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Rearrangement of the Angular Methyl Group in Dehydroabietic Acid Derivatives

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The rearrangement of the angular methyl group in dehydroabietic acid derivatives was examined. Treatment of 12-methoxy-5,8,11,13-abietatetraene (25) with boron trifluoride etherate afforded 12-methoxy-5β-methyl-10-norabieta-1(10),8,11,13-tetraene (26). On the other hand, 12-methoxy-7-oxo-5,8,11,13-abietatetraene (27) provided three naphthalene derivatives, 28, 29 and 30, on treatment with sulfuric acid in acetic anhydride. Methyl 7-oxo-5,8,11,13-abietatetraen-18-oate (5) was reduced with sodium borohydride in the presence of cerium(III) chloride heptahydrate and the resulting alcohol (32) was further treated with *p*-toluenesulfonic acid monohydrate to give methyl 5β-methyl-10-norabieta-1(10),6,8,11,13-pentaen-18-oate (33). On the other hand, under similar conditions, 7-oxo-5,8,11,13-abietatetraene (11) and its 12-methoxy derivative (27) were transformed into the naphthalene derivatives, 35 and 37, respectively, *via* the corresponding alcohols, 34 and 36.

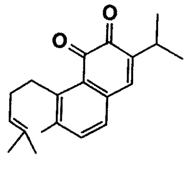
Keywords rearrangement; angular methyl group; dehydroabietic acid derivative

Recently, rearranged abietane-type diterpenes such as saprorthoquinone (**1**), 4-hydroxysapriparaquinone (**2**), and pygmaeocins B (**3**) and C (**4**) have been isolated from the roots of *Salvia prionitis* Hance (Labiatae)[1] and *Pygmaeopremna herbaceae* (Roxb.) Moldenke (Verbenaceae).[2] These natural diterpenes have a rare structural feature, possessing a rearranged angular methyl group at the C-5 position.

In order to devise an efficient synthetic route to these natural diterpenes, we conducted some preliminary experiments on the rearrangement of the angular methyl group in dehydroabietic acid derivatives to the C-5 position, although this type of rearrangement has been previously reported by several groups,[3−8] including our own.[9−12] The treatment of methyl 7-oxo-5,8,11,13-abietatetraen-18-oate (**5**) and its analogs (**7** and **9**), possessing a methoxycarbonyl group at the C-4 position, with sulfuric acid in acetic anhydride gave the corresponding rearranged acetates (**6**,[4,6] **8**, [11] and **10**,[11] respectively) with an intact C(4)–C(5) bond. Similar treatment of 7-oxo-5,8,11,13-abientatetraene (**11**) and its analog (**13**), possessing a geminal dimethyl group at the C-4 position, produced 4,5-seco diacetates, **12**[6] and **14**[8] respectively. We also reported the conversion of 12,13-dimethoxy-5,8,11,13-totaratetraene (**15**) and 1,10a-epoxy-1,2,3,4,4a,9,10,10a-octahydro-7-methoxy-4aβ-methylphenanthrene (**17**) into the 5β-methyl-10-nortotarane derivative[9] (**16**) and the 10aβ-methyl-1-phenanthrenol derivative[10] (**18**), respectively, by treatment with boron trifluoride etherate.

On the other hand, Cambie and Hayward[7] reported that the acid-catalyzed rearrangement of 7α-hydroperoxy- (**19**) or 7α-hydroxy-13-methoxy-5,8,11,13-totaratetraene (**20**) gave a naphthalene derivative to which the structure **21** was tentatively assigned, but an alternative structure **22** could not be excluded. In order to obtain further information on the rearrangement of the angular methyl group in dehydroabietic acid derivatives, we carried out the following experiments.

