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NEW NEUTRAL DITERPENES FROM SOUTHERN PINE TALL OIL

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Key Word Index—*Pinus banksiana*; *P. monticola*; *Pinus* spp.; tall oil; diterpenes; 8(14),15-pimaradiene-3β,18-diol; 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one; 8,13β-epoxy-14-labden-6α-ol; 8,11,13-abietatriene-15,18-diol; 9,10-secoabieta-8,11, 13-trien-18,10-olide.

Abstract—Five new diterpene natural products isolated from southern pine (*Pinus* spp.) tall oil were characterized as 8(14),15-pimaradiene-3β,18-diol, 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one, 8,13β-epoxy-14-labden-6α-ol, 8,11, 13-abietatriene-15,18-diol and 9,10-secoabieta-8,11,13-trien-18,10-olide.

INTRODUCTION

Tall oil, a byproduct of kraft (sulfate) pulping of conifer wood chips, is a complex mixture of fatty acids, resin acids, and neutral components. The neutral components have no commercial value but are found as contaminates in the commercially valuable resin and fatty acid fractions, and are major components of the forerun and the pitch obtained from distilling crude tall oil. The objective of a detailed analysis of the neutrals in tall oil of southern pine (*Pinus* spp.) was to gain useful information that could not only lead to new products but also could improve on the utilization of the tall oil fatty and resin acids [1]. During the course of the analysis five new natural products were isolated. The products have been characterized as 8(14), 15-pimaradiene-3β,18-diol† (**1**), 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one (**2**), 8,13β-epoxy-14-labden-6α-ol (**3**), 8,11,13-abietatriene-15,18-diol (**4**) and 9,10-secoabieta-8,11, 13-trien-18,10-olide (**5**). We have also isolated **2** from the benzene extractives from bark of jack pine (*P. banksiana* Lamb.) and **5** from bark of jack pine and western white pine (*P. monticola* Dougl.).

RESULTS AND DISCUSSION

8(14),15-Pimaradiene-3β,18-diol (**1**)

Compound **1** was isolated from the tall oil neutrals as its diacetate (**1a**) that on saponification gave the original diol (**1**). High resolution MS of the diol established the elemental composition as $C_{20}H_{32}O_2$. The IR and NMR spectra of the diol (**1**) and the diacetate (**1a**) indicated the presence of three tertiary methyls, primary and secondary hydroxyls (acetoxyls), and vinyl and trisubstituted double bonds typical of 8(14),15-pimaradiene diterpenes [2]. The primary and the secondary hydroxyls were confirmed by the expected shifts observed in the NMR spectrum for the protons geminal to the hydroxyls on addition of trichloroacetyl isocyanate [3].

The NMR spectrum of **1** was similar to that of 8(14), 15-pimaradien-18-ol (pimarol) except for (a) an additional absorption with the shape and the chemical shift characteristic of a proton geminal to an equatorial secondary hydroxyl, (b) the downfield shift of the C-4 Me by *ca* 0.12 ppm, and (c) the downfield shift of the C-4 hydroxymethyl protons by *ca* 0.3 ppm. These shift differences suggest that compound **1** is the 3β-hydroxyl analog of pimarol. The downfield shift of the C-4 Me can be explained by the deshielding of the C-3 equatorial hydroxyl and is not deshielded further by the C-4 hydroxymethyl; therefore, the hydroxymethyl must be equatorial (i. e. C-18 OH) [4]. The 3β,18-diol configuration is confirmed by the IR spectrum of the diol in a dilute CCl_4 solution that showed the expected absorptions for a secondary equatorial hydroxyl, a primary hydroxyl, and an intramolecular hydrogen bonding.

The 3β, 18-diol configuration is further confirmed by the ready formation of an acetonide derivative (**6**) and by comparison of the NMR spectra of the diol, the diacetate, and the acetonide with those of terpenoids of known configuration [5–12] (Table 1). The NMR spectrum of the acetonide is particularly informative. Of the four possible configurations, the acetonide of a 3β, 18-diol gives a singlet for the hydroxymethyl protons, whereas the other configurations give an AB doublet of doublets [10]. The acetonide of **1** has a 2H singlet at the position expected for the 3β, 18-diol configuration.

Oxidation of **1** and treatment of the resulting keto-aldehyde with base yielded 19-norpimara-8(14),15-dien-3-one (**7**), a known compound [13], thus the structure of **1** was established as 8(14),15-pimaradiene-3β,18-diol. Natural products with similar structures have been isolated: 8(14),15-isopimaradiene-3β,18 (and 19)-diol [11, 14–16]; 7,15-isopimaradiene-3β,19-diol [17]; *ent*-7,15-isopimaradiene-3β,19-diol [18]; 9(11),15-isopimaradiene-3β,19-diol [12]; *ent*-15-beyerene-3β,19-diol [19]; and *ent*-16-kaurene-3β,19-diol [19, 20].

