

Collins Oxidation of Methyl (+)-13 β -Abiet-8-en-18-oate and Absolute Configuration of Suaveolic Acid

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The oxidation of methyl (+)-13 β -abiet-8-en-18-oate with Collins reagent yielded nine oxidation products. Their structures were elucidated on the basis of spectroscopic and chemical data to be methyl (–)-14-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (1% yield), methyl (–)-11,14-dioxoabieta-8,12-dien-18-oate (1%), methyl (+)-11-oxo-13 β -abiet-8-en-18-oate (18%), methyl (–)-8 α ,9 α -epoxy-7-oxo-13 β -abietan-18-oate (2%), methyl (+)-7-oxoabieta-8,11,13-trien-18-oate (2%), methyl (+)-11,14-dihydroxy-7-oxoabieta-8,11,13-trien-18-oate (2%), methyl (+)-7,11-dioxo-13 β -abiet-8-en-18-oate (17%), methyl (+)-14-oxo-13 β -abiet-8-en-18-oate (**15**) (4%), and methyl (+)-7-oxo-13 β -abiet-8-en-18-oate (23%) respectively. It is noteworthy that oxygenation occurs not only at the C-7 and C-11 positions but also at the C-14 position. The oxygenated products obtained in this studies could be useful intermediates for the synthesis of the oxidized diterpenoids of abietane skeleton. To exemplify this, **15** was converted to methyl suaveolate and suaveolol. Hydrolysis of the former yielded suaveolic acid, thus confirming its absolute configuration to be 4R, 5R, 10S, 13S, and 14S.

The allylic oxygenated derivatives of methyl (+)-13 β -abiet-8-en-18-oate (**1**)¹⁾ seem to be useful intermediates for the partial syntheses of naturally occurring diterpenes possessing oxygen functions at the C-7, C-11, and/or C-14 positions. For this reason we attempted the oxidation of **1** with Collins reagent, which was superior to other reagents used for allylic oxidation,²⁾ and obtained the products oxygenated at the C-14 position in addition to those with oxygen functions at the C-7 and C-11 positions. This result is in contrast with the previously reported oxidation of **1** with *t*-butyl chromate.³⁾ A compound of the former type has been successfully converted to suaveolic acid;⁴⁾ this conversion

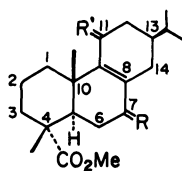
confirms its absolute configuration.

Collins Oxidation of Methyl (+)-13 β -Abiet-8-en-18-oate (1).

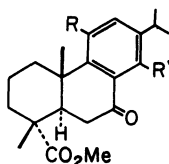
The oxidation of **1** was carried out with Collins reagent⁵⁾ in dichloromethane at room temperature for 24 h. The reaction mixture was carefully separated by repeated column chromatography on silica gel to give nine keto ester compounds: A (1%), B (1%), C (18%), D (2%), E (2%), F (2%), G (17%), H (4%), and I (23%), in the order of elution. The structure elucidation of these oxidation products was carried out as follows.

Compounds A and B were obtained as a mixture which could not be separated satisfactorily. Therefore the mixture was acetylated with refluxing acetic anhydride in the presence of sodium acetate and the resulting crude product was successfully separated by column chromatography on silica gel to give an acetylated A and the original ketone B. The more polar acetylated A showed the presence of an acetoxy group at 1763 cm^{–1} in its IR spectrum and a conjugated carbonyl group at 1673 cm^{–1}. Its ¹H NMR spectrum indicated signals due to a pair of ortho-coupling aromatic protons at δ 7.14 and 7.37 (each 1H, d, and *J* = 8 Hz). Consequently, the structure of the acetylated A was determined to be methyl 14-acetoxy-7-oxoabieta-8,11,13-trien-18-oate (**2**). Hydrolysis of the acetate **2** with sodium hydrogencarbonate in refluxing aqueous methanol gave the original ketone A, methyl 14-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**3**),⁶⁾ whose ¹H NMR spectrum showed a reasonable signal at δ 13.08 (1H, s), indicating the presence of a hydroxyl group chelated with a conjugated carbonyl group (IR: 1622 cm^{–1}). The compound B, which was less polar than the acetate **2**, showed the presence of a *p*-quinone moiety [IR: 1640, 1597 cm^{–1}; ¹H NMR: δ 6.32 (1H, d, *J* = 1 Hz); UV: $\lambda_{\text{max}}^{\text{EtOH}}$ 257 nm (ϵ 11800), 338 (340), 420 (40)]. On the basis of these spectral data and mass spectrum [*m/e* 344 (*M*⁺)] the structure of the compound B was determined to be methyl 11,14-dioxoabieta-8,12-dien-18-oate (**4**).⁷⁾

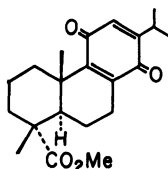
The compound C (mp 108–110 °C; IR: 1715, 1652 cm^{–1}) was identified as methyl 11-oxo-13 β -abiet-8-en-18-oate (**5**) by direct spectral comparison with an



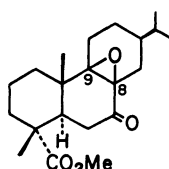
- 1 R = R' = H₂
 5 R = H₂, R' = O
 9 R = α -H- β -OH, R' = H₂
 14 R = R' = O
 16 R = O, R' = H₂



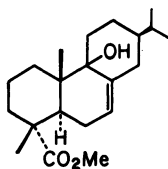
- 2 R = H, R' = OAc
 3 R = H, R' = OH
 11 R = OAc, R' = OH
 12 R = R' = OH
 13 R = R' = H