12-Methoxy-8,11,13-abietatrien-6β-ol[13] (**24**) prepared from (+)-dehydroabietic acid (**23**) was dehydrated with phosphoryl chloride in pyridine to give an olefin (**25**), whose proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed singlet signals at δ 1.13, 1.21 and 1.25 due to three



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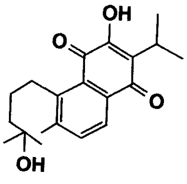

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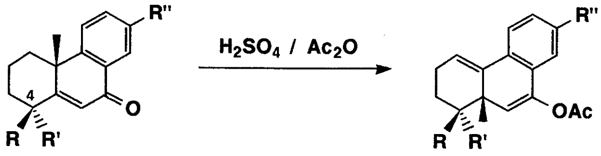
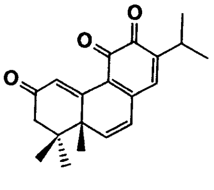


5	R=Me, R'=CO$_2$Me, R"=CHMe$_2$	6
7	R=Me, R'=CO$_2$Me, R"=OMe	8
9	R=CO$_2$Me, R'=Me, R"=OMe	10



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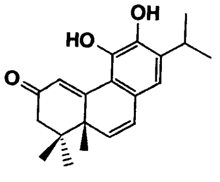

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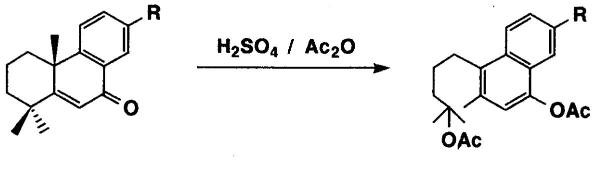
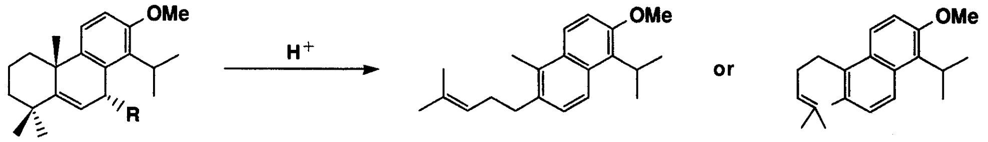


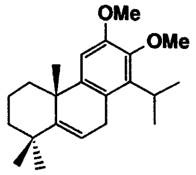
11	R=CHMe$_2$	12
13	R=OMe	14



19 : R=O$_2$H
20 : R=OH

21

22



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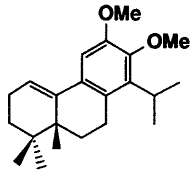

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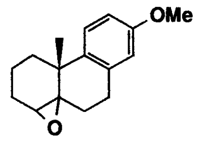

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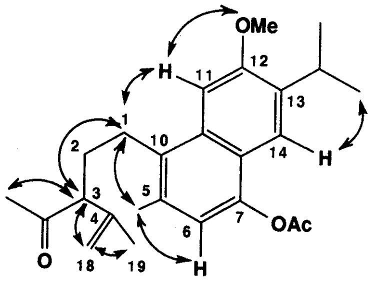
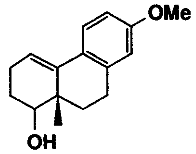


Fig. 1. NOESY Spectrum of Compound 29

Arrows show NOE relationships.



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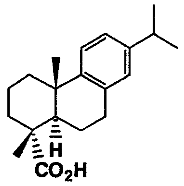

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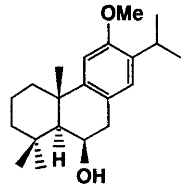

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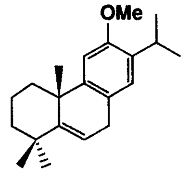

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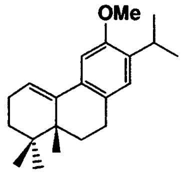

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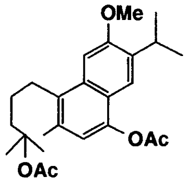

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tertiary methyl groups and a triplet signal at δ 5.70 (J=5 Hz) due to an olefinic proton. Treatment of **25** with boron trifluoride etherate at room temperature produced a rearranged compound (**26**) in 53.9% yield. The ^{1}H-NMR spectrum of **26** showed singlet signals at δ 0.89, 0.92, and 0.95 due to three tertiary methyl groups and a triplet signal at δ 5.98 (J=4 Hz) due to an olefinic proton. The appearance of these three methyl signals at higher field, and of the olefinic proton signal at lower field, than those in **25** suggested that the angular methyl group at the C-10 position had rearranged to the C-5 position, resulting in the formation of a new trisubstituted double bond between C-1 and C-10. Thus, the structure of **26** was assigned as 12-methoxy-5β-methyl-10-norabieta-1(10),8,11,13-tetraene.