19-Hydroxy-15,16-dinorlabd-8(17)-en-13-one (**2**)

The elemental composition of compound **2** was determined as $C_{18}H_{30}O_2$ by MS and elemental analysis. The IR and the NMR spectra indicated **2** contained two tertiary methyls, a methyl ketone, an exocyclic methylene,

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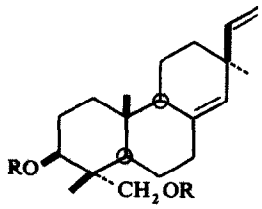
† The systematic nomenclature follows *The Common and Systematic Nomenclature of Cyclic Diterpenes* (with Addenda and Corrigenda, Feb. 1969), proposals of a committee chaired by J. W. Rowe.

Table 1. Comparison of reported NMR spectra of terpenoids containing 3,18- (or 19-) configuration* with those of 8(14),15-pimaradiene-3β,18-diol (1) and its derivatives

Compound	δ (ppm) Diol		Diacetate		Acetonide	
	C-3H	C-18H$_2$†	C-3H	C-18H$_2$†	C-3H	C-18H$_2$
3α,18-diol	3.62–3.68	3.40–3.44	4.86	3.88	3.60–3.65	3.40–3.47
3β,18-diol	3.60	3.48–3.54	4·81–4·82	3.74–3.78	3.48–3.60	3.46–3.61‡
1	3.67	3.59	4·80	3.80	3.52	3.52‡
3α,19-diol		3.64		4.09–4.10	4.40–4.43	3.67–3.72
3β,19-diol	3.47–3.50	3.81–3.90	4.51	4.20–4.30	3.38–3.56	3.56–3.59

* Refs [5–12].
† Centre of absorption [i.e. $(\delta_A^+ \delta_B)/2$].
‡ Singlet.



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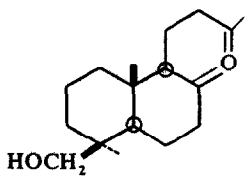

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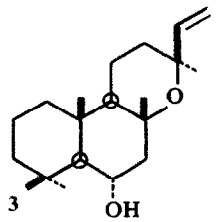

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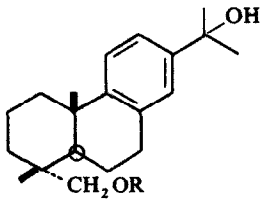

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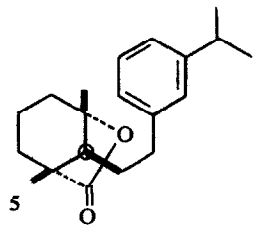

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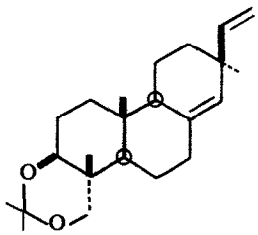

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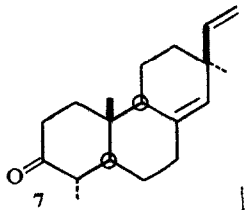

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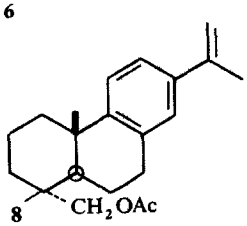

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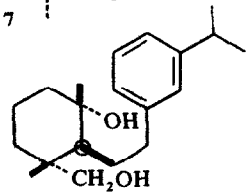

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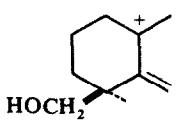

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and a hydroxymethyl. In the NMR spectrum the hydroxymethyl protons are an AB doublet of doublets with a chemical shift characteristic of an axial C-4 hydroxymethyl [5]. Addition of trichloroacetyl isocyanate produced the expected *ca* 0.7 ppm downfield shift in the doublet of doublets [3]. The NMR spectrum of **2** shows the expected downfield shift of the C-4 equatorial Me and the unshifted C-10 Me [4] compared with those for 15,16-dinorlabd-8(17)-en-13-one.

The MS contained ions that resulted from loss of H_2O (*m/e* 260) and of CH_2OH (*m/e* 274) that readily undergo McLafferty rearrangement to form ions at *m/e* 202 and 189. Cleavage of the methyl ketone gives a strong peak at *m/e* 43 as expected. The ion observed at *m/e* 153 (**10**) is characteristic of diterpenes of this type and results from cleavage through ring B [21]. This ion is accompanied by the expected peaks at *m/e* 135 and 121 due to the further loss of H_2O and MeOH, respectively.