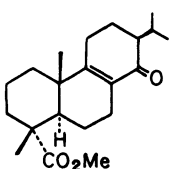
4



- 6 8 α ,9 α -epoxy
 8 8 β ,9 β -epoxy



- 7 9 α -OH
 10 9 β -OH



15

authentic sample.^{3,8)}

The compound D (mp 122–123 °C, C₂₁H₃₂O₄) showed absorption bands at 1718 and 1695 cm⁻¹ in its IR spectrum and no UV absorption band in the 220–250 nm region, indicating the presence of an ester group and a non-conjugated carbonyl group. The fourth oxygen atom should be an epoxide one. In its ¹H NMR spectrum a signal at δ 2.81 (1H, dd, *J* = 11.5 and 8 Hz) assignable to a C-5α proton⁹⁾ suggested that the structure of the ketone D was methyl 8α,9α-epoxy-7-oxo-13β-abietan-18-oate (**6**). This structure was subsequently confirmed by transformation of **6** to the known methyl 9α-hydroxy-13β-abiet-7-en-18-oate (**7**)¹⁰⁾ by refluxing with hydrazine hydrate in methanol containing a small amount of acetic acid under a stream of nitrogen. For comparison, methyl 8β,9β-epoxy-7-oxo-13β-abietan-18-oate (**8**) was also synthesized by epoxidation of methyl 7β-hydroxy-13β-abiet-8-en-18-oate (**9**)¹¹⁾ with *m*-chloroperbenzoic acid followed by oxidation of the resulting methyl 8β,9β-epoxy-7β-hydroxy-13β-abietan-18-oate with Jones reagent. The epoxide **8** was then converted to methyl 9β-hydroxy-13β-abiet-7-en-18-oate (**10**) by a similar treatment with hydrazine hydrate. The ¹H NMR signals corresponding to the methyl groups at the C-4 and C-10 positions in **6**, **7**, **8**, and **10** are shown in Table 1. The chemical shifts of the C-10 methyl groups in the 9β series are more deshielded than those in 9α series; this follows from the stereochemistry of their oxygen functions. The pyridine-induced solvent shift¹²⁾ (Δ = 0.21 ppm) of the C-10 methyl group in **10** also supported the conclusion that the stereochemistry of the hydroxyl group at the C-9 position was in β-configuration.

Compounds E and F were obtained as a mixture which contained one component possessing a free phenolic hydroxyl group [¹H NMR: δ 6.01 (1H, bs)]. Therefore, the mixture was acetylated with acetic anhydride in pyridine at room temperature and the resulting crude product was purified by column chromatography on silica gel to give the original E and an acetylated F. The acetylated F, mp 158.5–159.5 °C, which was less polar, showed the presence of an acetoxyl group [IR: 1757 cm⁻¹, ¹H NMR: δ 2.32 (3H, s)], an aromatic proton [¹H NMR: δ 6.95 (1H, s)], and a hydroxyl group [¹H NMR: δ 13.54 (1H, s)] chelated with a conjugated carbonyl group (IR: 1630 cm⁻¹). These spectral data suggested that the structure of the acetylated F was methyl 11-acetoxy-14-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**11**). Hydrolysis of the acetate **11** with sodium hydrogencarbonate in refluxing aqueous methanol gave the original ketone F, methyl 11,14-dihydroxy-7-oxoabieta-8,11,13-trien-18-oate (**12**), mp 233.5–234.5 °C, whose ¹H NMR spectrum showed a signal at δ 3.47 (1H, dm, *J* = 12 Hz) assignable to C-1β proton; this supported the presence of a hydroxyl group at the C-11 position.¹³⁾ The compound E isolated from the more polar fraction was identified as methyl 7-oxoabieta-8,11,13-trien-18-oate (**13**) by direct spectral comparison with an authentic sample.¹⁴⁾

Compound G (mp 87–89.5 °C; IR: 1720, 1670 cm⁻¹) was also identified as methyl 7,11-dioxo-13β-abiet-8-en-18-oate (**14**) by direct spectral comparison

TABLE 1. CHEMICAL SHIFTS OF C₄- AND C₁₀-METHYL GROUPS OF **6**, **7**, **8**, AND **10** (δ VALUE)

Solvent ^{a)}	9α Series			9β Series		
	6	7	8	10		
C ₄ -Me	1.18	1.30	1.39	1.15	1.30	1.37
C ₁₀ -Me	0.94	0.96	1.03	1.15	1.08	1.29

a) A, carbon tetrachloride; B, chloroform-*d*; C, pyridine-*d*₅.

with an authentic sample.^{3,8)}

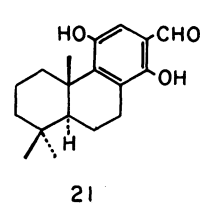
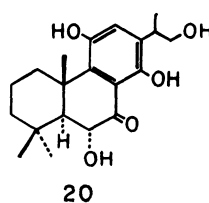
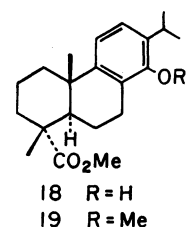
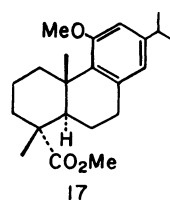
Compound H showed the presence of a conjugated carbonyl group in the IR spectrum (1655 cm⁻¹) and a characteristic isopropyl group in the ¹H NMR spectrum [δ 0.79 and 0.94 (each 3H, d, and *J* = 7 Hz)]. The IR and ¹H NMR spectra of ketone H were identical with those reported for methyl 14-oxo-13β-abiet-8-en-18-oate (**15**).⁴⁾

Compound I (mp 111–112 °C; IR: 1725, 1652 cm⁻¹) was identified as methyl 7-oxo-13β-abiet-8-en-18-oate (**16**) by direct spectral comparison with an authentic sample.^{3,8)}

Thus, the structures of nine oxidation products could be elucidated. The present oxidation of **1** with Collins reagent occurred not only at the C-7 and C-11 positions, as was the case with *t*-butyl chromate, but also at the C-14 position; this latter resulted in the formation of **3**, **4**, **12**, and **15**. The latter compounds would be useful intermediate for the synthesis of 14-oxygenated abietane diterpenes as illustrated below.

The compounds, **5** and **14**, were each converted¹⁵⁾ to methyl 11-methoxyabieta-8,11,13-trien-18-oate (**17**).¹⁶⁾ Treatment of **15** with copper(II) bromide and lithium bromide in refluxing acetonitrile afforded methyl 14-hydroxyabieta-8,11,13-trien-18-oate (**18**),¹⁷⁾ which was then methylated with methyl iodide and sodium hydride in *N,N*-dimethylformamide to give methyl 14-methoxyabieta-8,11,13-trien-18-oate (**19**).¹⁷⁾ These compounds, **17** and **19**, seem to be useful intermediates for the syntheses of nellionol (**20**),¹⁸⁾ premnolal (**21**),^{18,19)} and the like.¹⁸⁾

Absolute Configuration of Suaveolic Acid. Suaveolic acid and suaveolol have been isolated from the leaves and stems of *Hyptis suaveolens* (L) Poit (Labiatae) by Manchand *et al.*⁴⁾ On the basis of chemical and spectro-



scopic studies, the structures of suaveolic acid and suaveolol were assigned respectively to be **22** and **23**; their relative stereochemistry were further confirmed by an X-ray structure analysis of methyl suaveolate (**24**).⁴ In order to clarify the absolute configurations of these unusual⁴ tricyclic diterpenes, metal hydride reductions of the 14-oxo compound **15** were carried out.

