The nmr spectra of all compounds were recorded on Varian Associates DP-60 or HR-100 nmr spectrometer.

Registry No.—**1**, 1574-41-0; **2**, 926-56-7; **4**, 926-54-5; iron(III) acetylacetonate, 14024-18-1; triethylaluminum, 97-93-8; ethylene, 74-85-1; isoprene, 78-79-5; 2,3-dimethyl-1,3-butadiene, 513-81-5; 2-phenyl-1,3-butadiene, 2288-18-8; 1,3-butadiene, 106-99-0; propylene, 115-07-1; 4-methyl-1-*cis*-4-hexadiene, 761-76-2; 5-methyl-1,4-hexadiene, 763-88-2; 3-methyl-2-hexene, 10574-36-4; 2-methyl-2-hexene, 2738-19-4; 2,4-heptadiene, 14255-14-2; 4,5-dimethyl-1,4-hexadiene, 760-76-9; 2,3-dimethyl-2,4-hexadiene, 5678-98-8; 3,5-dimethyl-1,4-hexadiene, 761-87-5; 4-methyl-1-*cis*-4-heptadiene, 13857-54-0; 2,4-dimethyl-2-hexene, 14255-23-3; 4-methyl-3-heptene, 14255-24-4; 4-phenyl-1,4-hexadiene, 14255-25-5; 3-phenyl-2-hexene, 14255-26-6; 1-*cis*-5-heptadiene, 7736-34-7; 4-methyl-*cis*-3-hexene, 4914-89-0; 4-methyl-*trans*-3-hexene, 3899-36-3.

Some Reactions of 12α-Hydroxymethylabiet-7,8-enoic Acid

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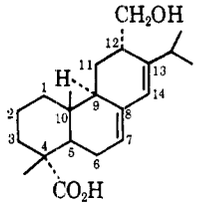
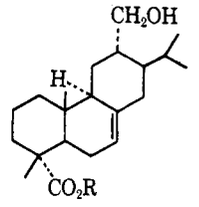
The position of the double bond in 12α-hydroxymethyldihydroabietic acid has been established by hydroboration and osmium tetroxide oxidation experiments. Cyclization of 12-hydroxymethylabiet-7,8-enoic acid and its 12-acetoxy derivative gave δ-lactones which on lithium aluminum hydride reduction and subsequent dehydration afforded new diterpene alcohols. Reaction of the dihydro compound with acetyl hypobromite afforded methyl 12-acetoxymethylabietate as the major product. The mechanistic implications of the latter are discussed.

Hydrogenation of readily available 12α-hydroxymethylabietic acid (**1**)[2] to a dihydro compound has been reported[3] but evidence as to its structure was not obtained. Physical data for this compound have now been obtained, and some of its reactions studied with a view to preparing new diterpene alcohols for polyurethane applications.

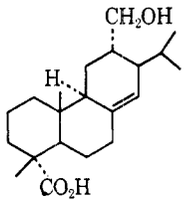
Absorption of one molecule of hydrogen by **1** may theoretically lead to the formation of dihydro compounds **2**, **3**, and **4**. However, it was found that low-



1



2a, R = H
b, R = Me



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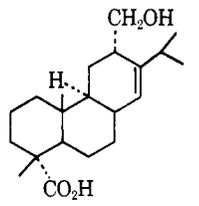
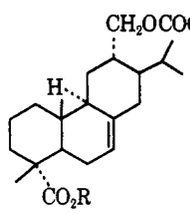


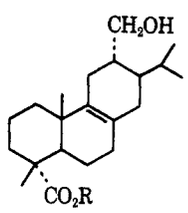
4

pressure hydrogenation followed by repeated recrystallization of the resulting product gave a single pure dihydro compound as the major product. The nuclear magnetic resonance (nmr) spectrum of the dihydro compound (as the methyl ester) suggests it to be 12α-hydroxymethylabiet-7,8-enoic acid (**2a**). The vinyl proton appeared as a broad signal centered at 5.34 ppm, it being rendered diffuse by possible long-range coupling. The vinyl proton signal in the corresponding 12-acetoxy compound **5b** is also found to be a broadened doublet (J = 4.0 cps) centered at 5.33 ppm very similar in shape and position to that found for the H-7 proton signal in methyl 12-acetoxymethylabietate (see later) and in authentic 7,8 compounds.[4,5]

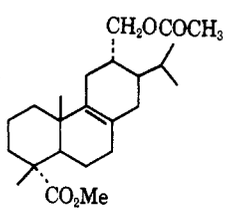
Passage of dry hydrogen chloride gas into a chloroform solution of **2a** at 0° resulted in proton rearrangement[6,7] to give 12α-hydroxymethylabiet-8,9-enoic acid (**6a**). Acetylation and esterification of **6a** gave methyl



5a, R = H
b, R = Me



6a, R = H
b, R = Me



7

12α-acetoxymethylabiet-8,9-enoate (**7**) which showed a deshielded C-10 Me singlet at 1.13 ppm and a broadened signal centered at 1.78 ppm (allylic protons).

Hydroboration of **2b** with lithium aluminum hydride–boron trifluoride followed by alkaline hydrogen peroxide oxidation[8] gave a saturated triol as major product. The nmr spectrum of the corresponding triacetate showed the H-7 proton signal as a broad triplet centered at 4.80 ppm, suggesting it to be axial and vicinal to other axial protons,[9] but no signals in the 2.20–3.40-

(1) (a) National Research Council Postdoctoral Resident Research Associate. (b) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) B. A. Parkin and G. W. Hedrick, *J. Org. Chem.*, **30**, 2356 (1965).