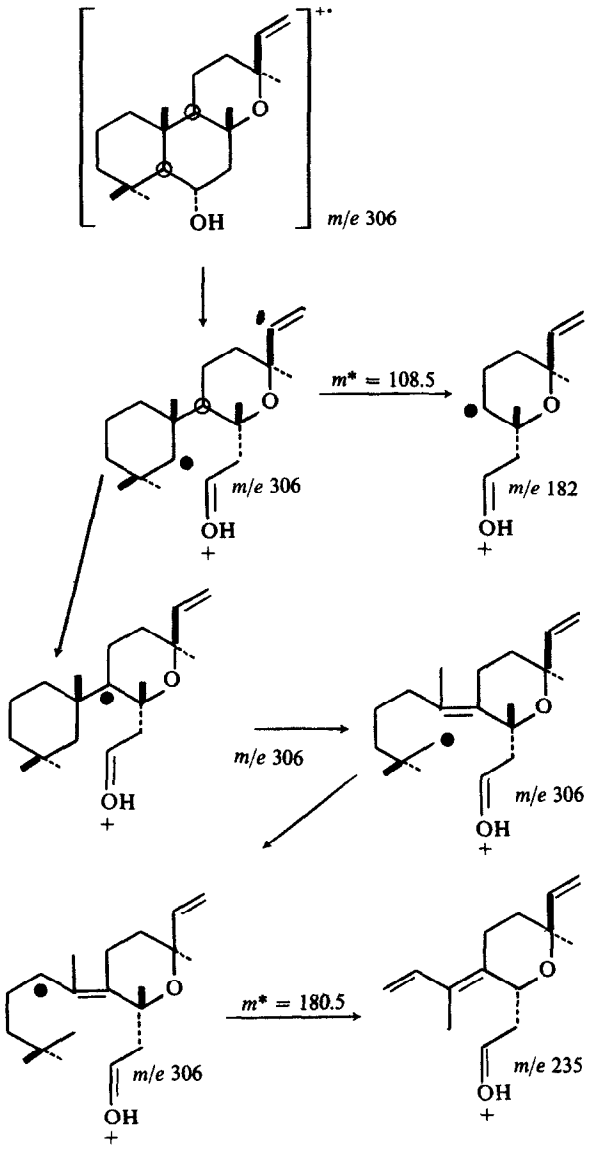
These data establish the structure of **2** as 19-hydroxy-15,16-dinorlabd-8(17)-en-13-one. The related compound 15,16-dinorlabd-8(17)-en-13-one has been isolated from *Pinus monticola* bark [22] and from *Dacrydium kirkii* [15].

8,13β-Epoxy-14-labden-6α-ol (6α-hydroxy-13-epimanoyl oxide) (**3**)

The NMR spectrum of **3** was almost identical to that of 8β,13-epoxy-14-labdene (8-epimanoyl oxide) except for an additional absorption characteristic of a proton geminal to a secondary hydroxyl. Comparison of the NMR spectrum with spectra of 8,13-epoxy-14-labdene (manoyl oxide) and 8,13β-epoxy-14-labdene (13-epimanoyl oxide) indicated that the C-8 Me of **3** was shielded by *ca* 0.1–0.3 ppm.

The IR spectrum of **3** contained absorptions for a secondary hydroxyl and a vinyl group, and further indicated that the hydroxyl was spatially near the epoxide oxygen as evidenced by a band due to intramolecular hydrogen bonding.

The high resolution MS of **3** contained M^+ at *m/e* 306 and ions resulting from the loss of H_2O (*m/e* 288), Me (*m/e* 291), and H_2O + Me (*m/e* 273) as expected. The ion observed at *m/e* 86 ($C_4H_6O_2$) indicates the maximum distance between the secondary hydroxyl and the epoxide because this ion is the lowest molecular weight fragment containing both oxygens. If the hydroxyl is at C-6 the *m/e* 86 ion will arise from C-6, C-7, C-8, and



Scheme 1. Mass spectral fragmentation of 8,13β-epoxy-14-labden-6α-ol.

C-17 of **3** and its structure will probably be [HOCH = C(Me)—CHO ⇌ OCH—C(Me) = CHOH]$^{+\cdot}$. Prominent peaks at *m/e* 235 and 182 can be explained as ring B fragmentations of **3** (Scheme 1) and establish that the secondary hydroxyl of **3** is at C-6.