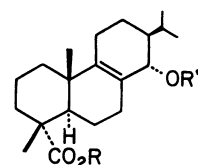
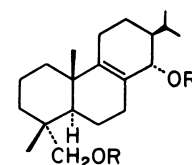
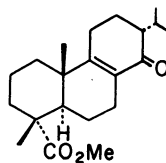
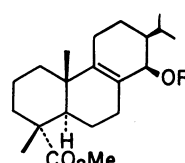
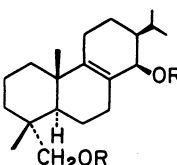
The compound **15** was reduced with sodium borohydride in refluxing tetrahydrofuran in the presence of aqueous sodium hydroxide to afford a mixture of alcohols. The mixture was then separated by column chromatography on silica gel to give four alcohols: W (24%), X (38%), Y (7.5%), and Z (15%), in the order of elution. Treatment of **15** with sodium methoxide in refluxing methanol provided an inseparable mixture of **15** and its C-13 epimer (**25**) [¹H NMR: δ 0.90 and 0.91 (each 3H, d, and $J=6$ Hz, $-\text{CH}(\text{CH}_3)_2$)]. The ¹H NMR spectrum of the mixture showed these epimers were present approximately in a 2 : 1 ratio. However, when **15** was treated with aqueous sodium hydroxide in refluxing tetrahydrofuran, the starting ketone **15** was recovered. Therefore, it is clear that no epimerization at the C-13 position in **15** occurred under the above reduction conditions.

The oily alcohol W ($[\alpha]_D^{25} +125^\circ$) showed the presence of a hydroxyl group (3620, 3460 cm^{-1}) and an ester group (1720 cm^{-1}) in the IR spectrum. Its ¹H NMR spectrum showed signals at δ 0.95 and 0.98 (each 3H, d, and $J=6$ Hz) due to an isopropyl group and at δ 3.78 (1H, br, $W_{1/2}=5.5$ Hz) due to C-14 α proton. These physical and spectral data were not identical with those of methyl suaveolate (**24**). Oxidation of the alcohol W with pyridinium chlorochromate in dichloromethane afforded the ketone **15**. The alcohol W was then acetylated with acetic anhydride in pyridine to give an oily monoacetate (**27**) ($[\alpha]_D^{25} +181^\circ$, IR: 1713 cm^{-1}). Thus, the structure of the alcohol W was identified as methyl 14 β -hydroxy-13 β -abiet-8-en-18-oate (**26**).

The alcohol X (mp 102–103 °C, $[\alpha]_D^{25} +59^\circ$; IR: 3600, 3450 br, 1720 cm^{-1}) was further characterized as its acetate (**28**) (mp 134.5–135 °C, $[\alpha]_D^{25} -41^\circ$, IR: 1720 cm^{-1}). Oxidation of the alcohol X with pyridinium chlorochromate in dichloromethane afforded the ketone **15**. The physical and spectral data, including optical rotation of the alcohol X and **28**, were identical with those of methyl suaveolate and its acetate.

The oily alcohol Y ($[\alpha]_D^{25} +92^\circ$; IR: 3625, 3450 cm^{-1}) showed the presence of hydroxyl groups [¹H NMR: δ 3.15 and 3.44 (each 1H, d, and $J=10.5$ Hz, $-\text{CH}_2\text{OH}$) and 3.77 (1H, br, $W_{1/2}=6$ Hz, $-\text{CHOH}$)] and the absence of an ester group. Acetylation of the alcohol Y with acetic anhydride in pyridine afforded the corresponding diacetate (**30**) (mp 93–95 °C, $[\alpha]_D^{25} +201^\circ$, IR: 1722 cm^{-1}). The physical and spectral data of the alcohol Y and **30** were different from those of suaveolol and its diacetate. Thus, the structure of the alcohol Y was identified as 13 β -abiet-8-ene-14 β ,18-diols (**29**).

The alcohol Z (mp 180–182 °C, $[\alpha]_D^{25} +84^\circ$; IR: 3620, 3290 cm^{-1}) showed signals at δ 2.97 and 3.46 (each 1H, d, and $J=11$ Hz) due to a hydroxymethyl group and at δ 3.77 (1H, bd, $J=7$ Hz) due to C-14 β

**22** R = R' = H**24** R = Me, R' = H**28** R = Me, R' = Ac**23** R = H**31** R = Ac**25****26** R = H**27** R = Ac**29** R = H**30** R = Ac

proton in the ¹H NMR spectrum. Acetylation of the alcohol Z with acetic anhydride in pyridine yielded an oily diacetate (**31**) ($[\alpha]_D^{25} -41^\circ$, IR: 1720 cm^{-1}). The physical and spectral data of the alcohol Z and **31** were identical with those of suaveolol and its diacetate.

Subsequently, the ketone **15** was reduced with lithium aluminium hydride in refluxing ether. Chromatographic purification of the crude product gave **23** (47%) and **29** (23%).

Finally, the synthetic methyl suaveolate **24** was hydrolyzed with potassium *t*-butoxide in dimethyl sulfoxide at room temperature to give suaveolic acid **22**, mp 188–190 °C, $[\alpha]_D^{25} +71^\circ$.

From the present study, the absolute configurations of suaveolic acid and suaveolol were conclusively assigned as 4R, 5R, 10S, 13S, and 14S.

Experimental

All melting points are uncorrected. The IR and optical rotations were measured in chloroform, and the ¹H NMR spectra in carbon tetrachloride at 90 MHz, with tetramethylsilane as an internal standard, unless otherwise stated. The chemical shifts are presented in terms of δ values; s: singlet, bs: broad singlet, d: doublet, bd: broad doublet, dd: double doublet, dm: doublet of multiplet, t: triplet, bt: broad triplet, m: multiplet. The low-resolution mass spectra were obtained by direct inlet (ion-source temperature 200 °C and ionizing voltage 70 eV). The column chromatography was performed using Merck silica gel (0.063 mm).

Methyl (+)-13 β -Abiet-8-en-18-oate (1). A suspension of (+)-13 β -abiet-8-en-18-oic acid¹ in acetone was methylated with diazomethane at room temperature for 3 h to give **1**³ as an oil, $[\alpha]_D^{25} +79^\circ$ (c 3.82), which without purification was used in the next reaction.

Oxidation of 1 with Collins Reagent.

