Phytochemistry, 1980, Vol. 19, pp. 1121–1131. Pergamon Press Ltd. Printed in England.

TERPENOID AND OTHER EXTRACTIVES OF WESTERN WHITE PINE BARK

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(*Received* 12 *September* 1979)

Key Word Index—*Pinus monticola*; Pinaceae; western white pine; bark extractives; resin acids; triterpenes; sterols; fatty acids.

Abstract—A detailed chemical analysis of the benzene extract of western white pine bark was conducted. The extract consisted of 13% phlobaphenes, 18% strong acids, 21% polar weak acids, 6.5% fatty acids, 9.5% resin acids, and 32% neutrals. The fatty acids consisted mainly of $C_{20:0}$, $C_{22:0}$, and $C_{24:0}$ acids. The resin acids were identified as: isopimaric, anticopalic, dehydroabietic, sandaracopimaric, abietic, 6,8,11,13-abietatetraen-18-oic and pimaric acids. The neutrals on saponification gave fatty acids, sterols, wax alcohols, nonsaponifiables, and other components. The esterified fatty acids consisted primarily of the $C_{16:0}$, $C_{18:0}$, $C_{20:0}$ and $C_{24:0}$ acids. The sterols included major amounts of sitosterol, campesterol, and stigmasterol, and traces of cholesterol. Over 70 individual compounds were isolated and identified from the nonsaponifiables. These included borneol, sesquiterpenes, diterpenes, steroidal ketones, as well as lanostane and serratane triterpenes. The characterization of 12 new natural products or natural products isolated for the first time from *Pinus* species is reported.

INTRODUCTION

The utilization of bark residues is a problem for the forest products industries. To assess the possible utilization of the millions of tons of waste bark from lumber and pulp production as an additional source of chemicals, detailed knowledge of the extractable chemical constituents in bark is needed.

Following a preliminary investigation of the chemistry of western white pine (*Pinus monticola* Dougl.) bark [1], a detailed analysis of the benzene extract was conducted to determine its chemical composition. Nonpolar organic solvents, such as benzene, extract the terpenes, waxes, fats, sterols, fatty (and wax) acids, wax alcohols, and resins contained in the bark. Marketable components of this nature are now recovered as byproducts of wood pulping (i.e. tall oil and related naval stores [2]) and waxes [3]. Reported here are the results of that analysis.

RESULTS AND DISCUSSION

The benzene extract (3.2%) of western white pine bark consisted of 18% 'strong' acids, 13% 'phlobaphenes', 37% weak fatty and resin acids, and 32% neutrals (Fig. 1). The 'strong' acids consisted, in part, of azelaic, adipic, and vanillic acids. Vanillic and other phenolic acids are known constituents of pine barks [4]. The phlobaphene fraction was irreversibly absorbed on the DEAE-Sephadex column used to separate the neutrals and acidics. This fraction was not examined further but contains condensed tannins and related polyphenols found in bark.

Weak acids

After methylation, the weak acids were fractionated into resin acids, fatty acids, and polar weak acids (components not readily eluted from alumina with *n*-pentane—e.g. simple phenolics, hydroxy acids, and auto-oxidation products).

The resin acids (9.5% of extract) consisted of pimaric, isopimaric, and abietic acids commonly found in *Pinus* spp. (Table 1). In addition the labdane diterpenic acid, anticopalic acid, was shown to be a major resin acid of the bark [4]. The fatty acids (6.5% of

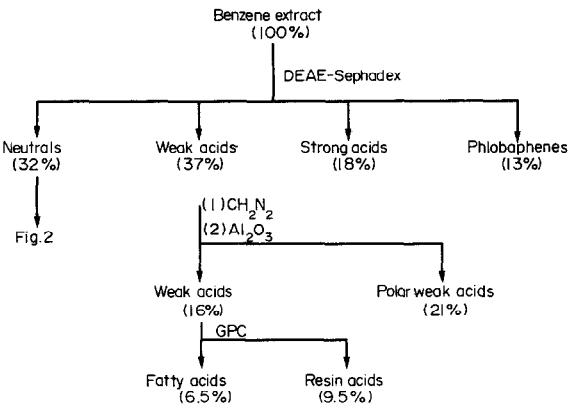

Fig. 1. Fractionation of western white pine bark benzene extractives.

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† Maintained in cooperation with the University of Wisconsin.

Table 1. Composition of the resin acids found in western white pine bark

Resin acid	Composition (%)
Isopimaric	51
Anticopalic	26
Dehydroabietic	15
Sandaracopimaric	5
Abietic	1
6,8,11,13-Abietatetraen-18-oic	1
Pimaric	trace

extract) consisted primarily of a homologous series of acids as shown in Table 2.

Neutrals

The neutrals were further fractionated (Fig. 2) into unesterified free sterols and esterified sterols, waxes, wax alcohols, esterified fatty acids, esterified strong acids, esterified polar weak acids, and the residual nonsaponifiables. The composition of the fatty acids, sterols, and wax alcohols are given in Tables 2 to 4, respectively. The waxes, the esterified polar weak acids, and the esterified strong acids were not studied further.

Residual nonsaponifiables

Over 70 individual compounds were isolated and identified from the residual nonsaponifiables. These included borneol, sesquiterpenes, diterpenes, steroid ketones, as well as lanostane and serratane triterpenes (Table 5). The majority of these compounds have been reported in *Pinus* species. However, several of the

Table 2. Composition of the fatty acids found in western white pine bark

Fatty acid*	Composition (%)	
	Unesterified	Esterified
12:0	trace	1
13:0	—	trace
14:0	trace	1
15:0	—	trace
16:0	5	11
16:1/17:0	2	trace
17:1	—	trace
18:0	2	2
18:1	6	10
$18:2^{9,12}$ *cis, cis*	2	3
20:0	16	14
20:1	—	1
21:0	trace	trace
22:0	24	24
23:0	2	1
24:0	33	26
24:1	—	2
25:0	trace	1
26:0	6	4

* The fatty acid shorthand designations of Burchfield and Storrs [69] are used.

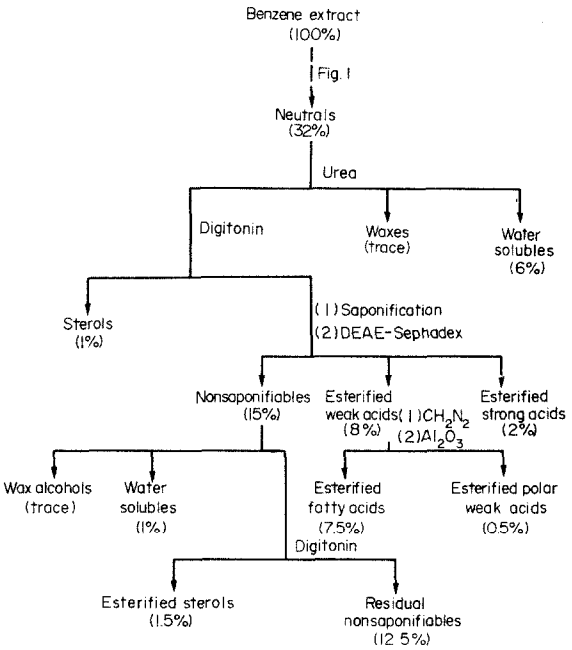


Fig. 2. Fractionation of western white pine bark neutrals.

compounds are new natural products or are reported from *Pinus* species for the first time.

(+)-8,11,13-*Abietatrien*-15-*ol* (**1**). High resolution MS gave an elemental composition of $C_{20}H_{30}O$ for this

Table 3. Composition of the sterols from western white pine bark

Compound*	Composition (%)	
	Unesterified	Esterified
Cholesterol	trace	—
Campesterol	13	3
Stigmasterol (?)	13	—
Sitosterol	74	97

* GLC: 1% SE-30, 260°, 10 ft × 1/8 in. O.D. SS column.

Table 4. Composition of wax alcohols from western white pine bark

Wax alcohol*	Composition (%)
16:0	14
17:0	23
18:0	47
18:1	9
20:0	trace
22:0	2
24:0	1
25:0	trace
26:0	trace
27:0	2
28:0	1

* The shorthand designations are analogous to those used by Burchfield and Storrs [69] for fatty acids.