A 6α-hydroxyl can participate in intramolecular hydrogen bonding with an 8,13-epoxide oxygen, as observed in the IR solution spectrum, if the conformation of ring B is a skewed boat. In this conformation the 6α-hydroxyl will be spatially near the epoxide oxygen allowing intramolecular hydrogen bonding and will be spatially distant from the C-4 methyls, which explains the lack of deshielding of these methyls as observed, for example, in the NMR spectrum of 8(17),14-labdadiene-6α,13β-diol (larixol). The skewed boat conformation of ring B will also relieve steric strain between the C-8 and C-10 methyls. The downfield shift of the C-8 Me is explained by a shielding effect of the vinyl. Thus the vinyl must be *cis* to the C-8 Me and **3** is 8,13β-epoxy-14-labden-6α-ol.

Oxygenated derivatives of manoyl oxide are reported as natural products. 2α-Hydroxymanoyl oxide [23], 2-oxomanoyl oxide [24], *ent*-3α-hydroxy-13-epimanoyl oxide [25], 3β-hydroxymanoyl oxide [26], 11β-hydroxymanoyl oxide [27], 12α-hydroxy-13-epimanoyl oxide [28, 29], 12-oxomanoyl oxide [30], and 12-oxo-13-epimanoyl oxide [30] have been isolated.

8,11,13-abietatriene-15,18-diol (**4**)

Compound **4** was isolated as its monoacetate (**4a**). The NMR spectrum of **4a** and that of 8,11,13-abietatrien-18-yl acetate (dehydroabietyl acetate) were the same except the doublet for the isopropyl methyls of dehydroabietyl acetate was shifted downfield *ca* 0.35 ppm and occurred as a singlet in the NMR spectrum of **4a**. The chemical shift of this singlet is the same as that for the isopropyl methyls of methyl 15-hydroxy-8,11,13-abietatrien-18-oate [31]. The IR and the UV spectra were characteristic of a dehydroabietane aromatic system [2]. The IR spectrum taken as a dilute solution in CCl_4 indicated that **4a** contained a tertiary hydroxyl. Compound **4a** was converted to dehydroabietyl acetate via dehydration with $POCl_3$ to 8,11,13,15-abietatetraen-18-yl acetate (**8**) and subsequent hydrogenation. The NMR and the UV spectra of 8,11,13,15-abietatetraen-18-yl acetate contained the expected absorptions due to an α-methyl styrene grouping. Thus **4a** is 8,11,13-abietatrien-15-ol-18-yl acetate and the original natural product is 8,11,13-abietatriene-15,18-diol (**4**).

Several related compounds have been isolated as natural products. 15-Hydroxy-8,11,13-abietatrien-18-oic acid was reported from *Agathis* spp. [32] and methyl 15-hydroxy-8,11,13-abietatrien-18-oate from *Pinus koraiensis* [33], *P. taeda* [31], and *Picea abies* [34].

9,10-secoabieta-8,11,13-trien-18,10-olide (**5**)

The elemental composition of **5** was determined as $C_{20}H_{28}O_2$ by high resolution MS. The IR spectrum was characteristic of a γ-lactone and a *m*-disubstituted benzene. The NMR spectrum contained peaks with the same chemical shifts, shapes, and relative intensities as the C-4 Me, the isopropyl methyls, the three benzylic hydrogens, and the four aromatic hydrogens of methyl 2*S*-[2′(*m*-isopropylphenyl)ethyl] 1*R*, 3*S*-dimethylcyclohexanecarboxylate (methyl secodehydroabietate) [2]. However the C-10 Me of **5** is a singlet and is deshielded as compared to the doublet for the secondary C-10 Me of methyl secodehydroabietate. These data indicate that **5** is the 18,10α-γ-lactone of a secodehydroabietane type compound.

Compound **5** was converted to the corresponding diol (**9**) on reduction. The IR spectrum of the diol as a dilute solution in CCl_4 showed the expected absorptions for tertiary and primary hydroxyls. The NMR spectrum of the diol contained peaks characteristic of an equatorial C-4 hydroxymethyl [5] geminal to an axial C-4 Me [4]. The tertiary hydroxyl at C-10 and the C-4 hydroxymethyl must be *cis* since they are derived from the γ-lactone. The preferred conformation of the cyclohexane ring would place the bulky 3-isopropylphenylethyl group in an equatorial orientation; therefore, the only relative configuration that allows both the hydroxymethyl and the 3-isopropylphenylethyl to be equatorial is that in which they are *trans*. This relative configuration is expected biogenetically, especially if **5** is formed as a rearrangement

product of 8(14),12-abietadien-18-oic acid (levopimaric acid) as postulated for similar compounds [35–37]. Thus **5** is 9,10-secoabieta-8,11,13-trien-18,10-olide.