Chromium trioxide

(113.2 g) was added to a mechanically stirred solution of pyridine (188 g) in dichloromethane (2.4 l) over a period of 20 min with cooling in an ice-bath. After the mixture had been stirred at room temperature for 2 h, a solution of **1** (24.0 g) in dichloromethane (200 ml) was added over a period of 30 min. The reaction mixture was further stirred at room temperature for 24 h and then decanted from a tarry residue, which was washed with ether (3.2 l). The combined organic solution was washed successively with aqueous sodium hydrogencarbonate, dilute hydrochloric acid, and brine. The solution was concentrated to ca. 2 l of volume, dried over sodium sulfate, and evaporated to give a reddish brown oil (24.0 g). The crude product (48.0 g) obtained from two runs of the oxidation was chromatographed on silica gel (1.5 kg), using benzene as the eluent, to give the recovered **1** (5.66 g; 12%).

Subsequent elution with benzene gave a mixture of two ketones (1.02 g), **A** (**3**) and **B** (**4**), whose separation and purification are described later.

Further elution with benzene afforded a ketone **C** (8.95 g; 18%) which was recrystallized from methanol, mp 108–110 °C, $[\alpha]_D^{25} + 104^\circ$ (*c* 0.743, EtOH) [lit.³ mp 108–109 °C, $[\alpha]_D^{25} + 104^\circ$ (EtOH)]; IR: 1715, 1652, 1608 cm⁻¹; ¹H NMR (CDCl₃): 0.90 (6H, bd, *J* = 5.5 Hz, –CH(CH₃)₂), 1.18 and 1.21 (each 3H and s, C₄–CH₃ and C₁₀–CH₃), 2.87 (1H, dm, *J* = 13 Hz, C_{1β}–H), 3.65 (3H, s, –CO₂CH₃). The IR and ¹H NMR spectra of the ketone **C** were identical with those of methyl 11-oxo-13β-abiet-8-en-18-oate (**5**).^{3,8}

Elution with ether–benzene (1 : 99) gave a fraction (1.36 g) containing a ketone **D**, which was further purified by column chromatography on silica gel (150 g) to afford the pure ketone **D** (0.84 g; 2%), methyl 8α,9α-epoxy-7-oxo-13β-abietan-18-oate (**6**). This was recrystallized from methanol to give colorless needles, mp 122–123 °C, $[\alpha]_D - 64^\circ$ (*c* 1.70); IR: 1718, 1695 cm⁻¹; ¹H NMR: 0.88 (6H, bd, *J* = 7 Hz, –CH(CH₃)₂), 0.94 (3H, s, C₁₀–CH₃), 1.18 (3H, s, C₄–CH₃), 2.81 (1H, dd, *J* = 11.5 and 8 Hz, C_{8α}–H), 3.65 (3H, s, –CO₂CH₃). Found: C, 72.33; H, 9.19%. Calcd for C₂₁H₃₂O₄: C, 72.38; H, 9.26%.

Elution with ether–benzene (1 : 99) afforded a mixture of two ketones (3.02 g), **E** (**13**) and **F** (**12**), whose separation and purification are described later.

Further elution with ether–benzene (1 : 99) gave a ketone **G** (8.96 g; 17%) which was recrystallized from methanol, mp 87–89.5 °C, $[\alpha]_D + 78^\circ$ (*c* 1.10) (lit.³ mp 88–89.5 °C, $[\alpha]_D^{25} + 87^\circ$); IR: 1720, 1670 vs cm⁻¹; ¹H NMR (CDCl₃): 0.94 (6H, bd, *J* = 6 Hz, –CH(CH₃)₂), 1.28 and 1.32 (each 3H and s, C₄–CH₃ and C₁₀–CH₃), 2.84 (1H, dm, *J* = 12 Hz, C_{1β}–H), 3.67 (3H, s, –CO₂CH₃). The IR and ¹H NMR spectra of the ketone **G** were identical with those of methyl 7,11-dioxo-13β-abiet-8-en-18-oate (**14**).^{3,8}

The next fraction (2.40 g) containing ketone **H** was rechromatographed on silica gel (240 g), using ether–hexane (1 : 4) as the eluent, to give the pure ketone **H** (1.91 g; 4%) as an oil, $[\alpha]_D + 99^\circ$ (*c* 0.985) (lit.⁴ $[\alpha]_D^{25} + 115.2^\circ$); IR: 1720, 1655, 1620 cm⁻¹; ¹H NMR (CDCl₃): 0.79 and 0.94 (each 3H, d, and *J* = 7 Hz, –CH(CH₃)₂), 1.11 (3H, s, C₁₀–CH₃), 1.21 (3H, s, C₄–CH₃), 3.66 (3H, s, –CO₂CH₃); UV: λ_{max}^{EtOH} 245.5 nm (ϵ 12700). Found: C, 75.96; H, 9.60%. Calcd for C₂₁H₃₂O₃: C, 75.86; H, 9.70%. The IR and ¹H NMR spectra of the ketone **H** were identical with those reported for methyl 14-oxo-13β-abiet-8-en-18-oate (**15**).⁴

Elution with ether–benzene (3 : 97) gave a ketone **I** (11.4 g; 23%) which was recrystallized from methanol; mp 111–112 °C; $[\alpha]_D + 110^\circ$ (*c* 5.54); IR: 1725, 1652, 1618 cm⁻¹; ¹H NMR: 0.95 (6H, bd, *J* = 6 Hz, –CH(CH₃)₂), 1.11 (3H, s, C₁₀–CH₃), 1.24 (3H, s, C₄–CH₃), 3.66 (3H, s, –CO₂CH₃).

Found: C, 75.96; H, 9.89%. Calcd for C₂₁H₃₂O₃: C, 75.86; H, 9.70%. The IR and ¹H NMR spectra of the ketone **I** were identical with those of methyl 7-oxo-13β-abiet-8-en-18-oate (**16**).^{3,8}

Separation and Purification of the Ketones **A** (**3**) and **B** (**4**).