Table 5. Composition of residual nonsaponifiables from western white pine bark

Compound	Composition (%)
MONOTERPENES	
(−)-Borneol	0.4
SESQUITERPENES	
Cadalene	0.1
(−)-Calamenene	trace
(+)-Longifolene	0.2
(±)-Torreyol	trace
DITERPENES	
Hydrocarbons	
(−)-Isopimaradiene	trace
(−)-Sandaracopimaradiene	0.1
19-Norabieta-3,8,11,13-tetraene‡	trace
19-Norabieta-4,8,11,13-tetraene‡	trace
(+)-19-Norabieta-4(18),8,11,13-tetraene‡	0.1
(−)-6,8,11,13-Abietatetraene	trace
(+)-Dehydroabietane	1.7
Alcohols	
(+)-Pimarol	0.1
(−)-Isopimarol	0.1
(−)-Sandaracopimarol	trace
Dehydroabietol	0.4
8,11,13-Abietatrien-15-ol (**1**)*	trace
(−)-8,11,13-Abietatrien-7α-ol (**2**)*	0.3
(+)-7-Oxo-8,11,13-abietatrien-18-ol	0.4
13-Epimanool	0.3
18-Norisopimarol	trace
18-Norsandaracopimarol	trace
18-Nordehydroabietol	0.4
19-Norabieta-4(18),8,11,13-tetraen-7α-ol (**3**)*	trace
Resin acid esters	
Methyl dehydroabietate	trace
Ethyl isopimarate*	0.1
Ethyl sandaracopimarate*	trace
Ethyl dehydroabietate*	0.1
Epoxides	
9,10-Epoxy-9,10-secoabieta-8,11,13-triene (**4**)*	0.02
(+)-Manoyl oxide	0.2
(+)-13-Epimanoyl oxide	0.07
8α,13*S*:13,17-Diepoxy-15,16-dinorlabdane (**5**)*	0.04
8β,13*R*:13,17-Diepoxy-15,16-dinorlabdane (**6**)*	0.09
Other	
(+)-8,11,13-abietatrien-7-one (**7**)*	0.6
15,16-Dinorlabd-8(17)-en-13-one	0.3
9,10-Secoabieta-8,11,13-trien-18,10-olide§	0.01
STEROIDS	
4-Campesten-3-one	0.02
4-Stigmasten-3-one	0.7
3,5-Stigmastadien-7-one	0.9
4,6-Cholestadien-3-one (**8**)*	trace
4,6-Campestadien-3-one	trace
4,6-Stigmastadien-3-one	0.03
TRITERPENES	
Cycloartanes	
24-Methylenecycloartanol	trace
Lanostanes	
3β-Methoxy-5α-lanost-9(11)-ene-24*S*,25-diol‖	6.0

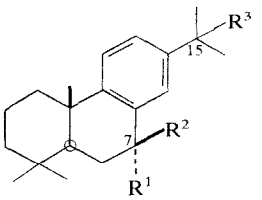
Table 5. (*Continued*)

Compound	Composition (%)
5α-Lanost-9(11)-en-3β,24S,25-triol‖	1.7
Nine other lanstane derivatives†	0.9
Serratenes	
Serratenediol	5.1
21-Episerratenediol	5.1
3,21-Diepiserratenediol	0.2
Serratenediol 3-methyl ether	9.4
21-Episerratenediol 3-methyl ether	0.4
21-Episerratenediol 21-methyl ether	0.9
Serratenediol dimethyl ether	0.2
21-Episerratenediol dimethyl ether	0.3
3β-Methoxy-14-serraten-21-one	4.3
3α-Hydroxy-14-serraten-21-one (**9**)*	0.03
3β-Hydroxy-14-serraten-21-one	0.3
16-Oxoepiserratenediol	0.03
Compound A†	0.02
Compound B†	0.09
Compound C†	0.04
Compound D†	0.03
Compound E†	0.09
Compound F†	0.01
Compound G†	0.01
Compound H†	1.7

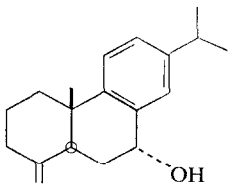
*New natural product or reported from *Pinus* species for the first time.
†Proof of structure in progress.
‡Characterization described in ref. [39].
§Characterization described in ref. [58].
‖Characterization described in ref. [63].

diterpene. The ^{1}H NMR was similar to that for dehydroabietane except that: (a) the isopropyl methine was absent; and (b) the isopropyl methyls were deshielded and occurred as a singlet at δ 1.57, indicating that the alcohol group was located at C-15. The IR and MS are consistent with the proposed structure. In the MS, the peak at *m/e* 271 corresponds to the expected loss of the C-10 Me from the molecular ion. The metastable peak at *m/e* 257 supports this fragmentation (*m/e* 286→*m/e* 271). The peak at *m/e* 253 corresponds to the expected loss of the benzylic alcohol at C-15 as H_2O from the 271 fragment. Further, the MS is analogous to that of dehydroabietane [5] showing characteristic fragment ions at *m/e* 175 (M^+-111), m/e 189 (M^+-97), and *m/e* 201 (M^+-85). These peaks are accompanied by weaker satellites 18 *m/e* units lower corresponding to the loss of water. These data indicate that this new natural product is (+)-8,11,13-abietatrien-15-ol.

(−)-8,11,13-*Abietatrien*-7α-*ol* (**2**). The natural product on oxidation gave 8,11,13-abietatrien-7-one. This fact, coupled with the ^{1}H NMR, IR, and MS data, indicated that the compound was 8,11,13-abietatrien-7α-ol (**2**). 8,11,13-Abietatrien-7-one on reduction ($LiAlH_4$) gave 8,11,13-abietatrien-7β-ol. Comparison of the ^{1}H NMR spectra of the epimeric alcohols confirmed the assignment of the natural product as the 7α-ol. Although the exact conformation of the B-ring in 4,4-disubstituted ring C aromatic diterpenoids with a *trans*-A/B ring junction and substitution at C-7 is not fully known, these compounds apparently possess either a half boat or half chair conformation [6, 7]. Thus as expected the C-10 Me of the 7β-ol is deshielded with respect to the C-10 Me of the 7α-ol.



1 $R^1=R^2=H$; $R^3=OH$
2 $R^1=OH$; $R^2=R^3=H$
7 $R^1, R^2=O$; $R^3=H$



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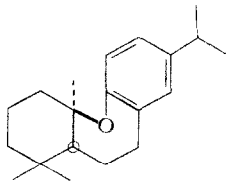

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Table 6. Changes in ^{1}H NMR chemical shifts of 9,10-epoxy-9,10-secoabieta-8,11,13-triene (13 mg) on adding the europium chelate of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione

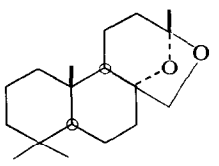
Peak	Change in chemical shift +5 mg	+10 mg	+25 mg	+50 mg
C-10 Me(δ 0.775)	−0.025	−0.055	−0.105	−0.145
C-4 eq Me (δ 1.00)	0.000	−0.020	−0.05	−0.06
C-4 ax Me (δ 1.00)	−0.075	−0.17	−0.27	−0.41
Isopropyl Me_2 (δ 1.225)	+0.01	0.00	0.00	0.00
Benzylic Hs (δ 2.75)	−0.03	−0.05	−0.15	−0.16

The coupling constant of the hydrogen geminal to the alcohol is small in the case of the 7α-ol ($W_{1/2} \sim 8$ Hz) as expected for a quasi-equatorial hydrogen and large in the case of the 7β-ol ($W_{1/2} \sim 18$ Hz) as expected for a quasi-axial hydrogen. In agreement with this is the 16 cm^{-1} lower position of the near IR maximum in the 7β-ol as expected for a quasi-equatorial alcohol vs a quasi-axial alcohol of the 7α-ol. These data are in agreement with that reported for the synthetic 7α-ol [8] and with the reassignment of configuration of 7β-acetoxydehydroabietic acid to 7α-acetoxydehydroabietic acid [9]. 8,11,13-Abietatrien-7α-ol has been isolated from *Juniperus oxycedrus* [10].

19-*Norabieta*-4(18),8,11,13-*tetraen*-7α-*ol* (**3**). The near IR of this product corresponds to that observed for 8,11,13-abietatrien-7α-ol. The narrow width of the C-7 H peak in the ^{1}H NMR (t, $J = 2.5$ Hz) is also consistent with a 7α-ol. The MS showed a molecular ion at *m/e* 270 which readily lost water to give the base peak at *m/e* 252. Further loss of the C-10 Me gives a strong peak at *m/e* 237. This fragmentation is supported by M* 223. The *m/e* 237 fragment loses propene (M* 160.5) to give an extremely strong *m/e* 195 ion with the expected structure (**10**). The ^{1}H NMR and IR spectral data obtained for this new natural product are consistent with the proposed structure (**3**).

9,10 - *Epoxy* - 9,10 - *secoabieta* - 8,11,13 - *triene* (**4**). High resolution MS of this compound gave a molecular formula of $C_{20}H_{30}O$. The spectral data clearly indicate the presence of 3 aromatic protons, an isopropyl group, 3 benzylic hydrogens, 3 angular methyls, and an aromatic ether, thus suggesting a 9,10-epoxy-9,10-secoabieta-8,11,13-triene structure. The addition of the europium chelate of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (Table 7) produced changes in the chemical shifts of the C-4 axial Me, the C-10 Me, and the C-7 benzylic protons. Because the C-4 axial methyl is more shifted than the C-10 Me, the C-10 Me must be equatorial (i.e. 10α Me and 5α H). This stereochemistry would explain the deshielded C-10 Me in the original ^{1}H NMR as compared to the C-10 Me of dehydroabietane since the C-10 Me would be in the face of the aromatic ring. The MS fragmentation of this molecule would be expected to fragment readily through ring B to give strong peaks at *m/e* 149 or 137 as observed. Thus, the spectral data are fully consistent with the proposed structure (**4**) for this new natural product.

8α,13S:13,17- and 8β,13R:13,17-*diepoxy*-15,16-*dinorlabdane* (**5** *and* **6**). These compounds have been



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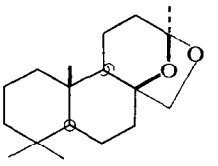

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synthesized [11, 12]. This is the first report of their occurrence as natural products.