Subsequently, 12-methoxy-7-oxo-5,8,11,13-abietatetraene[14] (**27**) was treated with sulfuric acid in acetic anhydride at room temperature to give a rearranged product with a naphthalene nucleus (**28**, 45.1% yield), together with the recovered starting compound (**27**, 42.2% yield). The mass spectrum of **28** gave a molecular ion peak at m/z 354.2173 (M$^+$), corresponding to the formula $\mathrm{C_{23}H_{30}O_3}$, and its infrared (IR) spectrum showed an absorption band at 1755 cm^{-1} due to an acetoxyl group on an aryl ring. In the ^{1}H-NMR spectrum, **28** exhibited the signals of two vinyl methyl groups at δ 1.62 and 1.73, methyl and acetoxyl groups on an aryl ring at δ 2.44 and 2.46, an olefinic proton at δ 5.33, and three aromatic protons at δ 6.90, 7.24 and 7.55. These spectral data suggested that the angular methyl group in **27** had rearranged to the C-5 position and ring B was aromatized with opening of ring A to form an unsaturated side chain. Thus, the structure of **28** was assigned as 4,5-seco-5,10-*friedo*-7-acetoxy-12-methoxyabieta-3,5(10),6,8,11,13-hexaene. A similar treatment of **27** with sulfuric acid in acetic anhydride was then carried out at 55—60 °C and this reaction, in addition to **28** (27.9% yield), produced two other naphthalene derivatives, **29** (24.2% yield) and **30** (14.7% yield), which were also obtained from **28** by a similar treatment. The molecular formulas of **29** and **30** were respectively assigned as $\mathrm{C_{25}H_{32}O_4}$ and $\mathrm{C_{27}H_{36}O_6}$ from their mass spectra, and their ^{1}H-NMR spectra were very similar to that of **28** except for signals due to the side chain. The ^{1}H-NMR spectrum of **29** exhibited signals due to the side chain at δ 1.70 (3H), 2.20 (3H), and 4.97 (1H) and 4.99 (1H), which were assigned to a vinyl methyl group, an acetyl group and terminal methylene protons, respectively. On the other hand, the ^{1}H-NMR spectrum of **30** showed four singlet signals at δ 1.45 (3H) and 1.50 (3H) due to a *gem*-dimethyl group, at δ 1.99 (3H) due to an acetoxyl group, and at δ 2.37 (3H) due to an acetyl group.

The nuclear Overhauser effect spectroscopy (NOESY) experiment on **29** gave cross peaks between 18-H and 4-CH$_3$, 18-H and 3-H, 3-H and 3-COCH$_3$, 3-H and 1-H$_2$, 1-H$_2$ and 5-CH$_3$, 1-H$_2$ and 11-H, 5-CH$_3$ and 6-H, 14-H and 13-CH(C$\underline{\mathrm{H}}_3$)$_2$, and 12-OCH$_3$ and 11-H, respectively, as shown in Fig. 1. On the basis of these spectral data, the structures of **29** and **30** were assigned as 4,5-seco-5,10-*friedo*-7-acetoxy-3-acetyl-12-methoxyabieta-4(18),5(10),6,8,11,13-hexaene and its 4-acetoxy derivative, respectively. It is of interest that the enone **27**, contrary to our expectation that it would give the diacetoxy compound (**31**), produced three new naphthalene derivatives, **28**, **29** and **30**. A possible mechanism for the rearrangement of the enone **27** with sulfuric acid in acetic anhydride is depicted in Chart 1.

The enone **27** first produced a C-10 carbonium ion intermediate (**27′**) by the enolization of the enone system