A part (125 mg) of the above mixture of ketones **A** and **B** was refluxed with acetic anhydride (5.5 mL) in the presence of sodium acetate (270 mg) for 5 h. After removal of the acetic anhydride *in vacuo*, the residue was mixed with brine and extracted with ether. The ether extract was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated to give an oil (136 mg), which was chromatographed on silica gel (20 g). The less polar fraction eluted with ether–hexane (5 : 95) afforded the ketone **B** (38 mg), $[\alpha]_D - 77^\circ$ (*c* 0.575) (lit.⁷ $[\alpha]_D - 68.9^\circ$); IR: 1715, 1640, 1597 cm⁻¹; UV: λ_{max}^{EtOH} 257 nm (ϵ 11800), 338 (340), 420 (40); ¹H NMR (CDCl₃): 1.11 (6H, d, *J* = 7 Hz, –CH(CH₃)₂), 1.26 and 1.31 (each 3H and s, C₄–CH₃ and C₁₀–CH₃), 3.67 (3H, s, –CO₂CH₃), 6.32 (1H, d, *J* = 1 Hz, C₁₂–H); MS (*m/e*): 344 (M⁺). The IR, ¹H NMR, and low-resolution mass spectral data were identical with those reported for methyl 11,14-dioxoabieta-8,12-dien-18-oate (**4**).⁷

The more polar fraction eluted with ether–hexane (4 : 6) afforded an acetylated ketone **A** (37 mg), methyl 14-acetoxy-7-oxoabieta-8,11,13-trien-18-oate (**2**), which was recrystallized from hexane, mp 160–161.5 °C, $[\alpha]_D + 19^\circ$ (*c* 0.520); IR: 1763, 1725, 1673 cm⁻¹; ¹H NMR: 1.16 and 1.21 (each 3H, d, and *J* = 7 Hz, –CH(CH₃)₂), 1.25 and 1.30 (each 3H and s, C₄–CH₃ and C₁₀–CH₃), 2.28 (3H, s, –OCOCH₃), 3.62 (3H, s, –CO₂CH₃), 7.14 and 7.37 (each 1H, d, and *J* = 8 Hz, C₁₁–H and C₁₂–H); MS (*m/e*): 386 (M⁺).

The acetoxy ketone (**2**) (20.5 mg) was refluxed with sodium hydrogencarbonate (17.5 mg) in 90% aqueous methanol (2.5 mL) for 1 h. After evaporation of the solvent *in vacuo*, the residue was mixed with brine, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel (5.0 g), using benzene as the eluent, to give the original hydroxy ketone **A** (14.0 mg) as an oil, $[\alpha]_D - 18^\circ$ (*c* 0.560); IR: 1725, 1622 cm⁻¹; ¹H NMR (CDCl₃): 1.21 and 1.23 (each 3H, d, and *J* = 7 Hz, –CH(CH₃)₂), 1.25 and 1.34 (each 3H and s, C₄–CH₃ and C₁₀–CH₃), 3.67 (3H, s, –CO₂CH₃), 6.77 and 7.36 (each 1H, d, and *J* = 8 Hz, C₁₁–H and C₁₂–H), 13.08 (1H, s, –OH); MS (*m/e*): 344 (M⁺). The IR and ¹H NMR spectra of the hydroxy ketone **A** were identical with those reported for methyl 14-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**3**).⁶

Methyl 9α-Hydroxy-13β-abiet-7-en-18-oate (7). A mixture of **6** (45.0 mg), 80% hydrazine hydrate (0.1 ml), and acetic acid (0.03 ml) in methanol (1.57 ml) was refluxed for 30 min under a stream of nitrogen. After the solvent had been removed, the residue was extracted with ether. The ether extract was washed successively with aqueous sodium hydrogencarbonate and brine, dried over sodium sulfate, and evaporated. The residual oil was chromatographed on silica gel (5.0 g), using ether–benzene (5 : 95) as the eluent, to afford **7**¹⁰ (7.9 mg; 18%), $[\alpha]_D - 120^\circ$ (*c* 0.395); IR: 3600, 3450 br, 1713 cm⁻¹; ¹H NMR (CDCl₃): 0.88 (6H, d, *J* = 7 Hz, –CH(CH₃)₂), 0.96 (3H, s, C₁₀–CH₃), 1.30 (3H, s, C₄–CH₃), 3.64 (3H, s, –CO₂CH₃), 5.41 (1H, bd, *J* = 4 Hz, C₇–H); MS (*m/e*): 334 (M⁺).

Methyl 8β,9β-Epoxy-7-oxo-13β-abietan-18-oate (8). Sodium borohydride reduction¹¹ of **16** afforded methyl 7β-hydroxy-13β-abiet-8-en-18-oate (**9**), mp 101–102 °C, $[\alpha]_D + 71^\circ$ (*c* 2.41, EtOH) [lit.¹¹ mp 100–101 °C, $[\alpha]_D^{25} + 66^\circ$ (EtOH)]; IR: 3600, 3425 br, 1720 cm⁻¹; ¹H NMR (CDCl₃): 0.89 (6H, d, *J* = 6.5 Hz, –CH(CH₃)₂), 1.04 (3H, s, C₁₀–CH₃), 1.20 (3H,

s, C₄-CH₃), 3.65 (3H, s, -CO₂CH₃), 4.07 (1H, bt, $J=8$ Hz, C_{7 α} -H).

A mixture of **9** (334 mg) and 85% *m*-chloroperbenzoic acid (406 mg) in dichloromethane (15 ml) was stirred at room temperature for 5 h and diluted with ether. The organic solution was washed successively with aqueous potassium iodide, aqueous sodium thiosulfate, aqueous sodium hydrogen-carbonate, and brine. After drying over sodium sulfate, the solution was evaporated *in vacuo*. The residual oil was chromatographed on silica gel (30 g), using ether-benzene (5 : 95) as the eluent, to give methyl 8 β ,9 β -epoxy-7 β -hydroxy-13 β -abietan-18-oate (165 mg); IR: 3575, 3400 br, 1718 cm⁻¹; ¹H NMR (CDCl₃): 0.85 (6H, d, $J=6.5$ Hz, -CH(CH₃)₂), 1.06 (3H, s, C₁₀-CH₃), 1.16 (3H, s, C₄-CH₃), 3.67 (3H, s, -CO₂CH₃), 3.78 (1H, bt, $J=8$ Hz, C_{7 α} -H).

A solution of the above epoxy compound (165 mg) in acetone (3.3 ml) was treated with Jones reagent (2.5 M: 0.5 ml) at 0 °C for 5 min. After the usual work-up, the crude product was purified by column chromatography on silica gel (15 g), using ether-benzene (1 : 99) as the eluent, to give **8** (107 mg: 31% from **9**) as an oil, $[\alpha]_D +32^\circ$ (c 2.11), IR: 1710 cm⁻¹; ¹H NMR: 0.88 (6H, bd, $J=6.5$ Hz, -CH(CH₃)₂), 1.15 (6H, s, C₄-CH₃ and C₁₀-CH₃), 3.65 (3H, s, -CO₂CH₃). Found: C, 72.23; H, 9.32%. Calcd for C₂₁H₃₂O₄: C, 72.38; H, 9.26%.