(+)-8,11,13-*Abietatrien*-7-*one* (**7**). This compound has been synthesized [8, 13, 14]. It has been found as a natural product in the cones of *Cedrus atlantica* [15]; this is the first report of its occurrence in *Pinus* spp.

Resin acid ethyl esters. Resin acid methyl esters have been reported as natural products, however ethyl esters have not. It is possible that the small amounts of ethyl isopimarate, ethyl sandaracopimarate, and ethyl dehydroabietate found in this investigation are artifacts of the isolation procedures.

Steroid ketones. 4-Campesten-3-one, 4-stigmasten-3-one, 3,5-stigmastadien-7-one, 4,6-cholestadien-3-one (**8**), 4,6-campestadien-3-one, and 4,6-stigmastadien-3-one are probably auto-oxidation products of sitosterol, campesterol, and cholesterol.

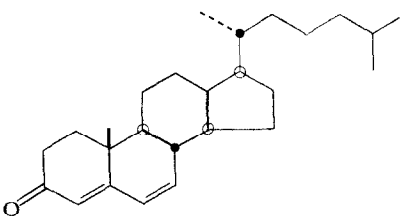
3α-*Hydroxy*-14-*serraten*-21-*one* (**9**). The spectral data were consistent with a 14-serratene structure containing a ketone and an axial alcohol. Oxidation gave serratenedione, a known compound [16, 17]. Thus, the alcohol and ketone were at C-3 and C-21. The CD is that expected for a 14-serraten-21-one [18]. Comparison with 3β-hydroxy-14-serraten-21-one, a known compound [18], showed that the two compounds were not the same. Thus, this new natural product must be 3α-hydroxy-14-serraten-21-one.

Unknown serratanes (*compounds A–H*). A number of compounds whose spectral properties suggested they were serratanes were isolated in small quantities. The structural elucidation of these compounds is in progress and will be reported later.

EXPERIMENTAL

Mps were measured in evacuated capillaries and are corrected. Rotations were obtained in $CHCl_3$ (*c* 1) and ^{1}H NMR spectra in $CDCl_3$ at 60 MHz with TMS (int. std) unless specified otherwise.

Fractionation of C_6H_6 *extract.* Western white pine (*Pinus monticola* Dougl.) whole bark ground in a Wiley mill to



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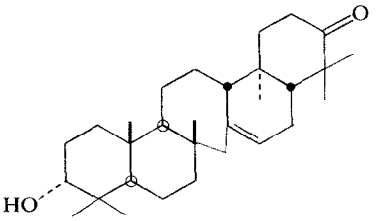

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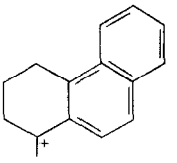

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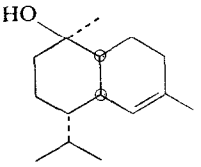

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pass a 2-mm mesh screen was C_6H_6-extracted in a Soxhlet as previously described [1]. Fractionation of C_6H_6 extract (3.2% of oven-dried bark) is summarized in Fig. 1. The C_6H_6 extract (4.56 g) was dissolved in 250 ml solvent (Et_2O–EtOH–H_2O, 90:10:1) and fractionated over 100 g DEAE-Sephadex [19, 20]. Elution with the solvent gave the neutrals (1.44 g). Elution with CO_2-saturated solvent gave the weak acids (1.67 g). Elution with a dilute formic acid solution in the solvent gave the 'strong' acids (0.85 g). The remaining material (0.59 g) was irreversibly absorbed on the DEAE-Sephadex column.

Weak acids. The weak acids were methylated with CH_2N_2 [20] and filtered through Al_2O_3 (Woelm, neutral, Act. II). The weak acid methyl esters (0.71 g) were eluted with pentane. Polar acid methyl esters (0.96 g) were retained by Al_2O_3 and were not investigated further. Gel permeation chromatography [21] separated the weak acid methyl esters into fatty acid methyl esters (0.29 g) and resin acid methyl esters (0.42 g). The fatty acid methyl esters were analysed by GLC [22] comparison with standard reference compounds (Table 2). The analysis of the resin acid methyl esters (Table 1) was reported earlier [23].

Neutrals. The neutrals (Fig. 2) were treated with urea to remove *n*-aliphatics (0.02 g) via the urea canal inclusion complex [24]. TLC (Si gel; petrol–C_6H_6, 1:1) indicated that the *n*-aliphatics were a mixture of waxes that included hydrocarbons, wax esters, and wax alcohols. 3β-Hydroxysterols (0.03 g) were isolated from the *n*-aliphatic free neutrals as the digitonides, that were subsequently cleaved by DMSO [25]. Trimethylsilylated sterols were analysed by GLC comparison with authentic standards (Table 4). Remaining neutrals were saponified in 2N refluxing ethanolic KOH for 4 hr under N_2. Acidification, extraction, and separation over DEAE-Sephadex as before yielded esterified weak acids (0.36 g), the nonsaponifiables (0.68 g), and the esterified strong acids (0.12 g) which were not investigated further.

Esterified weak acids. The esterified weak acids were methylated with CH_2N_2 and filtered through Al_2O_3 with pentane to give fatty acid methyl esters (0.33 g) that were analysed by GLC (Table 2). Esterified polar weak acids were retained on the Al_2O_3 and not investigated further.

Nonsaponifiables. Nonsaponifiables were treated with urea to remove wax alcohols (0.02 g) that were identified by GLC comparison with standard reference compounds (Table 4). Esterified 3β-hydroxysterols (0.06 g) were removed as the digitonides, that were cleaved by DMSO as before. Trimethysilylated sterols were identified by GLC (Table 3). Residual nonsaponifiables (0.56 g) were fractionated as described below.

Fractionation of the residual nonsaponifiables. Larger quantities of residual nonsaponifiables for further fractionation were obtained by direct saponification of a larger portion of the original C_6H_6 extract. Nonsaponifiables were obtained by classical extraction methods and freed of waxy materials via the urea canal inclusion complex and of sterols via the digitonides. Residual nonsaponifiables isolated in this manner represented 11.7% of the C_6H_6 extract, in close agreement with those isolated by the analytical methods described above. Residual nonsaponifiables were crystallized from C_6H_6, $CHCl_3$–EtOH, and C_6H_6 to yield a triterpene fraction (1% of C_6H_6 extract). Filtrate was crystallized from petrol to give a second triterpene fraction (2% C_6H_6 extract) and an oily fraction (8% C_6H_6 extract). The first crystalline triterpene fraction contained serratenediol 3-methyl ether, serratenediol, and 3 very polar serratane triterpenes: compounds A, B, and C. The second crystalline fraction contained episerratenediol dimethyl ether, 3β-methoxy-14-serraten-21-one, episerratenediol 21-methyl ether, episerratenediol 3-methyl ether, diepiserratenediol, episerratenediol, serratenediol, and the unknown serratane, compound H. The oily fraction contained borneol, sesquiterpenes, diterpene hydrocarbons, alcohols, resin acid esters, and epoxides, other diterpenes, ketosteroids, lanostane triterpenes, and serratene triterpenes (Table 5). Components in the crystalline fractions were further separated by column chromatography over Si gel and those in the oily fraction over Al_2O_3. These chromatographs were eluted with organic solvents of increasing polarity: petrol (PE), PE–C_6H_6 mixtures, C_6H_6, C_6H_6–diethyl ether mixtures, and finally C_6H_6–diethyl ether–MeOH mixtures. Fractions obtained from these chromatograms were combined on the basis of their similarity by GLC, TLC, IR, UV, and NMR. Numerous purification steps were often required for eventual isolation of individual components and often the same component was isolated from each of several combined fractions. Thus the combined fractions or the combined fraction after suitable derivatization (usually acetylation) were separated into individual chromatographically pure (TLC, GLC) compounds by a combination of techniques that included: rechromatography, preparative TLC and GLC, distillation, sublimation, and crystallization.

(−)-*Borneol.* Mp 190–192°, $[\alpha]_D^{22}$ −37°. Reported [26]: mp 204°, $[\alpha]_D$ −37.7°. TLC (Si gel), GLC (SE-30), IR identical with commercial sample of (+)-borneol.

Cadalene. TLC (Si gel), GLC (DEGS, SE-30), IR, ^{1}H NMR identical with authentic sample (S. Dev).

(−)-trans-*Calamenene*. $[\alpha]_D^{20}$ −60° (*c* 0.1). Reported [27–30]: $[\alpha]_D$ −46° to −68°. TLC (Si gel–$AgNO_3$), GLC (DEGS), IR, ^{1}H NMR identical with authentic sample [27, 31, 32].

(+)-*Longifolene*. $[\alpha]_D^{21}$ +44°. Reported [26]: $[\alpha]_D$ +45°. ν_{max}^{film} cm^{-1}: 3062, 1658, 874 (C=CH_2). ^{1}H NMR identical to reported [33].

(±)-*Torreyol* (**11**). Mp 102–103°, $[\alpha]_D^{25}$ +3°. Reported for (−)-torreyol [34]: mp 137–139°, $[\alpha]_D$ −109°. TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30), IR, and ^{1}H NMR identical with (−)-torreyol (W. G. Dauben). This is the first reported isolation of racemic torreyol as a natural product.