(3) B. A. Parkin, H. B. Summers, R. L. Settine, and G. W. Hedrick, *Ind. Eng. Chem., Prod. Res. Develop.*, **5**, 257 (1966).

(4) J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, **31**, 4128 (1966).

(5) W. Herz, H. J. Wahlborg, W. D. Lloyd, W. H. Schuller, and G. W. Hedrick, *ibid.*, **30**, 3190 (1965).

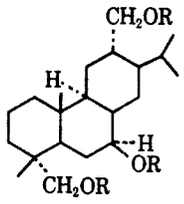
(6) *Cf.* L. Velluz, G. Müller, A. Petit, and J. Mathieu, *Bull. Soc. Chim. France*, 401 (1954).

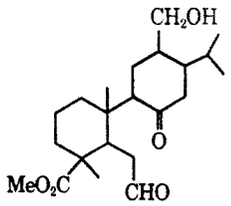
(7) O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).

(8) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(9) E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Am. Chem. Soc.*, **86**, 2218 (1964); W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels *J. Org. Chem.*, **30**, 1873 (1965).

ppm region[10] were found. The *cis* stereochemistry of the hydroboration oxidation process being established,[8] the structure of the triacetate may be given as **8b**.





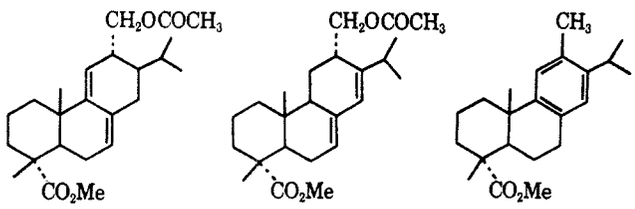
8a, R = H
b, R = $COCH_3$

9

Ozonolysis of 12α-hydroxymethylabiet-7,8-enoic acid (**2a**) gave inconclusive results. The product obtained gave a neutralization equivalent of 360 (theory for keto acid product is 366), the infrared spectrum of the methyl ester showing bands at 3400 (OH), 2800 (CHO), 1730 (aldehyde and ester C=O), and 1710 cm^{-1} (ketone C=O). However, gas–liquid partition chromatography of the product showed it to be a complex mixture of compounds.[11]

In order to obtain further chemical data on the position of the double bond in the dihydro compound, its oxidation with osmium tetroxide was studied. Lead tetraacetate cleavage of the resulting diol should give rise to a primary or secondary aldehyde group, depending on whether the initial double bond is 7,8 or 8,14. That the double bond is 7,8 was confirmed by the isolation of the aldehyde–ester **9**, the nmr spectrum of which showed a triplet centered at 9.63 ppm (J = 2.0 cps) for the $-CH_2CHO$ group.

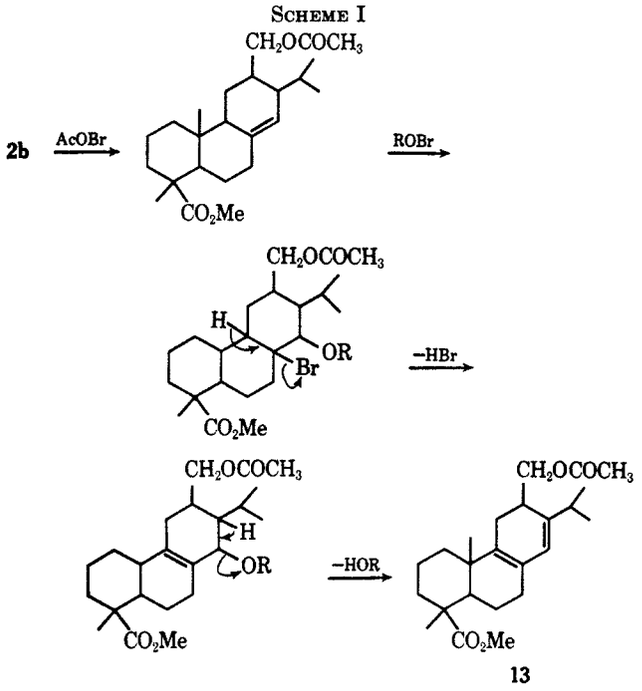
Oxidation of **5b** with mercuric acetate gave a low yield of methyl 12-acetoxymethylabieta-7,9(11)dienoate (**10**), having ultraviolet maxima at 235, 244, and 251 mμ, typical of a transoid diene.[12] The nmr spectrum showed a broad signal at 5.44 ppm for the H-7 and H-11 vinyl protons.



10 **11** **12**

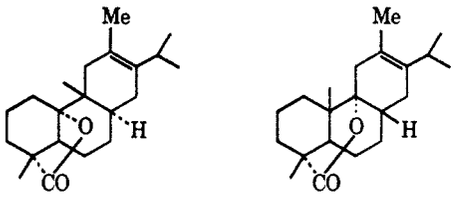
As a possible means of introduction of a functional group into the dihydro compound **2b**, its reaction with acetyl hypobromite[13] was studied. The major product was found to be methyl 12-acetoxymethylabietate **11**, together with methyl dehydroabietate and methyl 12-methyldehydroabietate **12**. Two mechanisms may be considered: (a) preferential proton abstraction at the less hindered C-14 site and (b) initial acetylation of the 12-acetoxymethyl group with liberation of HOBr, rearrangement of the double bond to the 8,14 position,[14] and addition of HOBr (or AcOBr) to the double bond followed by elimination of hydrogen bromide and acetic acid molecules to give the substituted palustric acid intermediate **13**. Proton rearrangement and eliminations readily account for the observed products. (See Scheme I.)