Methyl 9 β -Hydroxy-13 β -abiet-7-en-18-oate (10). A mixture of **8** (56 mg) and 80% hydrazine hydrate (0.12 ml), and acetic acid (0.04 ml) in methanol (1.86 ml) was treated as described for the preparation of **7**. The crude product was chromatographed on silica gel (5.0 g), using ether-benzene (3 : 97) as the eluent, to give **10** (14 mg: 26%) as an oil, $[\alpha]_D -66^\circ$ (c 0.455); IR: 3615, 3410 br, 1715 cm⁻¹; ¹H NMR (CDCl₃): 0.88 (6H, d, $J=6.5$ Hz, -CH(CH₃)₂), 1.08 (3H, s, C₁₀-CH₃), 1.30 (3H, s, C₄-CH₃), 3.65 (3H, s, -CO₂CH₃), 5.38 (1H, bd, $J=4$ Hz, C₇-H); MS (m/e): 334 (M⁺).

Separation and Purification of the Ketones E (13) and F (12). The mixture of the ketones (400 mg) E and F was treated with acetic anhydride (2.0 ml) in pyridine (2.0 ml) at room temperature for 2.5 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 methyl 11-acetoxy-14-hydroxy-7-oxoabieta-8,11,13-trien-18-oate (**11**) (99 mg) which was recrystallized from methanol, mp 158.5—159.5 °C, $[\alpha]_D +93^\circ$ (c 1.13); IR: 1757, 1723, 1630 cm⁻¹; ¹H NMR (CDCl₃): 1.23 (6H, d, $J=6$ Hz, -CH(CH₃)₂), 1.32 and 1.34 (each 3H and s, C₄-CH₃ and C₁₀-CH₃), 2.32 (3H, s, -OCOCH₃), 3.69 (3H, s, -CO₂CH₃), 6.95 (1H, s, C₁₂-H), 13.54 (1H, s, -OH). Found: C, 68.50; H, 7.62%. Calcd for C₂₃H₃₀O₆: C, 68.63; H, 7.51%. Subsequent elution gave a mixture of **11** and **13** (154 mg) (*ca.* 2 : 3 ratio by ¹H NMR analysis).

Further elution afforded the original ketone E (86 mg), $[\alpha]_D +20^\circ$ (c 3.91); IR: 1720, 1672, 1608 cm⁻¹; ¹H NMR: 1.25 (6H, d, $J=7$ Hz, -CH(CH₃)₂), 1.25 and 1.31 (each 3H and s, C₄-CH₃ and C₁₀-CH₃), 3.62 (3H, s, -CO₂CH₃), 7.20 (1H, d, $J=8.5$ Hz, C₁₁-H), 7.27 (1H, dd, $J=8.5$ and 2 Hz, C₁₂-H), 7.76 (1H, d, $J=2$ Hz, C₁₄-H). The IR and ¹H NMR spectra of the ketone E were identical with those of methyl 7-oxoabieta-8,11,13-trien-18-oate (**13**).¹⁴

A mixture of **11** (90 mg) and sodium hydrogencarbonate (80 mg) in 90% aqueous methanol (12 ml) was refluxed for 1 h and the solvent was removed *in vacuo*. The residue was extracted with ether and the ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was recrystallized from methanol to give methyl 11,14-dihydroxy-7-oxoabieta-8,11,13-trien-18-oate (**12**) (52 mg), mp 233.5—234.5 °C, $[\alpha]_D +121^\circ$ (c 0.595); IR: 3590, 3330 br, 1720, 1630 cm⁻¹; ¹H NMR (acetone-*d*₆): 1.16 and

1.17 (each 3H, d, and $J=7$ Hz, -CH(CH₃)₂), 1.33 and 1.45 (each 3H and s, C₄-CH₃ and C₁₀-CH₃), 3.47 (1H, dm, $J=12$ Hz, C_{1 β} -H), 3.66 (3H, s, -CO₂CH₃), 7.05 (1H, s, C₁₂-H), 7.87 (1H, s, disappeared with D₂O, C₁₁-OH), 13.02 (1H, s, disappeared with D₂O, C₁₄-OH). Found: C, 70.07; H, 8.05%. Calcd for C₂₁H₂₈O₅: C, 69.97; H, 7.83%.

Methyl 14-Hydroxyabieta-8,11,13-trien-18-oate (18). A mixture of **15** (332 mg), copper(II) bromide (402 mg), and lithium bromide (78 mg) in acetonitrile (16.6 ml) was refluxed for 6.5 h and then evaporated *in vacuo*. The residue was dissolved in ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated. The crude product was chromatographed on silica gel (40 g), using ether-benzene (1 : 99) as the eluent, to give **18**¹⁷ (190 mg: 57%) as an oil, $[\alpha]_D +38^\circ$ (c 0.635); IR: 3616, 1718, 1610, 1570 cm⁻¹; ¹H NMR (CDCl₃): 1.22 and 1.28 (each 3H and s, C₄-CH₃ and C₁₀-CH₃), 1.23 and 1.26 (each 3H, d, and $J=7$ Hz, -CH(CH₃)₂), 3.65 (3H, s, -CO₂CH₃), 4.69 (1H, bs, -OH), 6.83 and 6.99 (each 1H, d, and $J=8.5$ Hz, C₁₁-H and C₁₂-H). Found: C, 76.32; H, 9.10%. Calcd for C₂₁H₃₀O₃: C, 76.32; H, 9.15%. Further elution with ether-benzene (3 : 97) gave the recovered **15** (123 mg: 37%).

Methyl 14-Methoxyabieta-8,11,13-trien-18-oate (19). A mixture of **18** (1.18 g) and 55% sodium hydride (0.78 g) in *N,N*-dimethylformamide (39 ml) was stirred at room temperature for 45 min under a stream of nitrogen. After the addition of methyl iodide (0.30 ml), the mixture was stirred at 35—40 °C for 3 h and then some additional methyl iodide (0.30 ml) was added. The mixture was further stirred at the same temperature for 4 h, cooled, 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 chromatographed on silica gel (100 g), using benzene as the eluent, to give **19**¹⁷ (0.76 g: 67%) which was recrystallized from methanol, mp 102—104 °C, $[\alpha]_D +50^\circ$ (c 1.82); IR: 1712 cm⁻¹; ¹H NMR (CDCl₃): 1.20 (6H, d, $J=7$ Hz, -CH(CH₃)₂), 1.21 and 1.27 (each 3H and s, C₄-CH₃ and C₁₀-CH₃), 3.67 and 3.71 (each 3H and s, -CO₂CH₃ and -OCH₃), 7.04 (2H, s, C₁₁-H and C₁₂-H). Found: C, 76.71; H, 9.46%. Calcd for C₂₂H₃₂O₃: C, 76.70; H, 9.36%.