(−)-7,15-*Isopimaradiene*. $[\alpha]_D^{20}$ −35° (*c* 0.8). Reported: $[\alpha]_D$ −28° [35], −31.3° [36]. The ^{1}H NMR and IR were identical to those reported for 7,15-isopimaradiene [35, 37].

(−)-8(14),15-*Isopimaradiene* (*sandaracopimaradiene*). Mp 34–36°, $[\alpha]_D^{25}$ −12°. Reported [38]: mp 41–42°, $[\alpha]_D$ −12°. IR and ^{1}H NMR identical to reported [37, 38].

19-*Norabieta*-3,8,11,13-*tetraene*; 19-*norabieta*-4,8,11,13-*tetraene*; *and* 19-*norabieta*-4(18),8,11,13-*tetraene*. The characterization of the three 19-norabietatetraenes was reported earlier [39].

(−)-6,8,11,13-*Abietatetraene*. $[\alpha]_D^{22}$ −118°. $\lambda_{max}^{isooctane}$ nm (ε): 264 (8970), 219.5 (28 830). Reported [40]: λ_{max} nm (ε): 270 (9550). ν_{max}^{neat} cm^{-1}: 1605, 1570, 1490 (aromatic stretching); and 890, 825 (trisubstituted aromatic). ^{1}H NMR (100 MHz): δ 0.97 (3H, *s*, C-10 Me), 1.01 (3H, *s*, C-4β Me), 1.05 (3H, *s*, C-4α Me), 1.215 (6H, *d*, *J* = 7 Hz, $CH(CH_3)_2$), 2.09 (1H, *t*, *J* ~ 3 Hz, C-5H), 2.80 [1H, *heptet*, *J* = 7 Hz, $CH(Me)_2$], 6.93 (2H, *s*, C-11 and C-12 aromatic H's), 6.78 (1H, *br s*, C-14 aromatic H) and 6.17 [2H, AB *dd* (δ_A = 5.91, δ_B = 6.44), each peak of which is further split into a doublet by coupling (*J* = 3 Hz) with the C-5H, *J* = 9–1/2 Hz, C-6 and C-7 H's]. The ^{1}H NMR and IR were superimposable on those of the compound synthesized from 8,11,13-abietatrien-7β-ol. 8,11,13-Abietatrien-7β-ol was dissolved in C_6H_6 with a crystal of I_2 and refluxed for 45 min; a second crystal of I_2 was added and the soln refluxed for 3 hr. On cooling, the mixture was poured into 0.5 N NaOH and C_6H_6-extracted. The C_6H_6 extract was dried ($MgSO_4$), concd, and filtered through Al_2O_3 (basic, Act. I). 6,8,11,13-Abietatetraene was isolated from the filtrate by a combination of prep. GLC (SE-30/EGIP) and then liquid chromatography (alumina–40% $AgNO_3$). ^{1}H NMR, IR, and UV were identical to those of the natural product. However, the optical rotation ($[\alpha]_D^{23}$ −229°) was significantly greater than that of the natural product.

(+)-*Dehydroabietane*. Mp and mmp 42–43°, $[\alpha]_D^{19}$ +54° (*c* 1.2). Reported: mp 38–42° to 45° [8,40,41], $[\alpha]_D$ +49° and +63° [42]. TLC (Si gel), GLC (SE-30), ^{1}H NMR identical to authentic sample (E. Wenkert).

(+)-*Pimarol*. Mp 85–86°, $[\alpha]_D^{23}$ +81°. Reported: mp 85–86°, $[\alpha]_D^{20}$ +83° [43]; mp 87.5–89.5°, $[\alpha]_D^{22}$ +94° [44]. TLC (Si gel, Si gel–$AgNO_3$), GLC (PPE-20), IR, ^{1}H NMR identical to authentic sample prepared by $LiAlH_4$ reduction of methyl pimarate.

(−)-*Isopimarol*. Mp 65–68°, $[\alpha]_D^{22}$ −11°. Reported [43–46]: mp 81–82° to 86–87°, $[\alpha]_D$ −17° to −24.6°. TLC (Si gel, Si gel–$AgNO_3$), GLC (PPE-20), IR, ^{1}H NMR identical to authentic sample prepared by $LiAlH_4$ reduction of methyl isopimarate.

(−)-*Sandaracopimarol*. $[\alpha]_D^{23}$ −8° (*c* 0.5). Reported [47–49]: $[\alpha]_D$ −6.4° to −11°. IR, ^{1}H NMR identical to reported [47].

Dehydroabietol. TLC (Si gel), GLC (SE-30), UV, IR ^{1}H NMR identical to authentic sample prepared by $LiAlH_4$ reduction of methyl dehydroabietate.

(+)-8,11,13-*Abietatrien*-15-*ol* (**1**). Prep. TLC (Si gel. C_6H_6–ether, 9:1) yielded chromatographically pure [TLC (Si gel), GLC (SE-30)] 8,11,13-abietatrien-15-ol as a semisolid: $[\alpha]_D^{25}$ +49° (*c* 0.2). ^{1}H NMR,: δ 0.95 (6H, *s*, 2 Me), 1.20 (3H, *s*, tertiary Me), 1.57 (6H, *s*, isopropyl Me_2), 2.90 (2H, *m*, C-7 benzylic H's), and 7.2–7.4 (3H, *m*, aromatic H's). Reported for methyl 15-hydroxy abieta-8,11,13-trien-18-oate [50]: 1.47 (isopropyl Me_2) and 2.90 (C-7 benzylic H's). ν_{max}^{film} cm^{-1}: 3375 (OH); 3080, 1610, 1500 (aromatic); 892, 822 (trisubstituted aromatic). MS (probe) 70 eV *m/e* (rel. int.): 286 ($C_{20}H_{30}O$, M^+, 17), 271 ($C_{19}H_{27}O$, M^+−Me, 100), 257 (M*, 286→271), 253 ($C_{19}H_{25}$, M^+−Me−H_2O, 18), 201 ($C_{14}H_{17}O$, 28), 189 ($C_{13}H_{17}O$, 41), 185 ($C_{14}H_{17}$, 30), 183 ($C_{14}H_{15}$, 18), 175 ($C_{12}H_{15}O$, 32), 171 ($C_{13}H_{15}$, 30), 157 ($C_{12}H_{13}$, 32), 143 ($C_{11}H_{11}$, 33), 141 ($C_{11}H_9$, 30), 129 ($C_{10}H_9$, 40), 128 ($C_{10}H_8$, 38), 117 (C_9H_9, 24), 115 (C_9H_7, 31), 105 (C_8H_9, 21), and 91 (C_7H_7, 32). Found: M^+ *m/e* 286.2304. Calc. for $C_{20}H_{30}O$: M^+ *m/e* 286.2296.

(−)-8,11,13-*Abietatrien*-7α-*ol* (**2**). Chromatographically pure [TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30)] 8,11,13-abietatrien-7α-ol was isolated by chromatography over Al_2O_3: $[\alpha]_D^{22}$ −8° (*c* 1.6). $\nu_{max}^{CCl_4}$ cm^{-1}: 3614 (benzylic OH). $\nu_{max}^{CHCl_3}$ cm^{-1}: 1500, 830 (aromatic). ^{1}H NMR (100 MHz): δ 0.94 (3H, *s*, C-18 Me), 0.98 (3H, *s*, C-19 Me), 1.13 (3H, *s*, C-10 Me), 1.23 (6H, *d*, *J* = 7 Hz, isopropyl Me_2), 2.83 (1H, apparent *pentet*, *J* = 7 Hz, isopropyl methine), 4.79 (1H, sharp apparent *t*, *J* = 3 Hz, quasi-equatorial C-7 H), 6.66 (3H, *m*, aromatic H's). Reported ^{1}H NMR of synthetic compound (CCl_4) [8]: 0.93, 0.97, 1.08 (3 tertiary Me), 4.6 (C-7 H, *J* = 2.5–4 Hz). MS (probe) 70 eV *m/e* (rel. int.): 286 ($C_{20}H_{30}O$, M^+, 7), 268 ($C_{20}H_{28}$, M^+−H_2O, 2), 253 ($C_{19}H_{25}$, M^+−H_2O−Me, 16), 243 ($C_{17}H_{23}O$, 3), 211 ($C_{16}H_{19}$, 13), 183 ($C_{14}H_{15}$, 17), 141 ($C_{10}H_{21}/C_{11}H_9$, 14), 125 (C_9H_{17}, 13), 123 ($C_9H_{15}/C_8H_{11}O$, 13), 111 ($C_8H_{15}/C_7H_{11}O$, 19), 109 (C_8H_{13}/C_7H_9O, 21), 97 (C_7H_{13}/C_6H_9O, 32), 95 (C_7H_{11}/C_6H_7O, 32), 85 (C_6H_{13}, 32), 83 (C_6H_{11}/C_5H_7O, 32), 81 (C_6H_9, 21), 71 (C_5H_{11}/C_4H_7O, 51), 70 (C_5H_{10}, 18), 69 (C_5H_9/C_4H_5O, 46), 67 (C_5H_7, 16), 57 (100), 56 (42), 55 (42), 43 (74), 42 (17), and 41 (60). Found: M^+ *m/e* 286.2307. Calc. for $C_{20}H_{30}O$: M^+ *m/e* 286.2296. Oxidation of (−)-8,11,13-abietatrien-7α-ol gave 8,11,13-abietatrien-7-one (*vide infra*).