SCHEME I

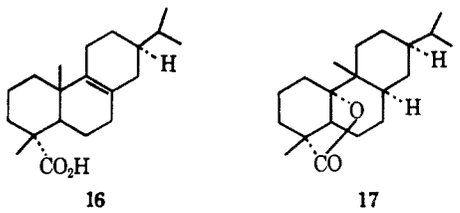


(R = H or $COCH_3$)

Treatment of **2a** with concentrated sulfuric acid at −5 to −10° (conditions of Fleck and Palkin[15,16]) effected lactonization to a mixture of γ- and δ-lactones (**14** and **15**, respectively), the cyclization being accompanied by dehydration of the 12-hydroxymethyl group. Gas–liquid partition chromatography and infrared spectroscopy (ν_{max} 1770 and 1745 cm^{-1}) showed the ratio of products to be approximately 4:1 in favor of the thermodynamically more stable δ-lactone. This contrasts with the findings of Velluz, Müller, Petit,



14 **15**



16 **17**

(10) J. W. Huffman, *et al.*,[4] have reported the hydroboration of methyl abiet-8,14-enoate to methyl 14-hydroxytetrahydroabietate which gave the H-14 signal as a broadened pair of doublets at 2.95 ppm.

(11) C. R. Enzell and B. R. Thomas (*Tetrahedron Letters*, No. 4, 225 (1965)) have obtained epoxides, rearrangement products, *etc.*, from ozonolysis of certain 7,8 compounds.

(12) L. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 365.

(13) Acetyl hypobromite has been found to add readily to isolated double bonds in steroids: S. G. Levine and M. E. Wall, *J. Am. Chem. Soc.*, **81**, 2826 (1959).

(14) That the 7,8 double bond migrates to the 8,14 position under acidic conditions is evidenced by the isolation of methyl 12,14-methyleneoxyabiet-8,9-enoate from the methyl 12-hydroxymethylabiet-7,8-enoate–paraformaldehyde reaction: D. K. Black and G. W. Hedrick, *J. Org. Chem.*, **32**, 3763 (1967).

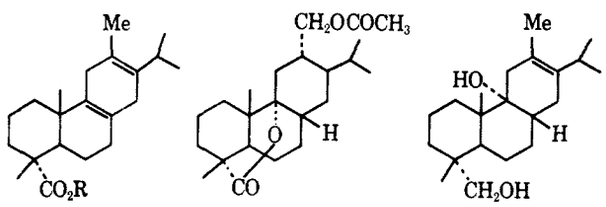
(15) E. E. Fleck and S. Palkin, *J. Am. Chem. Soc.*, **61**, 3197 (1939).

(16) E. E. Fleck and S. Palkin, *ibid.*, **62**, 2044 (1940).

and Mathieu[6] who obtained a γ-lactone as major product from the cyclization of dihydroabietic acid. Herz and Wahlborg[17] lactonized **16** to give **17**, formed by the Wagner–Meerwein rearrangement of the initially formed δ-lactone.

Although epimerization at C-8 in **15** is possible, none was observed. Such an epimerization would lead to a molecule in which the C-10 methyl group is strongly hindered.

Hydrolysis of the lactone **15** in ethylene glycol[18] gave the acid **18a** which resisted catalytic hydrogenation over platinum oxide or palladium. The nmr spectrum of the corresponding methyl ester **18b** confirmed the presence of the tetrasubstituted double bonds.

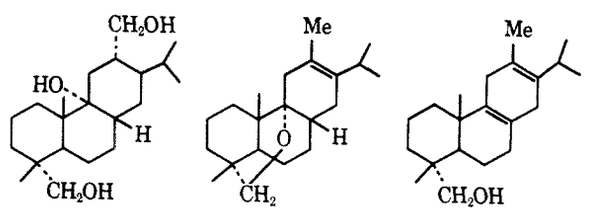


18a, R = H
b, R = Me

19 **20**

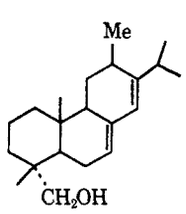
Lactonization of 12-acetoxymethylabiet-7,8-enoic acid (**5a**) gave a similar mixture of lactones (the crude reaction product showed infrared bands at 1770, 1750, and 1720 cm^{-1}) although recrystallization only afforded the δ-lactone **19**.

Lithium aluminum hydride reduction of **15** gave a 76% yield of diol **20**. A similar reduction of **19** gave an 82% yield of 9α-hydroxy-12-hydroxymethyltetrahydroabietol (**21**).



21 **22** **23**

Dehydration of **20** gave a mixture of products. Separation by fractional crystallization afforded the ether **22** (which on chromic acid oxidation yielded **15**) and the alcohol **23** as major products. The crude reaction mixture showed a low intensity ultraviolet maximum at 241 mμ suggesting some rearrangement of **23** to the corresponding abietadiene structure. This was confirmed by refluxing **23** in ethanolic hydrochloric acid solution with the formation, in low yield, of



24

12-methylabietadienol (**24**) (*Cf.* the acid-catalyzed isomerization of (+)-8,12-abietadienoic acid to (−)-abietic acid by Burgstahler and Worden[19]). Catalytic hydrogenation of **24** gave 12-methyltetrahydroabietol, identical with that isolated from the copper chromite reduction of levopimaric acid–formaldehyde adduct.[3]

(17) W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30**, 1881 (1965).
(18) L. van Thoi and J. Ourgaud, *Bull. Soc. Chim. France*, 209 (1956).