Isomerization of 15. a): A solution of **15** (67 mg) and sodium methoxide (44 mg) in absolute methanol (3.4 ml) was refluxed for 1 h. The solution was 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 (10 g), using ether-hexane (1 : 9) as the eluent, to give an inseparable mixture (62 mg) of **15** and its C-13 epimer (**25**) (*ca.* 2 : 1 ratio by ¹H NMR analysis). ¹H NMR (CDCl₃) signals assigned to **25**: 0.90 and 0.91 (each 3H, d, and $J=6$ Hz, -CH(CH₃)₂), 1.09 (3H, s, C₁₀-CH₃), 1.21 (3H, s, C₄-CH₃), 3.67 (3H, s, -CO₂CH₃).

b): A solution of **15** (67 mg) and 5% aqueous sodium hydroxide (0.3 ml) in tetrahydrofuran (3.4 ml) was refluxed for 10 h. The solution was poured into dilute hydrochloric acid and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give an oil (66 mg), whose IR and ¹H NMR spectra were identical with those of the starting **15**.

Reduction of 15 with Sodium Borohydride. A mixture of **15** (670 mg), sodium borohydride (1.52 g), and 5% aqueous sodium hydroxide (3.0 ml) in tetrahydrofuran (34 ml) was refluxed for 10 h. The mixture was 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 (65 g), using ether–benzene (3 : 97) as the eluent, to give methyl 14 β -hydroxy-13 β -abiet-8-en-18-oate (**26**) (159 mg; 24%) as an oil, $[\alpha]_D^{25} + 125^\circ$ (c 2.17); IR: 3620, 3460 br, 1720 cm^{-1} ; ^1H NMR (CDCl_3): 0.95 and 0.98 (each 3H, d, and $J=6$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.01 (3H, s, $\text{C}_{10}-\text{CH}_3$), 1.20 (3H, s, C_4-CH_3), 3.66 (3H, s, $-\text{CO}_2\text{CH}_3$), 3.78 (1H, br, $W_{1/2}=5.5$ Hz, $\text{C}_{14\alpha}-\text{H}$). Found: C, 75.68; H, 10.48%. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3$: C, 75.40; H, 10.25%.

Further elution with ether–benzene (3 : 97) gave methyl 14 α -hydroxy-13 β -abiet-8-en-18-oate (**24**) (256 mg; 38%), which was recrystallized from methanol; mp 102–103 $^\circ\text{C}$ (after drying *in vacuo* at 40 $^\circ\text{C}$ for 5 h), $[\alpha]_D^{25} + 59^\circ$ (c 0.625) (lit.⁴) mp 102–103 $^\circ\text{C}$, $[\alpha]_D^{25} + 66.7^\circ$; IR: 3600, 3450 br, 1720 cm^{-1} ; ^1H NMR (CDCl_3): 0.83 and 0.96 (each 3H, d, and $J=7$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.00 (3H, s, $\text{C}_{10}-\text{CH}_3$), 1.20 (3H, s, C_4-CH_3), 3.65 (3H, s, $-\text{CO}_2\text{CH}_3$), 3.80 (1H, bd, $J=7.5$ Hz, $\text{C}_{14\beta}-\text{H}$). Found: C, 75.35; H, 10.47%. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3$: C, 75.40; H, 10.25%. The identity of **24** with natural methyl suaveolate was confirmed by mixed melting point determination and by IR and ^1H NMR spectral comparison.²⁰

Elution with ether–benzene (1 : 1) afforded 13 β -abiet-8-ene-14 β ,18-diol (**29**) (46 mg; 7.5%) as an oil; $[\alpha]_D^{25} + 92^\circ$ (c 0.39); IR: 3625, 3450 br cm^{-1} ; ^1H NMR (CDCl_3): 0.81 (3H, s, C_4-CH_3), 1.03 (3H, s, $\text{C}_{10}-\text{CH}_3$), 0.95 and 0.98 (each 3H, d, and $J=6$ Hz, $-\text{CH}(\text{CH}_3)_2$), 3.15 and 3.44 (each 1H, d, and $J=10.5$ Hz, $-\text{CH}_2\text{OH}$), 3.77 (1H, br, $W_{1/2}=6$ Hz, $\text{C}_{14\alpha}-\text{H}$). Found: C, 78.40; H, 11.25%. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2$: C, 78.38; H, 11.18%.

Subsequent elution with ether–benzene (1 : 1) gave 13 β -abiet-8-ene-14 α ,18-diol (**23**) (95 mg; 15%) which was recrystallized from dichloromethane; mp 180–182 $^\circ\text{C}$; $[\alpha]_D^{25} + 84^\circ$ (c 0.285) (lit.⁴) mp 186–187 $^\circ\text{C}$, $[\alpha]_D^{25} + 81.3^\circ$; IR: 3620, 3290 br cm^{-1} ; ^1H NMR (CDCl_3): 0.76 (3H, s, C_4-CH_3), 0.82 and 0.95 (each 3H, d, and $J=6.5$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.00 (3H, s, $\text{C}_{10}-\text{CH}_3$), 2.97 and 3.46 (each 1H, d, and $J=11$ Hz, $-\text{CH}_2\text{OH}$), 3.77 (1H, bd, $J=7$ Hz, $\text{C}_{14\beta}-\text{H}$). Found: C, 78.15; H, 11.47%. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2$: C, 78.38; H, 11.18%. The identity of **23** with natural suaveolol was confirmed by mixed melting point determination and by IR and ^1H NMR spectral comparison.²⁰

Reduction of 15 with Lithium Aluminium Hydride. A mixture of **15** (166 mg) and lithium aluminium hydride (57 mg) in dry ether (5.0 ml) was refluxed for 4 h with stirring. The mixture was poured into aqueous ammonium chloride solution and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated. The residue was chromatographed on silica gel (20 g), using ether–benzene (3 : 7) as the eluent, to give an oil (35 mg; 23%). The IR and ^1H NMR spectra of the oil were superimposable with those of **29**.

Further elution with ether–benzene (1 : 1) gave a solid (72 mg; 47%). The IR and ^1H NMR spectra of the solid were identical with those of suaveolol.

Oxidation of 24 and 26 with Pyridinium Chlorochromate. a): A mixture of **24** (23 mg) and pyridinium chlorochromate (22 mg) in dichloromethane (1.0 ml) was stirred at room temperature for 2 h. The mixture was then decanted from a tarry residue, which was washed with ether. The combined organic solution was washed with brine, dried over sodium sulfate, and evaporated to give an oil (21 mg), whose IR and ^1H NMR spectra were identical with those of **15**.

b): A mixture of **26** (14 mg) and pyridinium chlorochromate (14 mg) in dichloromethane (1.0 ml) was treated as described in a) to give an oil (14 mg), which was shown to be identical with **15** by spectral comparison.