(+)-7-*Oxo*-8,11,13-*abietatrien*-18-*ol*. Isolated as the acetate derivative: mp 62–64°, $[\alpha]_D^{22}$ +20°. Reported [39]: mp 62–64°, $[\alpha]_D$ +18°. TLC (Si gel), GLC (SE-30), IR, ^{1}H NMR, and mmp of acetate identical to authentic sample [39].

13-*Epimanool*. TLC (Si gel), GLC (SE-30), IR, ^{1}H NMR identical to authentic sample [51]. (+)-13-Epimanool 3,5-dinitrobenzoate derivative was prepared [52]: mp and mmp 118–118.5°, $[\alpha]_D^{25}$ +32°. Reported [52]: mp 116.5–118°, $[\alpha]_D^{22}$ +33°.

18-*Norisopimaradienol*. TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30, DEGS—as TMS ether), IR, and ^{1}H NMR identical to an authentic sample (P. K. Grant).

18-*Norsandaracopimaradienol*. TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30, DEGS—as TMS ether), IR, and ^{1}H NMR identical to an authentic sample [53].

18-*Nordehydroabietol*. TLC (Si gel), GLC (SE-30), IR, ^{1}H NMR identical to an authentic sample (A. W. Burgstahler).

19-*Norabieta*-4(18),8,11,13-*tetraen*-7α-*ol* (**3**). A small amount of 90% pure (TLC) 19-norabieta-4(18),8,11,13-tetraen-7α-ol was isolated. ^{1}H NMR: δ 0.93 (3H, *s*, C-10 Me), 1.26 (6H, *d*, *J* = 7 Hz isopropyl Me_2), 2.85 (1H, *m*, isopropyl methine), 4.72 (2H, *d*, *J* = 15 Hz, C=CH_2), 4.85 (1H, *t*, *J* = 2–1/2 Hz, CHOH benzylic, quasi-equatorial) and 7.2 (3H, *m*, aromatic H's) ν_{max}^{film} cm^{-1}: 3390 (OH); 3180,

1650, and 890 (C=CH_2); 1616 and 1500 (aromatic); 905 and 825 (trisubstituted aromatic). $\nu_{max}^{CCl_4}$, cm^{-1}: 3613 (quasi-axial benzylic OH). MS (probe) 70 eV *m/e* (rel. int.): 270 (M^+, 16), 255 (20), 253 (30), 252 ($M^+ - H_2O$, 100), 238 (16), 237 ($M^+ - H_2O$ – Me, 48), 236 (M* 270 → 252), 224 (26), 211 (16), 210 (12), 209 (32), 195 ($M^+ - H_2O$ – Me – propene, 90), 193 (13), 192 (11), 181 (18), 169 (16), 167 (22), 165 (18), 141 (19), 123 (20), 109 (28), 108 (16), 107 (21), 105 (27), 95 (28), 93 (30), 91 (37), 81 (37), 79 (26), and 77 (18).

Methyl dehydroabietate. TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30), ^1H NMR identical to an authentic sample [54].

Ethyl isopimarate. The compound isolated by chromatography was identical to an authentic sample of ethyl isopimarate [55] by TLC (Si gel, Si gel–$AgNO_3$), GLC (DEGS, SE-30), IR, and ^1H NMR. The authentic sample was prepared by reacting isopimaric acid in Et_2O-EtOH (9:1, 20 ml) with a slight excess of $MeCH_2N_2$ in DMF. The mixture stood at room temp. for ~2 hr, and a slight excess of HOAc (20% solution in Et_2O–EtOH, (9:1)) was added to destroy the excess reagent. The solvent was removed by evapn *in vacuo* and the reaction product chromatographed over Al_2O_3 (neutral, Act. III) with pentane. ^1H NMR: δ 0.87, 0.91, and 1.28 (each 3H, *s*, tertiary Me), 1.23 (3H, *t*, $J = 7$ Hz, CH_3—CH_2—O), 4.12 (2H, *q*, $J = 7$ Hz, Me—CH_2—O—), and 4.7–6.2 (4H, typical isopimaradiene double bond pattern [54]). ν_{max}^{film} cm^{-1}: 1726 (carbonyl), 1240 (—CO—O—C) and 3080, 1640, 1405, 910 (vinyl).

Ethyl sandaracopimarate. Isolated material had the expected TLC (Si gel, Si gel–$AgNO_3$) and GLC (DEGS, SE-30) properties of ethyl sandaracopimarate [55]. ^1H NMR: δ 0.84 (3H, *s*, Me), 1.04 (3H, *s*, Me), 1.21 (3H, *s*, Me), 1.23 (3H, *t*, $J = 7$ Hz, CH_3—CH_2—O—), 4.14 (2H, *q*, $J = 7$ Hz, Me—CH_2—O—) and the typical sandaracopimarate double bond pattern between 4.5 and 6.2 [52]. ν_{max}^{film} cm^{-1}: 1725 (C=O), 1245 (CO—O—C) and 1638, 1000, 910 (vinyl).

Ethyl dehydroabietate. The material obtained by chromatography was identical with an authentic sample of ethyl dehydroabietate by TLC (Si gel, Si gel–$AgNO_3$), GLC [55] IR, and ^1H NMR. The authentic sample of ethyl dehydroabietate was synthesized from authentic dehydroabietic acid by the method given above for the synthesis of ethyl isopimarate. ^1H NMR: δ 1.22 (3H, *s*, Me), 1.28 (3H, *s*, Me), 1.225 (6H, *d*, $J = 7$ Hz, isopropyl Me_2), 1.23 (3H, *t*, $J = 7$ Hz, CH_3—CH_2—O—), 2.87 (3H, *m*, isopropyl methine + benzylic protons), 4.15 (2H, *q*, $J = 7$ Hz, Me—CH_2—O—), 6.8–7.4 (3H, *m*, aromatic protons). ν_{max}^{film} cm^{-1}: 1728 (C=O), 1245 (CO—O—C), and 1615, 1570, 1500, 820 (aromatic).

9,10-*Epoxy*-9,10-*secoabieta*-8,11,13-*triene* (**4**). The compound isolated by column chromatography was chromatographically pure [TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30, DEGS)]: $[\alpha]_D^{25} + 9°$ (*c* 1.2). ^1H NMR: δ 0.775 (3H, *s*, Me), 1.00 (6H, *s*, 2Me), 1.225 (6H, *d*, $J = 7$ Hz, isopropyl 2Me, decoupled by irradiation at 2.86), ~2.6 (3H, *m*, isopropyl methine + two benzylic hydrogens), and ~6.9 (3H, *m*, aromatic hydrogens). The shifts in the ^1H NMR spectrum on adding the europium chelate of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione are shown in Table 6. ν_{max}^{film} cm^{-1}: 1610, 1585, 1500 (aromatic); 1250 (asymmetrical C—O—aromatic) and 1100 (symmetrical C—O—aromatic). $\lambda_{max}^{isooctane}$ nm (ε): 272 (1010), 278 (930), 224 (*sh*), 215 (*sh*). MS (probe) 70 eV *m/e* (rel. int.): 286 (M^+, $C_{20}H_{30}O$, 49), 215 ($C_{15}H_{19}O$, 11), 189 ($C_{13}H_{17}O$, 18), 162 ($C_{11}H_{14}O$, 55), 162 (M*, 286 → 215), 150 ($C_{10}H_{14}O$, 57), 149 ($C_{10}H_{13}O$, 100), 137 ($C_{10}H_{17}$, 65), 135 ($C_9H_{11}O$, 22), 125 (M*, 286 → 189), 123 (C_9H_{15}, 33), 95 (C_7H_{11}, 32), 92 (M*, 286 → 162), 81 (C_6H_9, 35), 77.5 (M*, 286 → 149), 69 (C_5H_9, 25), 67 (C_5H_7, 18), 66 (M*, 286 → 137). Found: M^+ *m/e* 286.2281. Required for $C_{20}H_{30}O$: M^+ *m/e* 286.2296.

(+)-*Manoyl oxide.* $[\alpha]_D^{25} + 26°$ (*c* 1.3). Reported [44]: $[\alpha]_D^{22} + 19°$. TLC (Si gel–$AgNO_3$), GLC (SE-30), IR, and ^1H NMR identical to authentic compound [44].

(+)-13-*Epimanoyl oxide.* Mp 98.5–100.5°, $[\alpha]_D^{23} + 38°$ (*c* 0.9). Reported [44]: mp 97–99.5°, $[\alpha]_D^{22} + 38°$. TLC (Si gel–$AgNO_3$), GLC (SE-30), IR, ^1H NMR, mmp identical to authentic compound [44].

8α,13*S*:13,17-*Diepoxy*-15,16-*dinorlabdane* (**5**). The impure sample (80% by GLC) isolated by chromatography was sublimed at 95°/water aspirator: mp 90–100° undepressed on admixture with authentic 8α,13*S*:13,17-diepoxy-15,16-dinorlabdane (reported [11]: mp 115–116°). The IR and ^1H NMR spectra were superimposable on those of an authentic sample (Firmenich). The identity was further confirmed by GLC (SE-30, DEGS) and TLC (Si gel, Si gel–$AgNO_3$).