EXPERIMENTAL

Mp's were measured in evacuated capillaries and are corr. NMR were obtained as $CDCl_3$ soln with TMS as the int. stand. The initial isolation of these diterpenes from southern pine (*Pinus* spp.) tall oil has been described [1]. 8(14),15-Pimaradiene-3β,18-diol and 8,11,13-abietatriene-15,18-diol were isolated as the acetates from an acetylated polar fraction.

8(14),15-Pimaradiene-3β,18-diol (**1**). 8(14),15-Pimaradiene-3β,18-diyl diacetate (**1a**, 357 mg) was dissolved in C_6H_6–MeOH (4:1; 10 ml) and N methanolic NaOH (50 ml) added. The flask was flushed with N_2 and held at room temp. for 24 hr. This was partitioned between Et_2O and H_2O to yield a crystalline product (280 mg) that was crystallized alternately from C_6H_6 and hexane to constant mp 179.5–180.5°, $[\alpha]_D^{25}$ + 93° ($CHCl_3$, *c* 1.1). The crystalline material was pure by TLC (Si gel) and GLC (SE-30). IR, $\nu_{max}^{CCl_4}$ cm^{-1}: 3636 (primary OH), 3622 *sh* (secondary equatorial OH), and 3533 (br., intramolecular H-bonding); ν_{max}^{KBr} cm^{-1}: 3080, 1640, and 915 (vinyl). NMR (60 MHz): δ 0.79 (3H, *s*), 0.92 (3H, *s*), 0.99 (3H, *s*), 3.59 [2H, AB *dd* (δ_A = 3.32, δ_B = 3.86), J = 10–1/2 Hz], *ca* 3.67 (1H, *br.m* buried under AB *dd*, C<u>H</u>—OH), 4.6–6.1 (4H, typical 8(14),15-pimaradiene double bond patterns [2]). The addition of trichloroacetyl isocyanate to the NMR sample gave the following spectrum: δ 0.87 (3H, *s*), 1.02 (6H, *s*), 4.12 (2H, *s*, —C<u>H</u>$_2$—O—CO—NH—CCl_3), *ca* 4.8 (1H, obscured *br. m*, C<u>H</u>—O—CO—NH—CCl_3), 4.6–6.1 (4H, typical 8(14),15-pimaradiene double bond patterns [2]), and 8.43 (2H, N—<u>H</u>). MS (probe) 70 eV *m/e* (rel. int.): 304 (M^+, $C_{20}H_{32}O_2$; 27), 289 (M^+ −Me, $C_{19}H_{29}O_2$; 11), 286 (M^+-H_2O, $C_{20}H_{30}O$; 40), 273 (M^+ −CH_2OH, $C_{19}H_{29}O$; 27), 271 ($C_{19}H_{27}O$; 22), 255 ($C_{19}H_{27}$; 46), 168 ($C_{10}H_{16}O_2$; 13), 151 ($C_{10}H_{15}O$; 33), 148 ($C_{11}H_{16}$; 41), 137 ($C_9H_{13}O$; 32), 136 ($C_{10}H_{16}$; 32), 135 ($C_{10}H_{15}$; 38), 134 ($C_{10}H_{14}$; 22), 133 ($C_{10}H_{13}$; 56) 131 ($C_{10}H_{11}$; 16), 123 (C_9H_{15}; 29), 121 (C_9H_{13}; 100), 119 (C_9H_{11}; 41), 117 (C_9H_9; 16), 109 (C_8H_{13}; 49), and 93 (C_6H_5O; 57). Found: M^+ *m/e* 304.2412. Calculated for $C_{20}H_{32}O_2$: M^+ *m/e* 304.2401.

8(14),15-Pimaradiene-3β,18-diyl acetate (**1a**). Chromatographically pure (TLC, GLC) **1a** was distilled at 140–145°/0.02 mm Hg to yield an oil that solidified on standing. This was crystallized from 95% EtOH to constant mp 71–71·5°, $[\alpha]_D^{24}$ + 106° ($CHCl_3$, *c* 0.9). The crystalline material was pure by TLC (Si gel) and GLC (SE-30). IR, ν_{max}^{film} cm^{-1}: 3080, 1640, and 915 (vinyl); 1745, 1245, and 1040 (acetate). NMR (60 MHz): δ 0.80 (3H, *s*), 0.87 (3H, *s*), 1.00 (3H, *s*), 2.03 (3H, *s*, O—CO—C<u>H</u>$_3$), 2.07 (3H, *s* O—CO—C<u>H</u>$_3$), 3.80 [2H, AB *dd* (δ_A = δ_B = 3.80), J = 12–1/2 Hz, —C<u>H</u>$_2$OAc], *ca* 4.8 (1H, obscured *br. m*, C<u>H</u>-OAc), 4.6–6.1 (4H, typical 8(14),15-pimaradiene double bond patterns [2]).