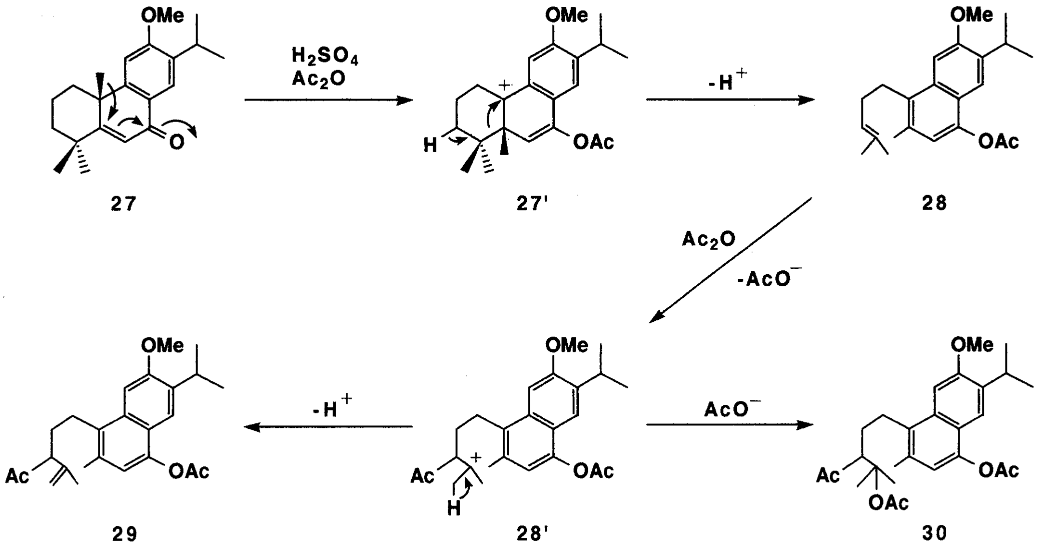

Chart 1

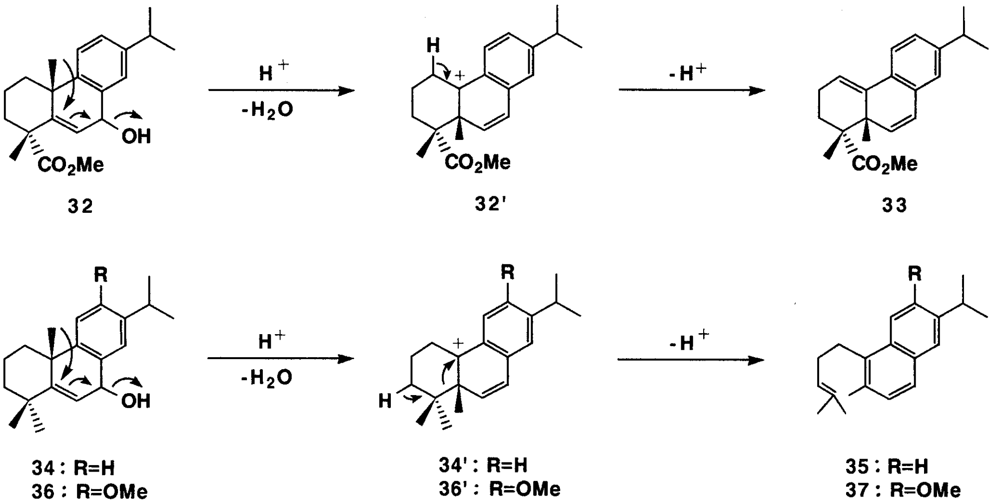

Chart 2

under acidic conditions, followed by the migration of the angular methyl group to the C-5 position. The cleavage of the C(4)–C(5) bond in the intermediate **27′** was accompanied by deprotonation at the C-3 position to give the naphthalene derivative **28**. Subsequent reaction of the trisubstituted double bond in **28** with acetic anhydride provided a 3-acetyl C-4 carbonium ion intermediate (**28′**), which was then transformed into **29** by the deprotonation of a methyl group at the C-18 position and into **30** by the addition of an acetate anion to the C-4 position.