Experimental Section[20]

12α-Hydroxymethylabiet-7,8-enoic Acid (2a).—Hydrogenation of 12α-hydroxymethylabietic acid[2] (5 g) in ethanol (200 cc) over Adams platinum oxide catalyst (0.1 g) for 8 hr at room temperature and 30 psi, filtration, concentration *in vacuo*, and repeated recrystallization from ethanol gave **2a** (4.0 g): mp 190–191°; $[\alpha]^{25}D$ +38° (*c* 1.02); ν_{max} 1700 (C=O), 1665 (C=C stretch), 828 cm^{-1} (C=CH); end absorption only in the ultraviolet region.

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.22; neut equiv, 334. Found: C, 75.35; H, 10.28; neut equiv, 336.

Methyl 12-hydroxymethylabiet-7,8-enoate (2b).—**2a** (3.3 g) in ether (50 cc) was treated with excess ethereal diazomethane at room temperature for 2 hr. Concentration and distillation gave **2b** (2.9 g, 83%) as a viscous liquid: bp 228–230° (0.4 mm); mp 37–39°; ν_{max} 3400 (OH), 1740 (C=O), 1665 and 827 cm^{-1} (C=CH); $[\alpha]^{24}D$ +34° (*c* 1.01); glpc gave a single peak, t = 4.2 min; nmr signals appeared at 0.84 and 0.95 (isopropyl group, J = 7.0 cps), 0.79 (C-10 Me), 1.15 (C-4 Me), 3.38 (OH), 3.57 (ester Me), and 5.34 ppm (H-7, broadened doublet, J = 4.0 cps).

Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.80; H, 10.42. Found: C, 75.42; H, 10.40.

Acetylation of 2a.—Acetic anhydride (1.5 cc) was added dropwise to a stirred solution of **2a** (1.6 g) in pyridine (10 cc) cooled in ice. After 2 hr, the mixture was poured onto ice and stirred 10 min, the pH adjusted to 8.0 with dilute sodium hydroxide solution, and ether extracted. The extracts were washed with water, dried ($MgSO_4$), and concentrated to give 12-acetoxymethylabiet-7,8-enoic acid (**5a**) (1.2 g, 81%) as a viscous liquid: ν_{max} 3500–3200 (H-bonded OH), 1730 (acetate C=O), 1700 (acid C=O), and 828 cm^{-1} (C=CH).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 73.35; H, 9.64; neut equiv, 376.5. Found: C, 73.60; H, 9.52; neut equiv, 378.

Methyl 12-Acetoxymethylabiet-7,8-enoate (5b).—Acetylation of **2b** (10.4 g) with acetic anhydride (10 cc) under reflux 2 hr gave the acetoxymethyl derivative as a viscous liquid (9.4 g, 80%): bp 214–216° (0.5 mm); $[\alpha]^{24}D$ +31.8° (*c* 1.02); ν_{max} 1735 (acetate Me), 1725 (ester C=O), 830 cm^{-1} (C=CH); nmr signals appeared at 0.96 and 0.87 (superimposed doublets for isopropyl group, J = 6.5 cps), 0.78 (C-10 Me), 1.16 (C-4 Me), 1.95 (acetate Me), 3.57 (ester Me), and 5.33 ppm (H-7, broadened doublet, J = 4.0 cps); glpc gave a single peak, t = 4.8 min.

Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.83; H, 9.81. Found: C, 73.60; H, 9.81.

12-Hydroxymethylabiet-7,8-enol Diacetate.—Methyl 12-hydroxymethylabiet-7,8-enoate (5 g) in ether (200 cc) was refluxed 3 hr with lithium aluminum hydride (4 g). Addition of water and aqueous HCl (1:1) to pH 2.0 and ether extraction afforded the diol as colorless crystals (3.8 g, 82%): mp 168–169°; ν_{max} (Nujol) 3300 (OH), 828 cm^{-1} (C=H).

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78,64; H, 11.30.

Acetylation of the above diol (3.2 g) with acetic anhydride (5 cc) under reflux 1 hr gave the **diacetate** as a viscous liquid (3.4 g 85%): glpc gave a single peak, t = 4.9 min; ν_{max} no OH, 1730 and 1235 cm^{-1} (acetate C=O); nmr signals at 0.86 and 0.97 (isopropyl group, J = 6.5 cps), 0.78 (C-10 Me), 0.89 (C-4 Me), 1.95 and 1.99 (acetate Me), and 5.36 ppm (H-7, broadened doublet, J = 4.0 cps).

(19) A. W. Burgstahler and L. R. Worden, *J. Am. Chem. Soc.*, **86**, 96 (1964).

(20) Melting points are uncorrected. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra (Nujol mulls or neat) were determined on a Perkin-Elmer Model 21 spectrophotometer; ultraviolet spectra and rotations were determined in 95% ethanol. Nmr spectra were run on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Frequencies are given in parts per million (ppm) measured downfield from tetramethylsilane as an internal standard. J values are in cycles per second (cps). Gas–liquid partition chromatography (glpc) was carried out at 280° on a 10 ft × 3/8 in. column 10% OV-1 on 100–120 mesh Chromosorb W using a Loenco, Inc., Model 15B instrument and a flow of 150 cc of helium min. Alumina for chromatography was Alcoa F-20, unless otherwise stated.