8β,13R:13,17-*Diepoxy*-15.16-*dinorlabdane* (**6**). The isolated material (95% pure by GLC) was sublimed at 65°/0.02 mmHg: mp 110–114° undepressed on admixture with authentic compound (reported: mp 119–121° [12] and 121–122° [11]). The identity of this compound as 8β,13R:13,17-diepoxy-15,16-dinorlabdane was confirmed by IR, ^1H NMR, TLC (Si gel, Si gel–$AgNO_3$), and GLC (SE-30, DEGS) comparison with an authentic sample (Firmenich).

(+)-8,11,13-*Abietatrien*-7-*one* (**7**). Chromatographically pure compound was sublimed at 105°/25 mmHg to give a white crystalline material: mp 87–90°, $[\alpha]_D^{24} + 14°$ (reported: mp 82–84° [8] and mp 83-84° [13]; $[\alpha]_D + 19°$ [13]). ν_{max}^{film}, cm^{-1}: 1688 (conjugated C=O); 1610, 1500 (aromatic); 820 (trisubstituted aromatic). ^1H NMR: δ 0.93 (3H, *s*, C-4 Me), 1.00 (3H, *s*, C-4 Me), 1.23 (3H, *s*, C-10 Me), 1.23 (6H, *d*, $J = 7$ Hz, isopropyl Me_2), 2.60 (1H, *d*, $J = 2$ Hz, C-6βH), 2.75 (1H, *s*, C-6αH), 2.90 (1H, apparent *pentet*, $J = 7$ Hz, isopropyl methine), 7.27 (2H, *m*, C-11 and C-12 Hs), 7.82 (1H, *d*, $J = 1$–1/2 Hz, C-14H). λ_{max}^{EtOH} nm (ε): 303 (2400), 254 (10 500), and 211 (24 500) (reported: λ_{max} 300 (1950) [8]; 300 (2000) and 256 (10 500) [13]). (Found: C, 84.54; H, 10.02. Calc. for $C_{20}H_{28}O$: C, 84.45; H, 9.92%). The compound was identical to an authentic sample of 8,11,13-abietatrien-7-one by mmp, TLC (Si gel, Si gel–$AgNO_3$), GLC (SE-30, DEGS), IR, and ^1H NMR.

Synthesis A. The authentic sample was synthesized by oxidizing dehydroabietane (710 mg) with CrO_3 in HOAc [14]. The yellow oil (702 mg) obtained from the oxidation was chromatographed over Si gel. PE–benzene (1:1) eluted chromatographically pure 8,11,13-abietatrien-7-one (400 mg) that was sublimed at 105°/20 mmHg to give a white crystalline material: mp 85–90°.

Synthesis B. (−)-8,11,13-Abietatrien-7α-ol (25 mg) was dissolved in Py (5 ml) and Py–CrO_3 complex (52 mg) added. The mixture stood under N_2 overnight. MeOH (2.2 ml) was added with stirring and the mixture stood for 0.5 hr. The soln was partitioned between dil HCl and C_6H_6. The C_6H_6 layer was washed with dil HCl, dil NaOH, and then H_2O; dried ($MgSO_4$); and taken to dryness *in vacuo*. 8,11,13-Abietatrien-7-one (16 mg) was obtained by prep. TLC on Si gel (C_6H_6–diethyl ether, 99:1). The oil was sublimed at 105°/25 mmHg to give a white crystalline material, mp 80.5–85.5°, $[\alpha]_D^{22} + 8°$ (*c* 1.2). λ_{max}^{EtOH} nm (ε): 302(2000), 255(10 000), 209(23 000). This material was identical to authentic 8,11,13-abietatrien-7-one by ^1H NMR, IR, GLC (SE-30), and TLC (Si gel, Si gel–$AgNO_3$).

Synthesis of 8,11,13-*abietatrien*-7β-*ol.* 8,11,13-Abietatrien-7-one (280 mg) was dissolved in dry Et_2O (10 ml). This

soln was added dropwise over a period of 0.5 hr to a cooled, stirred suspension of $LiAlH_4$ (290 mg) in dry Et_2O (50 ml). This mixture stood overnight. EtOAc (4 ml), Et_2O (20 ml), finally sat. and K Na tartarate (50 ml) was added slowly. The soln, which became turbid, was brought to room temp. and extracted with Et_2O, washed (H_2O), dried ($MgSO_4$) and evapd to dryness *in vacuo* to give a viscous oil (281 mg). Chromatography over Si gel with mixtures of PE–C_6H_6 gave 8,11,13-abietatrien-7β-ol. $\nu_{max}^{CCl_4}$ cm^{-1}: 3598. ν_{max}^{film} cm^{-1}: 1499 and 824 (aromatic). ^1H NMR: δ 0.95 (6H, *s*, C-4 Me_2), 1.22 (6H, *d*, $J = 7$ Hz isopropyl Me_2), 1.23 (3H, *s*, C-10 Me), 2.86 (1H, apparent *pentet*, $J = 7$ Hz, C-15 H), 4.77 (1H, apparent *triplet*, $J = 8$ Hz, C-7 quasi-axial H), 7.09 (2H, *m*, C-11 and C-12 H's), and 7.37 (1H, *br s*, C-14 H).

15,16-*Dinorlabd*-8(17)-*en*-13-*one*. $[\alpha]_D^{22} + 32°$ (*c* 2.9). Reported [56, 57]: $[\alpha]_D + 37°$ to +38.5°. TLC (Si gel, Si gel–$AgNO_3$), GLC (DEGS, SE-30), IR, ^1H NMR identical with authentic compound (O. Jeger). MS (probe) 70 eV *m/e* (rel. int.): 262 (M^+, $C_{18}H_{30}O$, 5), 247 ($M^+ - Me$, C_{17} $H_{27}O$, 4), 244 ($M^+ - H_2O$, $C_{18}H_{28}$, 6) 229 ($M^+ - Me - H_2O$, $C_{17}H_{25}$, 7), 204 ($C_{15}H_{24}$, 8), 191 ($C_{14}H_{23}/C_{13}H_{19}O$, 7), 190 ($C_{14}H_{22}$, 4), 189 ($C_{14}H_{21}$, 5), 179 ($C_{13}H_{23}$, 6), 178 ($C_{13}H_{22}/C_{12}H_{18}O$; 5), 177 ($C_{13}H_{21}/C_{12}H_{17}O$, 11), 176 ($C_{13}$ H_{20}, 5), 175 ($C_{13}H_{19}$, 7), 173 ($C_{13}H_{17}$, 5), 165 ($C_{11}H_{17}O$, 5), 163 ($C_{11}H_{15}O$, 6), 161 (C_{12} H_{17}, 8), 159 ($C_{12}H_{15}$, 10), 147 ($C_{11}H_{15}$, 9), 138 ($C_{10}H_{18}/C_9H_{14}O$, 12), 137 ($C_{10}H_{17}/C_9H_{13}O$, 33), 136 ($C_{10}H_{16}$, 18), 135 ($C_{10}H_{15}$, 16), 134 ($C_{10}H_{14}$, 8), 133 ($C_{10}H_{13}$, 14), 131 (C_{10} H_{11}, 7), 125 ($C_9H_{17}/C_8H_{13}O$, 13), 124 ($C_9H_{16}/C_8H_{12}O$, 15), 123 ($C_9H_{15}/C_8H_{11}O$, 34), 122 (C_9H_{14}, 18), 121 (C_9H_{13}, 29), 120 (C_9H_{12}, 10), 119 (C_9H_{11}, 20), 111 ($C_8H_{15}/C_7H_{11}O$, 15), 110 (C_8H_{14}, 10), 109 (C_8H_{13}/C_7H_9O, 40), 108 (C_8H_{12}, 14), 107 (C_8H_{11}, 27), 106 (C_8H_{10}, 9), 105 (C_8H_9, 20), 97 (C_7H_{13}/C_6H_9O, 24), 96 (C_7H_{12}, 17), 95 (C_7H_{11}/C_6H_7O, 60), 93 (C_7H_9, 30), 91 (C_7H_7, 27), 83 (C_6H_{11}/C_5H_7O, 31), 82 (C_6H_{10}, 22), 81 (C_6H_9, 56), 79 (C_6H_7, 27), 77 (C_6H_5, 18), 71 (C_5H_{11}/C_4H_7O, 28), 69 (C_5H_9/C_4H_5O, 52), 67 (C_5H_7, 37), 56 (45), 55 (51), 43 ($MeCO^+$, 100), 41 (64). Found: M^+ *m/e* 262.2276. Required for $C_{18}H_{30}O$: M^+ *m/e* 262.2296.

9,10-*Secoabieta*-8,11,13-*trien*-18,10-*olide*. The structure of this compound was proposed earlier [58].

4-*Stigmasten*-3-*one*. Mp 77–77.5°; λ_{max}^{EtOH} nm (ε): 242 (15 000). Reported: mp 90° [59]; λ_{max}^{EtOH} nm (ε): 241 (16 400) [26]. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical with authentic sample. The GLC showed this material contained ~6% 4-campesten-3-one. The UV also contained λ_{max}^{EtOH} 285 nm (ε 1620) probably due to 4,6-stigmastadien-3-one, an impurity expected from autooxidation.