As described above, Cambie and Hayward[7] reported a facile rearrangement of a 7α-hydroperoxide (**19**) or a 7α-hydroxy compound (**20**) into a naphthalene derivative, whose structure (**21**), however, could not be assigned conclusively. Therefore, it seemed to be necessary to examine this rearrangement in more detail, especially the structure of the rearranged product. For this purpose, the enones, **5**[15] and **11**,[6] were reduced with sodium borohydride in the presence of cerium(III) chloride heptahydrate[16] at room temperature and the resulting 7-hydroxy compounds, **32** and **34**, were further treated with *p*-toluenesulfonic acid monohydrate in benzene to give the rearranged products, **33** (78.3% yield from **5**) and **35** (74.7% yield from **11**), respectively. The molecular formulas of **33** and **35** were determined respectively to be $C_{21}H_{26}O_2$ and $C_{20}H_{26}$ from their mass spectra. The ^1H-NMR spectrum of **33** showed the presence of two tertiary methyl groups at δ 1.13 (3H) and 1.34 (3H), three olefinic protons at δ 6.03 (1H, t, J=4.0 Hz), 6.09 (1H, d, J=9.8 Hz), and 6.29 (1H, d, J=9.8 Hz), and three aromatic protons at δ 6.84 (1H, d, J=1.8 Hz), 6.99 (1H, dd, J=8.0, 1.8 Hz), and 7.36 (1H, d, J=8.0 Hz). Further, nuclear Overhauser effects were observed between the signals at δ 1.34 and 6.09 (15.1%), at δ 6.84 and 6.29 (18.3%), and at δ 7.36 and 6.03 (24.6%). These spectral data suggested the structure of **33** to be methyl 5β-methyl-10-norabieta-1(10),6,8,11,13-pentaen-18-oate. The ^1H-NMR spectrum of **35** also indicated the presence of an isopropyl group, two vinyl methyl groups, a methyl group on an aryl ring, an allylic methylene group, a benzylic methylene group, a trisubstituted olefinic proton, and five aromatic protons. Irradiation of the signal at δ 2.42 due to an aryl methyl group resulted in a 10.8% enhancement of the signal at δ 2.93—3.04 due to a benzylic methylene group and an 8.6% enhancement of the signal

Table I. Rearrangement of the Angular Methyl Group in Dehydroabietic Acid Derivatives

Substrate	Reagent	Product (yield, %)
25	$BF_3 \cdot OEt_2$	**26** (53.9)
27	H_2SO_4/Ac_2O	**28** (27.9), **29** (24.2), **30** (14.7)
27	1) $NaBH_4/CeCl_3$ 2) *p*-TsOH	**37** (67.8)
5	1) $NaBH_4/CeCl_3$ 2) *p*-TsOH	**33** (78.3)
11	1) $NaBH_4/CeCl_3$ 2) *p*-TsOH	**35** (74.7)

at δ 7.20 due to an aromatic proton at the C-6 position. From these spectral data the structure of **35** was assigned as 4,5-seco-5,10-*friedo*-abieta-3,5(10),6,8,11,13-hexaene. It is of interest that the enone (**5**) possessing a methoxycarbonyl group at the C-4 position produced the 5β-methyl-10-norabietane derivative (**33**) with an intact C(4)–C(5) bond, while the compound (**11**) possessing a *gem*-dimethyl group at the C-4 position produced a naphthalene derivative (**35**). Possible mechanisms of these rearrangements are also depicted in Chart 2.

That is, the alcohol **32** derived from the enone **5** undergoes dehydration with concomitant rearrangement of the angular methyl group to the C-5 position under acidic conditions, resulting in the formation of a C-10 carbonium ion intermediate (**32′**). This intermediate is then converted into the product (**33**) by deprotonation at the C-1 position. On the other hand, the alcohol **34** derived from the enone **11** is transformed into a C-10 carbonium ion intermediate (**34′**) as in the case of **32** and then the intermediate undergoes a cleavage of the C(4)–C(5) bond with concomitant deprotonation at the C-3 position to give the naphthalene derivative (**35**). Similarly, the enone (**27**) was also reduced with sodium borohydride in the presence of cerium(III) chloride heptahydrate and the resulting alcohol (**36**) was immediately treated with *p*-toluenesulfonic acid monohydrate to give a naphthalene derivative (**37**). The above results on the rearrangement of the angular methyl group in dehydroabietic acid derivatives are summarized in Table I.

From the present study, it seems that the rearranged product reported by Cambie and Hayward[7] has the structure **22**, not the structure **21**.

Experimental

All melting points are uncorrected. The IR spectra and optical rotations were measured in chloroform, and the ^1H-NMR spectra in deuteriochloroform with tetramethylsilane as an internal standard, unless otherwise stated. Column chromatography was performed using Merck silica gel (0.040—0.063 mm).