Methyl 14 β -Acetoxy-13 β -abiet-8-en-18-oate (27). A mixture of **26** (70 mg), acetic anhydride (1.0 ml), and pyridine (1.0 ml)

was allowed to stand overnight at room temperature. After the usual work-up, the crude product was chromatographed on silica gel (10 g), using ether–hexane (1 : 9) as the eluent, to give **27** (64 mg) as an oil; $[\alpha]_D^{25} + 181^\circ$ (c 0.575); IR: 1713 cm^{-1} ; ^1H NMR (CDCl_3): 0.90 (6H, d, $J=6$ Hz, $-\text{CH}(\text{CH}_3)_2$), 1.02 (3H, s, $\text{C}_{10}-\text{CH}_3$), 1.19 (3H, s, C_4-CH_3), 2.03 (3H, s, $-\text{OCOCH}_3$), 3.64 (3H, s, $-\text{CO}_2\text{CH}_3$), 5.32 (1H, br, $W_{1/2}=5$ Hz, $\text{C}_{14\alpha}-\text{H}$). Found: C, 73.97; H, 9.83%. Calcd for $\text{C}_{23}\text{H}_{36}\text{O}_4$: C, 73.67; H, 9.64%.

Methyl 14 α -Acetoxy-13 β -abiet-8-en-18-oate (28). The alcohol **24** (58 mg) was acetylated with acetic anhydride in pyridine, as described for the preparation of **27**. The acetate (**28**) (47 mg) was recrystallized from methanol; mp 134.5–135 $^\circ\text{C}$; $[\alpha]_D^{25} - 41^\circ$ (c 0.245) (lit.⁴) mp 132–133 $^\circ\text{C}$, $[\alpha]_D^{25} - 44.5^\circ$; IR: 1720 cm^{-1} ; ^1H NMR (CDCl_3): 0.82 and 0.92 (each 3H, d, and $J=6.5$ Hz, $-\text{CH}(\text{CH}_3)_2$), 0.99 (3H, s, $\text{C}_{10}-\text{CH}_3$), 1.19 (3H, s, C_4-CH_3), 2.06 (3H, s, $-\text{OCOCH}_3$), 3.65 (3H, s, $-\text{CO}_2\text{CH}_3$), 5.37 (1H, bd, $J=8$ Hz, $\text{C}_{14\beta}-\text{H}$). Found: C, 73.68; H, 9.79%. Calcd for $\text{C}_{23}\text{H}_{36}\text{O}_4$: C, 73.67; H, 9.64%.

14 β ,18-Diacetoxy-13 β -abiet-8-ene (30). The diol **29** (68 mg) was acetylated as described for the preparation of **27**. The crude product was chromatographed on silica gel (10 g), using ether–hexane (15 : 85) as the eluent, to give **30** (64 mg), which was recrystallized from methanol; mp 93–95 $^\circ\text{C}$; $[\alpha]_D^{25} + 201^\circ$ (c 1.695); IR: 1722 cm^{-1} ; ^1H NMR (CDCl_3): 0.88 (3H, s, C_4-CH_3), 1.04 (3H, s, $\text{C}_{10}-\text{CH}_3$), 0.92 (6H, d, $J=6$ Hz, $-\text{CH}(\text{CH}_3)_2$), 2.04 and 2.05 (each 3H and s, 2- OCOCH_3), 3.68 and 3.88 (each 1H, d, and $J=11$ Hz, $-\text{CH}_2\text{OAc}$), 5.35 (1H, br, $W_{1/2}=5.5$ Hz, $\text{C}_{14\alpha}-\text{H}$). Found: C, 74.09; H, 10.11%. Calcd for $\text{C}_{24}\text{H}_{38}\text{O}_4$: C, 73.80; H, 9.81%.

14 α ,18-Diacetoxy-13 β -abiet-8-ene (Suaveolol Diacetate) (31). The diol **23** (71 mg) was acetylated as described for the preparation of **27**. The crude product was chromatographed on silica gel (10 g), using ether–hexane (15 : 85) as the eluent, to give **31** (71 mg) as an oil; $[\alpha]_D^{25} - 41^\circ$ (c 0.590) (lit.⁴) $[\alpha]_D^{25} - 39.1^\circ$; IR: 1720 cm^{-1} ; ^1H NMR (CDCl_3): 0.83 and 0.95 (each 3H, d, and $J=6.5$ Hz, $-\text{CH}(\text{CH}_3)_2$), 0.89 (3H, s, C_4-CH_3), 1.02 (3H, s, $\text{C}_{10}-\text{CH}_3$), 2.06 and 2.07 (each 3H and s, 2- OCOCH_3), 3.72 and 3.85 (each 1H, d, and $J=11$ Hz, $-\text{CH}_2\text{OAc}$), 5.39 (1H, bd, $J=8.5$ Hz, $\text{C}_{14\beta}-\text{H}$). Found: C, 74.07; H, 10.09%. Calcd for $\text{C}_{24}\text{H}_{38}\text{O}_4$: C, 73.80; H, 9.81%.

Suaveolic Acid (14 α -Hydroxy-13 β -abiet-8-en-18-oic Acid) (22). A mixture of **24** (68 mg) and potassium *t*-butoxide (381 mg) in dimethyl sulfoxide (3.4 ml) was stirred at room temperature for 1 h. The mixture was poured into ice–water, acidified with 10% aqueous acetic acid, and extracted with ether. The ether extract was washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a pale yellow oil (70 mg). The crude product was chromatographed on silicic acid (Mallinckrodt, CC-4, 10g), using ether–benzene (3 : 7) as the eluent, to give **22** as a solid (34 mg; 55%). It was recrystallized from hexane to give needles, mp 188–190 $^\circ\text{C}$ after drying at 80 $^\circ\text{C}$ for 2 h, $[\alpha]_D^{25} + 71^\circ$ (c 0.14) (lit.⁴) mp 198–201 $^\circ\text{C}$ dec, $[\alpha]_D^{25} + 68.2^\circ$; IR (KBr): 3390–2630, 1698 cm^{-1} ; ^1H NMR (CDCl_3): 0.82 and 0.95 (each 3H, d, and $J=7$ Hz, $-\text{CH}(\text{CH}_3)_2$), 0.99 (3H, s, $\text{C}_{10}-\text{CH}_3$), 1.19 (3H, s, C_4-CH_3), 3.83 (1H, bd, $J=7.5$ Hz, $\text{C}_{14\beta}-\text{H}$), 6.02 (2H, br, $-\text{CO}_2\text{H}$ and $-\text{OH}$). The IR and ^1H NMR spectra of **22** were identical with those of natural suaveolic acid.²⁰

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