8(14),15-Pimaradiene-3β,18-diol acetonide (**6**). 8(14),15-Pimaradiene-3β,18-diol (85 mg) was dissolved in DMF (10 ml). 2,2-Dimethoxypropane (5 ml) and *p*-toluenesulfonic acid (35 mg) were added and the soln refluxed for 2 hr. After cooling the soln was neutralized by the addition of $NaHCO_3$, filtered, and evapd to dryness to yield a yellow oil. Chromatography over Si gel with C_6H_6 yielded a crystalline product (77 mg) which was recrystallized from MeOH to constant mp 124–125°, $[\alpha]_D^{24}$ + 76° ($CHCl_3$, *c* 0.8). This product was pure by GLC (OV-17, SE-30). IR, ν_{max}^{KBr} cm^{-1}: 3095, 1640, 995, and 915 (vinyl). NMR (60 MHz): δ 0.80 (3H, *s*), 0.99 (3H, *s*) 1.09 (3H, *s*), 1.43 (3H, *s*), 1.45 (3H, *s*), 3.52 (2H, *s*, —C<u>H</u>$_2$—O—), 3.52 (1H, *br. m*, —C<u>H</u>—O—), and 4.6–6.1 (4H, typical 8(14),15-pimaradiene double bond patterns [2]). MS (probe) 70 eV *m/e* (rel. int.): 344 (M^+, $C_{23}H_{36}O_2$, ·1), 329 (100), 286 (20), 269 (37), 241 (17), 229 (16), 220 (M*, 329 → 269), 201 (15), 187 (18), 173 (16), 161 (18), 160 (14), 159 (21), 157 (14), 151 (14), 148 (13), 147 (21), 145 (22), 135 (26), 134 (21), 133 (50), 131 (20), 123 (13), 121 (46), 120 (24), 119 (39), 117 (17), 109 (30), 107 (50), 106 (18), 105 (46), 59 (7), and 43 (71).

19-Norpimara-8(14),15-dien-3-one. (**7**). 8(14),15-Pimaradiene-3β,18-diol (30 mg) was dissolved in Me_2CO (20 ml) at 0°. Jones reagent [38] (0.4 ml) was added dropwise under N_2 until a slight reddish-yellow color remained after stirring for 4 min. MeOH (5 ml) was added to stop the reaction. This mixture was partitioned between Et_2O and N H_2SO_4. The ether layer was washed with N NaOH and H_2O and evapd to yield a colorless oil (33 mg). The oil was dissolved in MeOH (25 ml) to which was added 3N NaOH (1 ml). This soln was held at room temp. overnight under N_2, then partitioned between H_2O and Et_2O. The ether layer was filtered through dry $MgSO_4$ and evapd to yield a slightly yellowish oil that was chromatographed over Si gel. C_6H_6–Et_2O (9:1) eluted a compound (16 mg) identical to an authentic sample of 19-norpimara-8(14),15-dien-3-one by IR, NMR, GLC (SE-30, Silar), and TLC (Si gel, Al_2O_3). The center fractions from the Si gel chromatography were filtered through a small bed of Al_2O_3 (neutral, Act. III) with pentane–CH_2Cl_2 (19:1) to give a crystalline material: mp 82° (with extensive sintering from *ca* 60°), mmp undepressed $[\alpha]_D^{25}$ + 97° ($CHCl_3$, *c* 0.6) [reported [13]: mp 85–[illegible] $[\alpha]_D$ + [illegible]° ($CHCl_3$, *c* 0·5)].

19-Hydroxy-15,16-dinorlabd-8(17)-en-13-one (**2**). 19-Hydroxy-15,16-dinorlabd-8(17)-en-13-one was purified by chromatography on $AgNO_3$–Al_2O_3 (1:4) to yield a colorless oil that was pure by GLC (SE-30). This oil was distilled for analysis: bp 159–163°/0.2 mm Hg, $[\alpha]_D^{21}$ + 63° ($CHCl_3$, *c* 2.5). Found: C, 77.34; H, 10.89%. Calculated for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86%. IR, $\nu_{max}^{CCl_4}$ cm^{-1}: 3639 (primary OH); ν_{max}^{neat} cm^{-1}: 1717 (C = O); and 3078, 1646, 1411, and 892 (C = CH_2). NMR (100 MHz): δ 0.66 (3H, *s*, C-10 Me), 0.96 (3H, *s*, C-4 Me), 3.54 [2H, AB *dd* (δ_A = 3.37, δ_B = 3.72), J = 11 Hz, —C<u>H</u>$_2$ − OH], and 4.42 (*br. s*) and 4.81 (*br. s*) (2H, C = CH_2). Addition of trichloroacetyl isocyanate [3] to the NMR sample shifted the AB *dd* to δ 4.03 and 4.48 (2H, J = 11 Hz) and gave a *br. s* at 8.95 (1H, N-<u>H</u>). MS (probe) 70 ev *m/e* (rel. int.): 278 (M^+; 13), 260 (M^+-H_2O; 14), 247 (M^+-CH_2OH; 29), 202 (11), 189 (17), 153 (15), 135 (18), 121 (28), and 43 (100).