12-Methoxy-5,8,11,13-abietatetraene (25) A mixture of 12-methoxy-8,11,13-abietatrien-6β-ol[13] (**24**) (240 mg) and phosphoryl chloride (0.38 ml) in pyridine (3.8 ml) was stirred at room temperature for 8 h. 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 *in vacuo*. The residue was chromatographed on silica gel (20 g), using hexane–benzene (4:1) as an eluent, to give **25** as an oily material (146 mg, 64.6% yield), $[\alpha]_D$ $-62.1°$ ($c=0.79$). ^1H-NMR (60 MHz, CCl_4) δ: 1.13 and 1.16 (each 3H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 1.13 (3H, s) and 1.21 (3H, s) (4-$(CH_3)_2$), 1.25 (3H, s, 10-CH_3), 3.06 (1H, d, $J=5$ Hz) and 3.19 (1H, d, $J=5$ Hz) (7-H_2), 3.66 (3H, s, $-OCH_3$), 5.70 (1H, t, $J=5$ Hz, 6-H), 6.48 (1H, s) and 6.57 (1H, s) (aromatic protons). *Anal.* Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.62; H, 10.31.

Treatment of 25 with Boron Trifluoride Etherate A mixture of **25** (102 mg) and boron trifluoride etherate (0.2 ml) in dichloromethane (5.0 ml) was stirred at room temperature for 1 h. The mixture was diluted with ether, washed successively with dilute hydrochloric acid and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (20 g), using hexane–benzene (85:15) as an eluent, to give 12-methoxy-5β-methyl-10-norabieta-1(10),8,11,13-tetraene (**26**) as an oily material (55 mg, 53.9% yield). ^1H-NMR (60 MHz, CCl_4) δ: 0.89 (3H, s, 5-CH_3), 0.92 (3H, s) and 0.95 (3H, s) (4-$(CH_3)_2$), 1.13 and 1.16 (each 3H, d, $J=7$ Hz, $-CH(C\underline{H}_3)_2$), 3.72 (3H, s, $-OCH_3$), 5.98 (1H, t, $J=4$ Hz, 1-H), 6.60 (1H, s) and 6.73 (1H, s) (aromatic protons). *Anal.* Calcd for $C_{21}H_{30}O$: C, 84.51; H, 10.13. Found: C, 84.44; H, 10.27.

Rearrangement of 12-Methoxy-7-oxo-5,8,11,13-abietatetraene (27) with Sulfuric Acid in Acetic Anhydride a) At Room Temperature: A solution of **27** (180 mg) in acetic anhydride (1.8 ml) was treated with 0.5% concentrated sulfuric acid in acetic anhydride (1.8 ml), and the mixture was stirred at room temperature for 5 h, then diluted with ether, washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using hexane–benzene (15:85) as an eluent, to give 4,5-seco-5,10-*friedo*-7-acetoxy-12-methoxyabieta-3,5(10),6,8,11,13-hexaene (**28**) (92 mg, 45.1% yield). IR: 1755 cm^{-1}. ^1H-NMR (250 MHz) δ: 1.29 (6H, d, $J=6.9$ Hz, $-CH(C\underline{H}_3)_2$), 1.62 (3H, s, $-CH_3$), 1.73 (3H, s, $-CH_3$), 2.29 (2H, m, 2-H_2), 2.44 (3H, s) and 2.46 (3H, s) (5-CH_3 and 7-$OCOCH_3$), 2.98 (2H, m, 1-H_2), 3.38 (1H, m, $J=6.9$ Hz, $-C\underline{H}(CH_3)_2$), 3.95 (3H, s, $-OCH_3$), 5.33 (1H, t, $J=7.0$ Hz, 3-H), 6.90 (1H, s, 6-H), 7.24 (1H, s, 11-H), 7.55 (1H, s, 14-H). HRMS *m/z*: Found: 354.2173 (M^+). Calcd for $C_{23}H_{30}O_3$: M, 354.2195.

Further elution with the same solvent gave the starting **27** (76 mg: 42.2% yield).