Anal. Calcd for $C_{25}H_{40}O_4$: C, 74.21; H, 9.96. Found: C, 74.16; H, 9.92.

12-Hydroxymethylabiet-8,9-enoic Acid (6a).—**2a** (1.0 g) in dry chloroform (50 cc) was cooled in ice and dry hydrogen chloride gas passed for 8 hr with stirring. After washing with three 50-cc portions of water and drying, concentration *in vacuo* gave **6a** as a colorless solid (0.9 g); recrystallization from ethanol gave mp 137–139° with $[\alpha]^{24}D$ +34° (*c* 1.10) and neut equiv 336 (theory 384.3).

Esterification with ethereal diazomethane gave the Me ester **6b** as a colorless viscous liquid: ν_{max} 3300 (OH), 1735 (ester C=O); glpc gave a major peak (>95%), t = 3.5 min, with a single impurity having t = 4.2 min.

Methyl 12-Acetoxymethylabiet-8,9-enoate (7).—Acetylation of **6b** (2.0 g) with acetic anhydride (3 cc) under reflux 2 hr gave **7** as a viscous liquid (2.0 g): bp 225–230° (0.5 mm); ν_{max} 1734 (ester C=O), 1725 (acetate C=O); nmr signals at 0.97 and 0.85 (isopropyl group, J = 6.5 cps), 1.13 (C-10 Me), 1.16 (C-4 Me), 1.98 (acetate Me), 3.58 (ester Me), and a broadened signal centered at 1.78 ppm (allylic protons).

Anal. Calcd for $C_{24}H_{38}O_4$: C, 73.83; H, 9.81. Found: C, 73.69; H, 9.78.

Osmium Tetroxide Oxidation of 2b.—Methyl 12-hydroxymethylabiet-7,8-enoate (1.3 g) in dry ether (20 cc) and pyridine (10 cc) was left at room temperature 24 hr with osmium tetroxide (1.0 g). The resulting solid was suspended in water (20 cc) containing sodium hydroxide (1 g) and mannitol (5 g) and the mixture heated on a steam bath for 1 hr. After cooling, the solution was neutralized and extracted with chloroform–ether (1:1). Concentration gave the crude **triol** (0.9 g, 60%) as a resinous solid.

The above triol ester (0.8 g) in acetic acid (50 cc) was left at room temperature with lead tetraacetate (0.8 g) for 24 hr. Addition of ethylene glycol (0.2 cc), standing 30 min, dilution with aqueous sodium chloride solution, extraction with ether, washing with aqueous sodium bicarbonate solution and water, and concentration gave **9** as a viscous liquid (0.6 g, 75%): ν_{max} 3430 (OH), 2680 (CHO), 1735 (ester and aldehyde C=O), 1240–1230 (C–O stretch) and 1430 cm^{-1} ($-CH_2CO$); nmr signals at 0.86 and 0.97 (broadened doublets for isopropyl group, J = 6.5 cps), 1.19 (C-4 Me), 1.03 (C-10 Me), 3.66 (ester Me), and a triplet centered at 9.63 ppm (J = 2.0 cps, $-CH_2CHO$).

Anal. Calcd for $C_{22}H_{36}O_5$: C, 69.41; H, 9.54. Found: C, 69.26; H, 9.38.

Hydroboration of Ester 2b.—Lithium aluminum hydride (1.2 g) and **2b** (3.2 g) in dry ether (100 cc) was cooled in ice, boron trifluoride–etherate (6 cc) in ether (50 cc) added over 3 hr, and the mixture left overnight at room temperature. Saturated aqueous sodium sulfate solution was slowly added and the ether layer separated, dried, and concentrated. The residue was dissolved in 80% aqueous ethanol (200 cc) containing sodium hydroxide (3 g), 30% hydrogen peroxide (20 cc) added slowly, and the mixture refluxed 6 hr. Addition of water, ether extraction, and concentration of extracts gave the triol **8a** as a solid (2.4 g, 71%), mp 213–214° (from acetic acid).

Anal. Calcd for $C_{21}H_{36}O_3$: C, 74.50; H, 11.31; OH determination, 15.1. Found: C, 74.39; H, 11.21; OH determination, 14.9.

Acetylation of **8a** with acetic anhydride under reflux 2 hr gave the triacetate **8b** as a viscous liquid: nmr signals at 0.87 and 0.98 (superimposed doublets, J = 6.5 cps), 0.89 (C-10 Me), 1.08 (C-4 Me), 2.00 (acetate Me), a quartet centered at 3.88 ppm (acetate CH_2), and a broad signal at 4.80 (H-7).

Anal. Calcd for $C_{27}H_{44}O_6$: C, 69.79; H, 9.77. Found: C, 69.80; H, 10.71.

Ozonolysis of 12-Hydroxymethylabiet-7,8-enoic Acid.—Ozonized oxygen (from a Welsbach ozonizer) was passed into a solution of **2a** (3.4 g) in methanol (40 cc) until no further absorption of ozone occurred. Water (50 cc) was added followed by slow addition of sodium bisulfite (10 g). The mixture was allowed to stand at room temperature overnight, water added, and ether extracted. Concentration of the dried extracts gave a colorless resinous solid (3.0 g), neut equiv, 360.

Esterification with excess ethereal diazomethane afforded a resinous solid: ν_{max} ($CHCl_3$) 3400 (OH), 2800 (CHO), 1730 (aldehyde and ester C=O), 1710 (ketone C=O); glpc showed a complex mixture of products.

