for 15 min. After the usual work-up, the crude product was purified by column chromatography on silica gel (5.0 g). Elution with benzene gave **31** (15 mg: 43%) as an oil; $[\alpha]_D$ +266° (*c* 1.02); IR: 1695, 1618, 1580 cm^{-1}; NMR: 1.13, 1.19, and 1.60 (each 3H and s, $-\dot{C}(CH_3)_2$ and C_{10}–CH_3), 1.24 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 3.73 (3H, s, C_{11}–OCH_3), 5.77 and 6.16 (each 1H, d, and J=10 Hz, C_2–H and C_3–H), 6.43 and 6.54 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 80.55; H, 9.19%. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03%.

Demethylation of 31. A solution of **31** (10.0 mg) and boron tribromide (0.015 ml) in dichloromethane (0.50 ml) was stirred at 0 °C for 30 min, poured into a mixture of ice and water, and 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 (5.0 g), using benzene as the eluent, to give 11-hydroxyabieta-2,8,11,13-tetraen-1-one (**1**) (4.7 mg: 49%) as an oil; $[\alpha]_D$ +470° (*c* 0.35); IR: 3200br, 1657, 1615, 1567 cm^{-1}; UV (λ_{max}^{EtOH}): 222.5 nm (ε 15500), 281.5 (2220); NMR: 1.21 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.22 (6H, s, $-\dot{C}(CH_3)_2$), 1.58 (3H, s, C_{10}–CH_3), 5.88 and 6.56 (each 1H, d, and J=10 Hz, C_2–H and C_3–H), 6.37 and 6.60 (each 1H and bs, C_{12}–H and C_{14}–H). Found: C, 80.28; H, 8.93%. Calcd for $C_{20}H_{26}O_2$: C, 80.49; H, 8.78%.

Further elution with benzene gave 3β-bromo-11-hydroxyabieta-8,11,13-trien-1-one (**32**) (6.0 mg: 50%) as an oil; IR: 3320br, 1690 cm^{-1}; NMR: 1.18 (6H, d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.22 and 1.24 (each 3H and s, $-\dot{C}(CH_3)_2$), 1.64 (3H, s, C_{10}–CH_3), 2.91 (1H, dd, J=12 and 4.5 Hz, $C_{2\alpha}$–H), 3.60 (1H, dd, J=13 and 12 Hz, $C_{2\beta}$–H), 4.04 (1H, dd, J=13 and 4.5 Hz, $C_{3\alpha}$–H), 5.63 (1H, bs, –OH), 6.41 and 6.52 (each 1H and bs, C_{12}–H and C_{14}–H).

A mixture of **32** (6.0 mg), lithium carbonate (8.0 mg), and lithium bromide (6.0 mg) in *N,N*-dimethylformamide (1.0 ml) was heated at 120—125 °C for 3 h under a stream of nitrogen. After the same work-up as described for the preparation of **26**, the crude product was chromatographed on silica gel (5.0 g). Elution with benzene gave a colorless oil (4.9 mg: 96%), whose IR and NMR spectra were identical with those of **1**.

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