b) At 55—60 °C: A solution of **27** (98 mg) in acetic anhydride (0.98 ml) was treated with 0.5% concentrated sulfuric acid in acetic anhydride (0.98 ml), and the mixture was heated at 55—60 °C for 3 h. After work-up as described in a), the crude product was chromatographed on silica gel (10 g), using hexane–benzene (1:3) as an eluent, to give **28** (31 mg, 27.9% yield). Subsequent elution with benzene and ether–benzene (5:95) afforded 4,5-seco-5,10-*friedo*-7-acetoxy-3-acetyl-12-methoxyabieta-4(18),5(10),6,8,11,13-hexaene (**29**) (30 mg, 24.2% yield), mp 80.5—81.5 °C (from hexane). IR: 1760, 1710 cm^{-1}. ^1H-NMR (400 MHz) δ: 1.28 (6H, d, $J=7.0$ Hz, $-CH(C\underline{H}_3)_2$), 1.70 (3H, dd, $J=1.5$, 1.0 Hz, 4-CH_3), 1.62 (1H, m) and 2.20 (1H, m) (2-H_2), 2.20 (3H, s, 3-$COCH_3$), 2.42 (3H, s, 5-CH_3), 2.43 (3H, s, 7-$OCOCH_3$), 2.87 (2H, m, 1-H_2), 3.31 (1H, dd, $J=9.0$, 5.0 Hz, 3-H), 3.39 (1H, m, $J=7.0$ Hz, $-C\underline{H}(CH_3)_2$), 4.05 (3H, s, $-OCH_3$), 4.97 (1H, br s) and 4.99 (1H, dq, $J=1.5$, 1.5 Hz), (18-H_2), 6.88 (1H, s, 6-H), 7.38 (1H, s, 11-H), 7.54 (1H, s, 14-H). HRMS *m/z*: Found: 396.2307 (M^+). Calcd for $C_{25}H_{32}O_4$: M, 396.2301.

Further elution with ether–benzene (5:95) afforded 4,5-seco-5,10-*friedo*-4,7-diacetoxy-3-acetyl-12-methoxyabieta-5(10),6,8,11,13-pentaene (**30**) (21 mg, 14.7% yield). IR: 1760, 1730, 1710 cm^{-1}. ^1H-NMR (250 MHz) δ: 1.28 (6H, d, $J=6.9$ Hz, $-CH(C\underline{H}_3)_2$), 1.45 (3H, s, $-CH_3$), 1.50 (3H, s, $-CH_3$), 1.59 (1H, m) and 2.12 (1H, m) (2-H_2), 1.99 (3H, s, 4-$OCOCH_3$), 2.37 (3H, s, 3-$COCH_3$), 2.41 (3H, s, 5-CH_3), 2.44 (3H, s, 7-$OCOCH_3$), 2.80 (2H, m, 1-H_2), 3.39 (1H, m, $J=6.9$ Hz, $-C\underline{H}(CH_3)_2$), 3.62 (1H, dd, $J=9.0$, 5.0 Hz, 3-H), 4.05 (3H, s, $-OCH_3$), 6.88 (1H, s, 6-H), 7.14 (1H, s, 11-H), 7.54 (1H, s, 14-H). HRMS *m/z*: Found: 456.2510 (M^+). Calcd for $C_{27}H_{36}O_6$: M, 456.2512.

Rearrangement of Methyl 7-Oxo-5,8,11,13-abietatetraen-18-oate (5) Sodium borohydride (19.3 mg) was added to a stirred mixture of **5** (160 mg) and cerium(III) chloride heptahydrate (190 mg) in methanol and tetrahydrofuran (1:1, 2.0 ml) at room temperature for 3 min. The mixture was further stirred at this temperature for 10 min, diluted with ether, washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a crude alcohol (**32**) (170 mg).

A solution of the above crude alcohol (**32**, 170 mg) and *p*-toluenesulfonic acid monohydrate (17 mg) in benzene (3.5 ml) was stirred at room temperature for 1 h. The solution was diluted with ether, washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (15 g), using hexane–benzene (15:85) as an eluent, to give methyl 5β-methyl-10-norabieta-1(10),6,8,11,13-pentaen-18-oate (**33**) (119 mg, 78.3% yield), mp 59—60 °C (from methanol), $[\alpha]_D$ $-348°$ ($c=1.54$). ^1H-NMR (200 MHz) δ: 1.13 (3H, s, 4-CH_3), 1.23 (6H, d, $J=6.9$ Hz, $-CH(C\underline{H}_3)_2$), 1.34 (3H, s, 5-CH_3), 2.84 (1H, m, $J=6.9$ Hz, $-C\underline{H}(CH_3)_2$), 3.58 (3H, s, $-CO_2CH_3$), 6.03 (1H, t, $J=4.0$ Hz, 1-H), 6.09 (1H, d, $J=9.8$ Hz, 6-H), 6.29 (1H, d, $J=9.8$ Hz, 7-H), 6.84 (1H, d,

$J = 1.8$ Hz, 14-H), 6.99 (1H, dd, $J = 8.0$, 1.8 Hz, 12-H), 7.36 (1H, d, $J = 8.0$ Hz, 11-H). MS m/z: 310 (M^+). *Anal.* Calcd for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44. Found: C, 81.41; H, 8.37.