8,13β-Epoxy-14-labden-6α-ol. (**3**). Compound **3** (3 mg) was isolated by preparative GLC on 3% OV-17 (60/80 Gas Chrom Q; 1.8 m × 5 mm ss column, 60 ml He/min; 210°). The collected material was >95% pure by GLC (SE-30, OV-17) and was purified by chromatography on 1 g Al_2O_3 (neutral, Act III) to yield 1 mg of chromatographically pure material. IR, $\nu_{max}^{CCl_4}$ cm^{-1}: 3627 (secondary OH) and 3570 (intramolecular H-bonding); ν_{max}^{film} cm^{-1}: 3090, 1640, and 915 (vinyl). NMR (60 MHz, time averaged): δ 0.83 (9H, *s*, C-4 Me_2 and C-10 Me), 0.98 (3H, *s*, C-8 Me), 1.20 (3H, *s*, C-13 Me), 3.34 (1H, *br. m*, —COH—<u>H</u>$_{axial}$), 4.82 (1H, *q*, J_{AB} ~ 2 Hz, J_{AX} = 10 Hz, H_A of vinyl ABX system), 4.88 (1H, *q*, J_{AB} ~ 2 Hz, J_{BX} = 18 Hz, H_B of vinyl ABX system), and 5.80 (1H, *q*, J_{AX} = 10 Hz, J_{BX} = 18 Hz, H_x of vinyl ABX system). MS (probe) 70 eV *m/e* (rel. int.): 306 (M^+, $C_{20}H_{34}O_2$; 100), 291 (M^+-Me, $C_{19}H_{31}O_2$; 56), 288 (M^+ −H_2O, $C_{20}H_{32}O$; 76), 277 (M*, 306 → 291), 273 (M^+ −H_2O—Me, $C_{19}H_{29}O$; 22), 256 (M*, 291 → 273), 235 ($C_{15}H_{23}O_2$; 73), 182 ($C_{11}H_{18}O_2$; 39), 180.5 (M*, 306 → 235), 123 (C_9H_{15}; 53), 109 (C_8H_{13}; 56), 108.5 (M*, 306 → 182), 95 (C_7H_{11}; 43), 91 (C_7H_7; 31), 86 ($C_4H_6O_2$; 8), 81 (C_6H_9; 49), and 69 (C_5H_9; 63). Found: M^+ *m/e* 306.2561. Calculated for $C_{20}H_{34}O_2$: M^+ *m/e* 306.2561.

*8,11,13-Abietatriene-15, 18-diol 18-*acetate (**4a**). Chromatographically pure 8,11,13-abietatriene-15,18-diol 18-acetate (oil, 55 mg) was obtained by rechromatography over Si gel–$AgNO_3$ (4:1), $[\alpha]_D^{24}$ + 45° ($CHCl_3$, *c* 0.8). NMR (60 MHz): δ 0.95 (3H, *s*, C-4 Me), 1.22 (3H, *s*, C-10 Me), 1.57 [6H, *s*, —C(OH)(C<u>H</u>$_3$)$_2$], 2.03 (3H, *s*, O—CO—C<u>H</u>$_3$), 2.87 (2H, *m*, benzylic hydrogens), 3.87 [2H, AB *dd* (δ_A = 3.74, δ_B = 4.00), J = 11 Hz, —C<u>H</u>$_2$OAc], 7.08–7.34 (3H, *m*, aromatic hydrogens). IR, $\nu_{max}^{CCl_4}$ cm^{-1}: 3606 (tertiary OH); ν_{max}^{film} cm^{-1}: 1610, 1570, and 1500 (aromatic); 1740, 1250, and 1040 (acetate); 895 and 828 (1,2,4-trisubstituted aromatic). UV, λ_{max}^{EtOH} nm: 275 and 267 (shape and relative intensities same as for methyl dehydroabietate [2]). **4a** (55 mg) was dissolved in dry C_5H_5N (10 ml). $POCl_3$ (2 ml) was added in small portions with stirring. This mixture was held at 0° for 48 hr under N_2. The mixture was poured into H_2O and extracted with Et_2O. The Et_2O layer was washed with 0.5 N HCl and H_2O, dried over $MgSO_4$, and evapd to dryness to yield 37 mg of impure 8,11,13,15-abietatetraen-18-yl acetate (**8**) NMR (60