Oxidation of Methyl 12-Acetoxymethylabiet-7,8-enoate.—Ester **5b** (0.5 g) in ethanol (25 cc) was refluxed 3 hr with mercuric acetate (1.2 g) in glacial acetic acid (2 cc) and ethanol (2 cc). After cooling, the mixture was filtered, concentrated *in vacuo*, and extracted with hot chloroform. Evaporation of the extract gave a viscous liquid (0.41 g); glpc showed two major peaks with retention times t = 4.7 min and t = 4.8 min (**5b**, ~20%). Preparative glpc (similar conditions) gave the diene **10**: λ_{max} 235, 244 (ε 6200) and 251 mμ; nmr signals appeared at 0.82 and 0.92 (isopropyl group, J = 6.5 cps), 0.97 (C-10 Me), 1.20 (C-4 Me), 1.95 (acetate Me), 3.55 (ester Me), and 5.44 ppm (broad, H-7 and H-11).

Anal. Calcd for $C_{24}H_{36}O_4$: C, 74.19; H, 9.34. Found: C, 74.23; H, 9.24.

Hydrogenation of Methyl 12-Acetoxymethylabieta-7,9(11)-dienoate (10).—Impure **10** (0.2 g) (from above) in ethanol (50 cc) was hydrogenated overnight at 50 psi using platinum oxide catalyst (0.1 g). Filtration, concentration *in vacuo*, and preparative glpc gave a colorless viscous liquid (0.2 g), identified as **methyl 12-acetoxymethyltetrahydroabietate:** ν_{max} 1730 (ester C=O), 1725 and 1240 cm^{-1} (acetate C=O).

Anal. Calcd for $C_{24}H_{40}O_4$: C, 73.40; H, 10.28. Found: C, 73.10; H, 10.20.

Reaction of Methyl 12-Hydroxymethylabiet-7,8-enoate with Acetyl Hypobromite.—Ester **2b** (4.2 g) in carbon tetrachloride (20 cc) was cooled at 0° and stirred 0.5 hr with acetyl hypobromite solution[13] (150 cc, 0.1 *M* in CCl_4). The mixture was shaken with ice-cold 5% sodium bisulfite solution, washed with water, dried, and concentrated. The residue was dissolved in pyridine (20 cc) and left overnight at room temperature, ether (100 cc) added, and the pyridine removed by washing with dilute HCl and water. Removal of solvent gave a pale yellow viscous liquid (3.0 g).

Chromatography of the above mixture (2.0 g) over Fisher neutral alumina (50 g) and elution with *n*-hexane afforded the following.

A. **Methyl dehydroabietate** (0.2 g) had mp 69°, λ_{max} 268 and 276 mμ (ε 770).

B. **Methyl 12-methyldehydroabietate (12)** (0.6 g) also was obtained as colorless needles: mp 112–113° (from aqueous ethanol); $[\alpha]^{23}D$ +51° (*c* 1.04); λ_{max} 269 mμ (ε 760) and 278 mμ (ε 800); nmr signals appeared at 1.10 and 1.20 (isopropyl group, J = 6.5 cps), 1.18 (C-10 Me), 1.21 (C-4 Me), 2.22 (C-12 Me), 3.59 (ester Me), 6.73 and 6.84 ppm (H-11 and H-14, J_{AB} = 11.0 cps).

Anal. Calcd for $C_{22}H_{32}O_2$: C, 80.40; H, 9.82. Found: C, 80.52; H, 9.76.

C. **Methyl 12-acetoxymethylabietate (11)** (0.7 g) had λ_{max} 235, 242 mμ (ε 21,000) and 250 mμ; nmr signals at 0.98, 1.09 and 1.01, 1.12 (doublets for isopropyl group, J = 6.5 cps), 0.80 (C-10 Me), 1.21 (C-4 Me), 1.98 (acetate Me), 3.57 (ester Me), 5.78, (H-14), and a broadened doublet (J = 4.0 cps) centered at 5.32 ppm (H-7) identical with those of an authentic sample.[21]

D. A mixture (0.3 g) of component C and methyl 12-hydroxymethyldihydroabietate was also present.

Lithium Aluminum Hydride Reduction of 11.—Methyl 12-acetoxymethylabietate (**11**) (0.39 g) in dry ether (100 cc) was refluxed 2 hr with lithium aluminum hydride (0.5 g). Addition of water and aqueous HCl to pH 2.0 and ether extraction gave a colorless solid which on recrystallization from ethanol afforded **12-hydroxymethylabietol** (0.27 g, 84%) as colorless needles: mp 180–181° (lit.[2] 179.5–181.3°); λ_{max} 235, 242 (ε 23,100), and 250 mμ.

Lactonization of 12-Hydroxymethylabiet-7,8-enoic Acid.—**2a** (3.0 g) was added to concentrated sulfuric acid (30 cc) cooled at −5°. After stirring 1 hr, the mixture was poured onto ice and ether extracted. The extracts were washed with cold aqueous 5% sodium hydroxide solution and water, then dried. Concentration *in vacuo* gave a colorless solid (1.0 g) which on boiling with *n*-hexane and filtering gave the δ-lactone **15** (0.9 g, 32%): mp 180–181° (from MeOH); $[\alpha]^{25}D$ +19.5° (*c* 1.05); ν_{max} 1745 (lactone C=O); glpc gave a single peak, t = 7.0, min; nmr (pyridine) signals at 0.84 and 0.95 (isopropyl group, J = 6.5 cps), 0.75 (C-10 Me), 1.07 (C-4 Me), and 1.47 ppm (C-12 Me).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.68; H, 10.19. Found: C, 79.59; H, 10.06.