3,5-*Stigmastadien*-7-*one*. Mp and mmp 106–107°, $[\alpha]_D^{22} -$ 304°. Reported: mp 106–107° [60], $[\alpha]_D - 288°$ [61]. TLC (Si gel), GLC (SE-30), UV, IR, ^1H NMR identical to authentic samples (R. A. Abramovitch).

4,6-*Stigmastadien*-3-*one*. Isolated material was distilled at 210°/0.002 mmHg to give a semisolid: $[\alpha]_D^{25} + 43°$. λ_{max}^{EtOH} nm (ε): 284 (21 400). The material was identical to authentic 4,6-stigmastadien-3-one by TLC (Si gel), IR, UV, and ^1H NMR. GLC (SE-30) showed the material consisted of 4,6-stigmastadien-3-one (90%), 4,6-campestadien-3-one (10%), and 4,6-cholestadien-3-one (**8**) (trace). The authentic sample of 4,6-stigmastadien-3-one was prepared by a method analogous to that reported for the preparation of 4,6-cholestadien-3-one [62]. A mixture of 4-stigmasten-3-one (100 mg) and tetrachloro-1,4-benzoquinone (180 mg) in 10 ml *t*-BuOH was refluxed for 3 hr with stirring. After cooling the residual tetrachloro-1,4-benzoquinone was removed by filtration. Filtrate was evapd to dryness and dissolved in $CHCl_3$. The $CHCl_3$ extract was washed with H_2O, 1 N NaOH, and H_2O and then evapd to dryness. Residue (125 mg) was chromatographed over Si gel. Benzene-eluted chromatographically pure (TLC–Si gel) 4,6-stigmastadien-3-one (27 mg) that was distilled at 210°/0.002 mmHg: mp 66–70°, $[\alpha]_D^{21} + 33°$. λ_{max}^{EtOH}, nm (ε): 284 (26 130). ^1H NMR, δ: 0.76 (3H, *s*, C-18 Me), 0.84 (6H, *d*, $J = 7$ Hz, isopropyl Me_2), 0.90 (3H, *t*, $J = 5$ Hz, CH_2—CH_3), 0.93 (3H, *d*, $J = 6$ Hz, C-21 Me), 1.12 (3H, *s*, C-19 Me), 2.45 (2H, *m*, CH_2—C=O), 2.58 (1H, *m*, $CH(Me)_2$), 5.90 (2H, *d*, $J = 27$ Hz, *cis* HC=CH), and 6.13 (1H, *s*, C-4 H). ν_{max}^{film} cm^{-1}: 3040, 1670 (conj. C=O); 1620, 1588, and 875 (conj. diene).

24-*Methylenecycloartanol*. TLC (Si gel and alumina–$AgNO_3$), GLC(SE-30), IR, and ^1H NMR identical to authentic sample (G. Ourisson).

3β-*Methoxy*-5α-*lanost*-9(11)-*ene*-24S,25-*diol and* 5α-*lanost*-9(11)-*en*-3β,24S,25-*triol*. Isolation and characterization of these lanostanes was reported earlier [63].

Serratenediol. Mp 302–305°, $[\alpha]_D^{21} - 19°$ (*c* 0.7). Reported [16]: mp 302.5–304.5°, $[\alpha]_D^{22} - 19°$ (*c* 0.9). TLC (Si gel), GLC (SE-30), IR identical to an authentic sample [16].

21-*Episerratenediol*. Mp and mmp 296–298°. Reported [16]: mp 303–308°. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical to an authentic sample [16].

3,21-*Diepiserratenediol*. Mp 287–291°. Reported [16]: mp 300–301°. TLC (Si gel) identical to authentic sample [16]. Acetylation (Py–Ac_2O) give the diacetate: mp 240–244°, $[\alpha]_D^{25} - 67°$. Reported [64]: mp 240–242°. TLC (Si gel), IR, and ^1H MNR identical to authentic 3,21-diepiserratenediol diacetate [64].

Serratenediol 3-*methyl ether*. Mp and mmp 319–321°, $[\alpha]_D^{21} - 4°$ (*c* 0.7). Reported [18]: mp 319–322.5°, $[\alpha]_D - 5°$. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical to authentic sample [18]. Acetylation (Py–Ac_2O) gave serratenediol 3-methyl ether monoacetate: mp 320.5–321°. ν_{max}^{KBr} cm^{-1}: 1738 (C=O), and 1247 (—CO—O). ^1H NMR: δ 0.70 (3H, *s*, Me), 0.76 (3H, *s*, Me), 0.845 (3H, *s*, Me), 0.91 (3H, *s*, Me), 0.96 (3H, *s*, Me), 2.06 (3H, *s*, O—CO—CH_3), 2.56 (1H, *br m*, —CH_{ax}—OMe), 3.34 (3H, *s*, equatorial OCH_3), 4.54 (1H, *br m*, —CH_{ax}—OAc), and 5.35 (1H, *br s*, olefinic H). (Found: C, 79.16; H, 10.74. Required for $C_{33}H_{54}O_3$: C, 79.46; H, 10.92%).

21-*Episerratenediol* 3-*methyl ether*. Mp and mmp 320.5–322.5°. Reported [65]: 307.5–308°. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical with authentic compound [65].

Serratenediol dimethyl ether. Mp and mmp 321.5–322.5°. Reported [18]: mp 320.5–323.5°. TLC (Si gel), GLC (SE-30), IR ^1H NMR identical with authentic compound [18].

21-*Episerratenediol dimethyl ether*. Mp 298–300°, $[\alpha]_D^{18} -$ 22°. Reported [65]: mp 277–278°, $[\alpha]_D - 16.4°$. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical with authentic sample [65].

21-*Episerratenediol* 21-*methyl ether*. Mp and mmp 250.5–251.5°, $[\alpha]_D^{22} - 44.5°$ (*c* 0.8). Reported [66]: mp 250.5–252°, $[\alpha]_D^{21} - 43.5°$. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical with authentic sample [66].

3β-*Hydroxy*-14-*serraten*-21-*one*. Mp 268.5–270°. Reported [18]: mp 268–268.5°. TLC (Si gel), IR, ^1H NMR identical with authentic sample [18].

3β-*Methoxy*-14-*serraten*-21-*one*. Mp and mmp 272.5–273°, $[\alpha]_D^{23} - 29°$. Reported [18]: mp 267–270°, $[\alpha]_D^{23} - 29°$. TLC (Si gel), GLC (SE-30), IR, ^1H NMR identical with authentic sample [18].

3α-*Hydroxy*-14-*serraten*-21-*one* (**9**). This compound was isolated as its acetyl derivative which was crystallized alternately from CH_2Cl_2–hexane and CH_2Cl_2–MeOH to constant

mp 251–253°, $[\alpha]_D^{25}$ −67° (*c* 0.6). ν_{max}^{KBr} cm^{-1}: 1735 (acetyl); 1712 (C=O); 1250 (C—O); 1630 and 800 (C=C). ^1H NMR, δ: 0.85 (3H, *s*, Me), 0.89 (3H, *s*, Me), 0.94 (3H, *s*, Me), 1.06 (3H, *s*, Me), 1.10 (3H, *s*, Me), 2.08 (3H, *s*, $OCOCH_3$), 4.65 (1H, sharp *t*, CH_{eq}–OAc), 5.41 (C=CH). CD (*c* 0.002, $CHCl_3$): $[\theta]_{299}$ −3000. 3α-Acetoxy-14-serraten-21-one (33 mg) was dissolved in C_6H_6 (2 ml) and saponified with 1.5 N methanolic NaOH at room temp. for 3 days. Extraction of the reaction mixture with Et_2O in the usual manner gave 3α-hydroxy-14-serraten-21-one (30 mg). 3α-Hydroxy-14-serraten-21-one was dissolved in Me_2CO (30 ml). The soln was cooled to 0° (ice bath) and Jones' reagent (~0.1 ml) [67] added with stirring under N_2. After 8 min, excess MeOH was added to destroy the reagent. Extraction with Et_2O in the usual manner gave impure serratenedione (33 mg). Chromatography over Si gel gave chromatographically pure serratenedione that was crystallized (CH_2Cl_2–hexane): mp 210.5–212°, $[\alpha]_D^{25}$ −3°. Reported: mp 211.5–212°, $[\alpha]_D^{21}$ −6.5° [16]; and mp 209–210° [17]. This material was identical to authentic serratenedione by mmp, TLC (Si gel), GLC (SE-30), IR, and ^1H NMR.

3β,21β-Dihydroxy-14-serraten-16-one (16-oxoepiserratenediol). This compound was isolated as its diacetate: mp 237–238°, $[\alpha]_D^{24}$ +2° (*c* 0.8), λ_{max}^{EtOH} nm (ε): 245 (12 000). Reported [68]: mp 242–245°, λ_{max} nm (ε): 245 (13 000). TLC (Si gel), IR, ^1H NMR identical with authentic sample [68].