MHz): δ 0.92 (*s*, C-4 Me), 1.22 (*s*, C-10 Me), 2.02 (3H, *s*, O—CO—C<u>H</u>$_3$), 2.12 (3H, *br. s*, C-15 Me), 3.84 [2H, AB *dd* (δ_A = 3.70, δ_B = 3.98), J = 11 Hz, —C<u>H</u>$_2$-OAc], 5.00 (1H, *br. s*, C = C<u>H</u>), 5.30 (1H, *br. s*, C = C<u>H</u>), 7.05–7.30 (3H, *m*, aromatic hydrogens). UV. λ_{max}^{EtOH} nm: 247 [reported for α-methyl styrene [39]: λ_{max}^{EtOH} 243 nm]. The 8,11,13,15-abietatetraen-18-yl acetate (37 mg) obtained was hydrogenated (1 atm) over Pd/C (*ca* 100 mg) in absolute EtOH at room temp. for 48 hr. This mixture was filtered to remove the Pd/C and evapd to dryness to give 28 mg of a mixture that contained 8,11,13-abietatrien-18-yl acetate (dehydroabietyl acetate) by comparison with an authentic sample (TLC: Si gel; GLC: SE-30 and OV-17). Pure dehydroabietyl acetate could not be isolated due to the small amount of material and the nature of the impurities.

9,10-Secoabieta-8,11,13-trien-18,10-olide (**5**). Chromatographically pure (TLC) **5** was distilled at 105–110°/0.02 mm Hg to yield a pure (GLC: SE-30) oil, $[\alpha]_D^{25}$ + 19° ($CHCl_3$, *c* 1.1). NMR (60 MHz): δ 1.16 (3H, *s*, C-4 Me), 1.25 (6H, *d*, isopropyl Me_2), 1.38 (3H, *s*, C-10 Me), 2.73 (3H, *m*, benzylic hydrogens), and 6.9–7.2 (4H, *m*, aromatic hydrogens), IR, ν_{max}^{film} cm^{-1}: 1775 (γ-lactone); 1610, 1590, 1490 (aromatic); and 925, 795, 710 (*m*-disubstituted aromatic). MS (probe) 70 eV *m/e* (rel. int.): 300 (M^+, $C_{20}H_{28}O_2$; 23), 256 ($C_{19}H_{28}$; 5), 218.5 (M^*, 300 → 256), 146 ($C_{11}H_{14}$; 14), 133 ($C_{10}H_{13}$; 35), 131 ($C_{10}H_{11}$; 12), 123 (C_9H_{15}; 48), 122 (C_9H_{14}; 15), 117 (C_9H_9; 17), 111 (C_7H_{11}; 28), 110 (C_8H_{14}; 30), 109 (C_8H_{13}; 100), 108 (C_8H_{12}; 14), and 91 (C_7H_7; 20). Found: M^+ *m/e* 300.2057. Calculated for $C_{20}H_{28}O_2$: M^+ *m/e* 300.2088.

9,10-Secoabieta-8,11,13-trien-10,18-diol (**9**). 9,10-Secoabieta-8,11,13-trien-18,10-olide (48 mg) was reduced in the usual manner with $LiAlH_4$ to yield **9** (54 mg) that was crystallized to constant mp 141.5–143° (hexane), $[\alpha]_D^{21}$ −3° ($CHCl_3$, *c* 0.7). NMR (60 MHz): δ 0.79 (3H, *s*, C-4 Me), 1.24 (3H, *s*, C-10 Me), 1.24 (6H, *d*, J = 7 Hz, isopropyl Me_2), 2.81 (3H, *br. m*, benzylic hydrogens), 3.38 (2H, *br. s*, —C<u>H</u>$_2$—O—), 7.12–7.30 (4H, *m*, aromatic hydrogens). IR, $\nu_{max}^{CCl_4}$ cm^{-1}: 3641 (primary OH), 3609 *sh* (tertiary OH), 3580 (intramolecular H-bonding); ν_{max}^{KBr} cm^{-1}: 1605, 1585, and 1486 (aromatic); 1048 and 1038 (C-O); 792 and 704 (*m*-disubstituted aromatic).

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