The above hexane filtrate was concentrated and chromatographed over neutral alumina (50 g). Elution with *n*-hexane gave a small unidentified forerun followed by the γ-lactone **14** (0.11 g): mp 112–114° (from ethanol); ν_{max} 1770 (lactone C=O);

(21) This was obtained from levopimaric acid–formaldehyde adduct.[2]

glpc gave a major peak, t = 7.2 min (~90%), contaminated with **15**, t = 7.0 min.

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.68; H, 10.19. Found: C, 79.51; H, 10.12.

Elution with hexane–ether (4:1) gave **15** (0.32 g), identical with the material isolated as the hexane-insoluble fraction.

Hydrolysis of Lactone 15.—A mixture of lactone (2.4 g) and potassium hydroxide (1.5 g) in ethylene glycol (20 cc) was refluxed 1.5 hr in a nitrogen atmosphere; the mixture was cooled, diluted with water, and ether extracted. The extracts were washed with aqueous sodium chloride solution, dried, and concentrated to give unchanged **15** (0.1 g). The aqueous phase was cooled to 0°, acidified with cold 0.5 *N* acetic acid, saturated with sodium chloride, and ether extracted. The extracts were washed with water, dried, and concentrated *in vacuo* to give a pale yellow solid (1.0 g). The crude acid was decolorized and esterified with excess ethereal diazomethane solution. The resulting product was recrystallized from aqueous ethanol then *n*-hexane to give the ester **18b** (0.9 g, 36%) as colorless needles: mp 143–144°; ν_{max} 1738, 1200 cm^{-1} (C=O), no OH or C=C bands; end absorption only in the ultraviolet region; glpc gave a single peak, t = 5.0 min.

Anal. Calcd for $C_{22}H_{34}O_2$: C, 79.93; H, 10.37. Found: C, 79.82; H, 10.29.

Lactonization of 12-Acetoxymethylabiet-7,8-enoic Acid (5a).—Acetate **5a** (1.0 g) in chloroform (20 cc) cooled at 0° was added with stirring to concentrated sulfuric acid (20 cc) cooled at −5°. The mixture was shaken 0.5 hr, poured onto ice, and ether extracted. The extracts were washed with water, decolorized, and concentrated to give a semisolid mass which was dissolved in hot *n*-hexane and the solution filtered. The filtrate on standing afforded colorless crystals of lactone **19** (0.52 g, 52%): mp 147–148°; ν_{max} 1750 (lactone C=O), 1725 cm^{-1} (acetate C=O); glpc gave a major peak (~ 95%), t = 10.0 min; nmr (pyridine) signals at 0.80 and 0.92 (isopropyl group, J = 7.0 cps), 0.74 (C-10 Me), 1.07 (C-4 Me), and 1.96 ppm (C-12 acetate Me).

Anal. Calcd for $C_{23}H_{36}O_4$: C, 72.95; H, 10.12. Found: C, 72.76; H, 9.91.

9α-Hydroxy-12-methyl-12,13-abietenol (20).—The δ-lactone **15** (1.3 g) in dry ether (200 cc) was refluxed 3 hr with lithium aluminum hydride (1.0 g), excess hydride decomposed by the addition of water, and aqueous HCl solution (1:1) added to obtain pH 2.0. Ether extraction and concentration of the extracts gave a solid which on recrystallization from ether afforded the diol **20** (1.0 g, 76%): mp 211–212°; $[\alpha]^{25}D$ −41° (*c* 1.07); ν_{max} 3380 and 3270 (OH), 1053 and 1167 cm^{-1} (primary and tertiary C–O stretch); strong end absorption only in the ultraviolet region; glpc gave a single peak, t = 7.8 min; nmr (pyridine) signals at 0.83 and 0.95 (isopropyl group, J = 7.0 cps), 0.89 (C-10 Me), 0.99 (C-4 Me), 1.46 (C-12 Me), and a broad signal centered at 3.82 ppm (–CH_2OH).

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.43; H, 11.29. Found: C, 78.40; H, 11.27.

Dehydration of Diol 20.—Diol **20** (0.8 g) in ethanol (80 cc) was refluxed 18 hr with concentrated sulfuric acid (0.3 g). Concentration *in vacuo*, addition of saturated sodium chloride solution (100 cc) and ether extraction gave a pale yellow solid (0.65 g). Dissolution in hot *n*-hexane and standing at room temperature gave an unidentified product as colorless crystals (0.1 g): mp 140–142°; glpc gave a major peak, t = 4.3 min; nmr signals at 1.20, 1.03, 0.90, 0.87, 0.79, 3.87, and 5.40 ppm.

The mother liquors from above on further standing at 20° gave colorless needles (0.30 g), mp 148–149° (from hexane), identified as the alcohol **23**: ν_{max} 3400 (OH), strong end absorption in the ultraviolet region; nmr (pyridine) signals at 0.79 and 0.90 (isopropyl group, J = 6.5 cps), 0.97 (C-10 Me), 1.09 (C-4 Me), 1.48 (C-12 Me), and a broad signal at 3.79 ppm (OH); glpc gave a single peak, t = 4.8 min.

Anal. Calcd for $C_{21}H_{34}O$: C, 83.36; H, 11.33. Found: C, 83.29; H, 11.30.