Rearrangement of 7-Oxo-5,8,11,13-abietatetraene (11) Sodium borohydride (166 mg) was added to a stirred solution of **11** (1.236 g) and cerium(III) chloride heptahydrate (1.632 g) in methanol and tetrahydrofuran (1 : 1, 15 ml) at room temperature for 15 min. The mixture was further stirred at this temperature for 5 min and then treated as described above to give a crude alcohol (**34**) (1.218 g).

A solution of the above crude alcohol (**34**) (1.218 g) and *p*-toluenesulfonic acid monohydrate (122 mg) in benzene (24 ml) was refluxed for 1 h. The solution was cooled and then treated as described above to give an oily product (1.114 g). This was chromatographed on silica gel (110 g), using hexane as an eluent, to give 4,5-seco-5,10-*friedo*-abieta-3,5(10),6,8,11,13-hexaene (**35**) as an oil (871 mg, 74.7% yield). ^{1}H-NMR (200 MHz) δ: 1.28 (6H, d, $J = 6.9$ Hz, $-CH(C\underline{H}_3)_2$), 1.55 (3H, s, $-CH_3$), 1.67 (3H, s, $-CH_3$), 2.18—2.29 (2H, m, 2-H_2), 2.42 (3H, s, 5-CH_3), 2.93—3.04 (3H, m, $-C\underline{H}(CH_3)_2$ and 1-H_2), 5.27 (1H, t, $J = 7.2$ Hz, 3-H), 7.20 (1H, d, $J = 7.5$ Hz, 6-H), 7.33 (1H, dd, $J = 8.8$, 1.9 Hz, 12-H), 7.51 (1H, d, $J = 7.5$ Hz, 7-H), 7.53 (1H, s, overlap, 14-H), 7.92 (1H, d, $J = 8.8$ Hz, 11-H). MS m/z: 266 (M^+). *Anal.* Calcd for $C_{20}H_{26}$: C, 90.16; H, 9.84. Found: C, 90.04; H, 9.67.

Rearrangement of 12-Methoxy-7-oxo-5,8,11,13-abietatetraene (27) Sodium borohydride (36 mg) was added to a stirred mixture of **27** (300 mg) and cerium(III) chloride heptahydrate (358 mg) in methanol and tetrahydrofuran (1 : 1, 2.4 ml) at room temperature for 10 min. The mixture was further sitrred at this temperature for 8 min and then treated as described above to give a crude alcohol (**36**) (303 mg).

A solution of the above crude alcohol (**36**) (303 mg) and *p*-toluenesulfonic acid monohydrate (50 mg) in benzene (6.0 ml) was stirred at room temperature for 1 h. The solution was treated as described above and the crude product was purified by repeated column chromatography on silica gel, using hexane–benzene (7 : 3 and then 1 : 1) as eluents, to give 4,5-seco-5,10-*friedo*-12-methoxyabieta-3,5(10),6,8,11,13-hexaene (**37**) (133 mg, 52.0% yield). ^{1}H-NMR (60 MHz) δ: 1.30 (6H, d, $J = 7.0$ Hz, $-CH(C\underline{H}_3)_2$), 1.63 (3H, s, $-CH_3$), 1.73 (3H, s, $-CH_3$), 2.47 (3H, s, 5-CH_3), 3.96 (3H, s, $-OCH_3$), 5.35 (1H, t, $J = 7.0$ Hz, 3-H), 7.12 (1H, d, $J = 8.5$ Hz, 6-H), 7.25 (1H, s, 11-H), 7.53 (1H, d, $J = 8.5$ Hz, 7-H), 7.55 (1H, s, 14-H). *Anal.* Calcd for $C_{21}H_{28}O$: C, 85.08; H, 9.52. Found: C, 85.27; H, 9.39. Further elution with benzene afforded unchanged **27** (63 mg, 23.3% yield).

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