Compound A. Impure compound A was acetylated with Py–Ac_2O at room temp. for 36 hr. The reaction product was isolated in the usual manner and purified by column chromatography on Si gel. C_6H_6–Et_2O (98:2) eluted compound A diacetate: mp 237–239° (CH_2Cl_2–hexane). ^1H NMR :δ 0.69 (3H, *s*, Me), 0.73 (3H, *s*, Me), 0.79 (3H, *s*, Me), 0.81 (3H, *s*, Me), 0.93 (3H, *s*, Me), 0.96 (3H, *s*, Me), 2.05 (6H, *s*, 2 OAc), 2.6 (1H, *br m*, CHOMe), 3.31 (3H, *s*, OMe), 4.29 [2H, AB *dd* (δ_A = 4.15, δ_B = 4.43; *J* = 12 Hz), CH_2OAc], 4.57 (1H, *br t*, CHOAc), and 5.29 (1H, *m*, C=CH). M^+ *m/e* 556 ($C_{35}H_{56}O_5$).

Compound B. Impure compound B was acetylated with Py–Ac_2O at room temp. for 36 hr in the usual manner. The reaction product was crystallized (3×) from C_6H_6–hexane: mp 237–239°, $[\alpha]_D^{24}$ +44°. ν_{max}^{KBr} cm^{-1}: 1745 and 1245 (OAC), 1635 and 790 (C=CH). ^1H NMR :δ 0.73 (3H, *s*, Me), 0.77 (3H, *s*, Me), 0.83 (3H, *s*, Me), 0.86 (3H, *s*, Me), 0.90 (3H, *s*, Me), 0.97 (3H, *s*, Me), 2.025 (3H, *s*, OAc), 2.06 (3H, *s*, OAc), 2.65 (1H, *br m*, CHOMe), 3.35 (3H, *s*, OMe), 3.8 [2H, AB *dd* (δ_A = 3.53, δ_B = 3.83; *J* = 12 Hz), CH_2OAc], 4.75 (1H, *br t*, CHOAc), and 5.31 (1H, *m*, C=CH). Found: C, 75.13; H, 10.20%. Calc. for $C_{35}H_{56}O_5$: C, 75.49; H, 10.14%. M^+ *m/e* 556 ($C_{35}H_{56}O_5$).

Compound C. Impure compound C was acetylated with Py–Ac_2O at room temp. for 60 hr in the usual manner. The resulting diacetate was purified by chromatography over Si gel. C_6H_6–Et_2O (98 : 2) eluted chromatographically pure compound C diacetate: mp 241–242° (CH_2Cl_2–hexane, 3×), $[\alpha]_D^{22}$ −30°. ν_{max}^{KBr} cm^{-1}: 1745 and 1245 (OAc), 1640 and 790 (C=CH). ^1H NMR :δ 0.71 (3H, *s*, Me), 0.76 (3H, *s*, Me), 0.83 (3H, *s*, Me), 0.87 (3H, *s*, Me), 0.96 (6H, *s*, 2 Me), 2.05 (3H, *s*, OAc), 2.08 (3H, *s*, OAc), 2.6 (1H, *br m*, CHOMe), 3.35 (3H, *s*, OMe), 4.18 [2H, AB *dd* (δ_A = 4.11, δ_B = 4.25; *J* = 12 Hz), CH_2OAc], 5.04 (1H, *t*, CHOAc), and 5.34 (1H, *m*, C=CH). (Found: C, 75.72; H, 10.03. Calc. for $C_{35}H_{56}O_5$: C, 75.49; H, 10.14%). M^+ *m/e* 556 ($C_{35}H_{56}O_5$).

Compound D. Chromatographically pure compound D was isolated as its diacetate that was crystallized alternately from CH_2Cl_2–MeOH and CH_2Cl_2–hexane to constant mp 299–303°, $[\alpha]_D^{21}$ +20° (*c* 0.4). ^1H NMR (100 MHz) :δ [0.76, 0.85, 0.89, 0.96 (18H, 6 Me)], 2.05 (6H, *s*, 2 OAc), 4.3–4.7 (2H, *br m*, 2 CHOAc), 9.53 (1H, *d*, *J* = 2 Hz, CHO). ν_{max}^{KBr} cm^{-1}: 2720 (CHO), 1731 *br* (C=O), 1250 (OAc).

Compound E. Chromatographically pure (TLC: Si gel) compound E was obtained after sublimation at 250°/0.02 mmHg: mp 326–327.5°, $[\alpha]_D^{24}$ +24.5°. ^1H NMR :δ [0.70, 0.73, 0.75, 0.83, 0.88, and 0.95 (6 or 7 Me)], 2.6 (1H, *br m*, CH_{ax}–OMe), 3.39 (3H, *s*, OMe) and 9.5 (1H, *s*, CHO). $\nu_{max}^{CCl_4}$ cm^{-1}: 3626 (secondary equatorial OH). ν_{max}^{KBr} cm^{-1}: 3468 (OH), 2720 (CHO), 1725 (C=O). Compound E was acetylated (Py–Ac_2O and the resulting acetate isolated by column chromatography (Si gel). The chromatographically pure (TLC: Si gel and Si gel–$AgNO_3$) acetate was crystallized alternately from CH_2Cl_2–MeOH and MeOH–hexane to constant mp 277–278.5°, $[\alpha]_D^{22}$ +38° (*c* 0.7). ^1H NMR (100 MHz) :δ [0.70, 0.73, 0.77, 0.80, 0.89, 0.90, and 0.95 (6 or 7 Me)], 2.01 (3H, *s*, OAc), ~2.5 (1H, *m*, CHOMe), 3.35 (3H, *s*, OMe), 4.45 (1H, *br m*, CHOAc), 9.5 (1H, *s*, CHO). ν_{max}^{KBr} cm^{-1}: 2700 and 1729 (CHO); 1740 and 1248 (OAc). M^+ *m/e* 514 ($C_{33}H_{54}O_4$).

Compound F. The acetate of compound F isolated by chromatography was crystallized from CH_2Cl_2–hexane and then CH_2Cl_2–MeOH: mp 238–244°. ν_{max}^{KBr} cm^{-1}: 1740 and 1250 (OAc). ^1H NMR, :δ 0.73 (3H, *s*, Me), 0.84 (12H, *br s*, 4 Me), 0.93 (3H, *s*, Me), 0.97 (3H, *s*, Me), 2.05 (6H, *s*, 2 OAc), 2.10 (3H, *s*, OAc), ~4.34 (1H, *br m*, CHOAc), ~4.50 (1H, *br m*, CHOAc), 4.72 (1H, *t*, CHOAc), 6.05 (1H, *m*, C=CH —CHOAc).

Compound G. The compound isolated by chromatography had mp 264–266° (dec) $[\alpha]_D^{25}$ −20° (*c* 0.3). $\nu_{max}^{CCl_4}$, cm^{-1}: 3520 (secondary equatorial OH). ν_{max}^{KBr} cm^{-1}: 3540 (OH) and 1630 (C=CH). ^1H NMR :δ [0.71, 0.72, 0.80, 0.85, 0.95 (6–7 Me)], ~2.7 (2H, *br m*, 2 CHOMe), 3.22 (1H, CH_{eq}—OH), 3.35 (3H, *s*, OMe), 3.36 (3H, *s*, OMe) and 5.3 (1H, *m*, C=CH).

Compound H. The chromatographically pure material [TLC(SiO_2, $AgNO_3$–SiO_2): GLC(SE-30, QF-1)] had mp 277–278.5°, $[\alpha]_D^{22}$ −0.6°. ^1H NMR :δ 0.76 (3H, *s*, Me), 0.81 (3H, *s*, Me), 0.83 (3H, *s*, Me), 0.90 (3H, *s*, Me), 0.91 (3H, *s*, Me), 0.96 (3H, *s*, Me), 1.03 (3H, *s*, Me), ~2.70 (1H, *br m*, CH_{ax} OMe), 3.34 (3H, *s*, OMe), and 5.36 (1H, *m*, C=CH). ν_{max}^{KBr} cm^{-1}: 1710 (C=O), 1630 and 797 (C=CH), and 1100 (C—O—C). CD: $[\theta]_{286}$ +5165 (*c* 0.1, $CHCl_3$). (Found: C, 81.94; H, 11.26. Calc. for $C_{31}H_{50}O_2$: C, 81.88; H, 11.08%).

Acknowledgements—The authors thank the following for samples of authentic reference compounds: R. A. Abramovitch (3,5-stigmastadien-7-one), A. W. Burgstahler (18-nordehydroabietol), W. G. Dauben ((−)-torreyol), S. Dev (cadalene), P. K. Grant (18-norisopimaradienol), O. Jeger (15,16-dinorlabd-8(17)-en-13-one), G. Ourisson (24-methylenecycloartanol), Y. Tsuda (16-oxoepiserratenediol), E. Wenkert ((+)-dehydroabietane), and C. A. West (NMR of (+)-sandaracopimaradiene), and Firmenich *et Cie*, Geneva (8α,13*S*:13,17-diepoxy-15,16-dinorlabdane and 8β,13*R*: 13,17-diepoxy-15,16-dinorlabdane). MS were obtained by the High Resolution Mass Spectrometry Laboratory, Department of Chemistry, Florida State University. The authors thank J. K. Toda, E. (Dewey) Spalding, and M. A. (Lintner) Turnbow for their technical assistance. This article was written and prepared by U.S. Government employees on official time, and it is therefore in the public domain.

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