Concentration of the mother liquors gave a viscous liquid (0.22 g) which slowly crystallized to give colorless needles, mp 92–94°, identified as the ether **22**: ν_{max} 1042 cm^{-1}; nmr (pyridine) signals at 0.80 and 0.91 (isopropyl group, J = 6.5 cps), 0.98 (C-10 Me), 1.10 (C-4 Me), 1.47 (C-12 Me), and a singlet at 3.73 ppm (–CH_2–O–C); glpc gave a major component (~95%), t = 3.8 min.

Anal. Calcd for $C_{21}H_{34}O$: C, 83.36; H, 11.33. Found: C, 83.02; H, 11.13.

Oxidation of Ether 22.—Ether **22** (0.2 g) in glacial acetic acid (10 cc) was warmed to 60°, excess Jones reagent[22] added, and the mixture heated 10 min on a steam bath. Methanol (20 cc) was added, the mixture poured onto ice, and ether extracted. The extracts were washed with cold 5% aqueous sodium hydroxide and concentrated, and the residue recrystallized from methanol to give the δ-lactone **15** (0.11 g, 52%), mp 180–181°, spectroscopically identical with that previously obtained.

Rearrangement of 23 to 12-Methylabietadienol (24).—Compound **23** (0.2 g) in ethanol (5 cc) was refluxed 6 hr with concentrated hydrochloric acid (1.0 cc), the mixture diluted with water, and ether extracted. The extracts were washed with water, dried, decolorized, and concentrated to give a viscous liquid (0.1 g) which on glpc showed two major peaks at t = 4.3 min (unchanged **22**) and t = 4.7 min. Preparative glpc[23] afforded 12-methylabietadienol **24**, λ_{max} 241 mμ (ε 18,100).

Anal. Calcd for $C_{21}H_{34}O$: C, 83.37; H, 11.33. Found: C, 83.29; H, 11.17.

Hydrogenation of 24.—Compound **24** (50 mg) in ethanol (50 cc) was hydrogenated overnight at 50 psi using platinum oxide catalyst (20 mg). Filtration, concentration *in vacuo*, and recrystallization from ethanol gave **12-methyltetrahydroabietol**: mp 162–163°; glpc gave a single peak, t = 3.2 min; the nmr (pyridine) spectrum showed methyl singlets at 0.74 (C-10), 0.80 and 0.89 (isopropyl group, J = 6.0 cps), 1.06 (C-4), and a quartet centered at 3.13 ppm (–CH_2OH), J = 11.5 cps).

Anal. Calcd for $C_{21}H_{38}O$: C, 82.26; H, 12.49. Found: C, 82.21; H, 12.33.

9α-Hydroxy-12-hydroxymethyltetrahydroabietol (21).—The lactone **19** (0.3 g) in ether (25 cc) was refluxed 2 hr with lithium aluminum hydride (0.1 g) in ether (25 cc). Usual work-up and removal of solvent gave the triol **21** as colorless crystals (0.23 g, 85%): mp 206–207°; ν_{max} 3390 and 3275 (OH), 1055 (C–O stretch); no absorption in the ultraviolet region; nmr (pyridine) signals at 0.83 and 0.94 (isopropyl group, J = 6.5 cps), 0.87 (C-10 Me), 0.98 (C-4 Me), 3.36 (C-12, –CH_2OH), 3.52 (C-9 OH), and 3.82 ppm (C-4, –CH_2OH).

Anal. Calcd for $C_{21}H_{38}O_3$: C, 74.50; H, 11.31. Found: C, 74.34; H, 11.42.

Dehydration of Triol 21.—Triol **21** (0.2 g) in ethanol (25 cc) containing concentrated sulfuric acid (0.1 cc) was refluxed 18 hr. Evaporation *in vacuo*, addition of water (50 cc), ether extraction, decolorization, drying ($MgSO_4$), and concentration gave a viscous liquid (0.12 g): ν_{max} 3300 (OH) and 1040 (C–O–C); strong end absorption only in the ultraviolet region; glpc showed the presence of four components with retention times t = 3.8, 4.0, 4.3, and 4.8 min. Addition of ether (2 cc) and standing at 0° for 2 hr afforded colorless needles (40 mg), mp 148–149°, identified as **23**, no depression of melting point with a sample of **23** obtained from **20**; glpc gave a single peak, t = 4.8 min. The components present in the mother liquors failed to crystallize.

Registry No.—**2a**, 15094-96-9; **2b**, 15094-97-0; **5a**, 15094-98-1; **5b**, 15153-23-8; 12-hydroxymethylabiet-7,8-enol, 15094-99-2; 12-hydroxymethylabiet-7,8-enol diacetate, 15095-00-8; **6a**, 15095-01-9; **6b**, 15095-20-2; **7**, 15095-02-0; **8a**, 15095-03-1; **8b**, 15215-71-1; **9**, 15095-04-2; **10**, 15095-05-3; methyl 12-acetoxymethyltetrahydroabietate, 15095-06-4; methyl dehydroabietate, 1235-74-1; **11**, 14909-67-2; **12**, 15095-09-7; **14**, 15095-10-0; **15**, 15095-11-1; **18b**, 15095-12-2; **19**, 15095-13-3; **20**, 15095-14-4; **21**, 15095-15-5; **22**, 15095-16-6; **23**, 15095-17-7; **24**, 15095-18-8; 12-methyltetrahydroabietol, 15095-19-9.

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(22) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon *J. Chem. Soc.*, 39 (1946).

(23) Glpc was carried out at 280° on a 5 ft × ⅜ in. column 20% SE-52 on Gas-Chrom Z using an Aerograph Autoprep A-700 instrument and a flow of 120 cc of helium per min.