the steam bath for 1 hr. The reaction mixture was acidified with concentrated hydrochloric acid and extracted with four portions of ether. The extracts were dried, the solvent was removed, and the residual acid was converted to the methyl ester with diazomethane. Glc analysis indicated that there were two components present in the mixture in a ratio 3:1 (A:B). The retention time of the major component was the same as that of the starting acid, while that of the minor component was the same as that of the isomer present in intermediate amount in the original reaction mixture.

B.—Keto acid **10** was converted to the methyl ester with diazomethane and 0.010 g was heated at reflux for 16 hr in 2.0 ml of methanolic sodium methoxide. The methanol was removed, 5 ml of water was added, and the solution was acidified (pH 1) with conentrated hydrochloric acid. The turbid solution was extracted with ether, the extracts were dried over magnesium sulfate, and the solvent was removed to give 0.005 g (50%) of a mixture of esters. Glc analysis indicated that there were two components present in a ratio 3:5 (A:D). The retention time of the minor component was the same as that of the starting ester, while the major product was a new ester of longer retention time. The infrared spectrum of this mixture showed absorption at 5.75 and 5.83 μ while the nmr showed two singlets, at δ 0.81 and 0.91, of relative intensities of *ca.* 2.2:1.

4aβ-Methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronaphthalene-2α-carboxylic Acid (13).—To a solution of methylene triphenylphosphorane, from 4.40 g of methyltriphenylphosphonium bromide in 45 ml of dimethyl sulfoxide, was added 0.500 g of the mixture of isomeric acids, A, B, and C, described above in 10 ml of dimethyl sulfoxide. The deep orange solution was stirred and heated at 62–65° for 36 hr. After cooling to room temperature, the reaction mixture was poured into water, and the basic solution was brought to pH 1 with concentrated hydrochloric acid and extracted with ether. The extracts were washed with water and dried, and the solvent was removed under reduced pressure at steam bath temperature, leaving 2 g of a yellow oil. The oil was dissolved in anhydrous ether–hexane and filtered through a column of silica gel. Elution with hexane gave in the first fraction 0.030 g of a colorless oil which was not characterized. Elution with hexane–anhydrous ether (1:1) gave 0.415 g of yellow oil (84%) which crystallized on standing. Analysis by glc of the methyl ester of this material showed that it consisted of 40% of the desired acid (**12**), and 60% of a mixture of two other compounds in a ratio of *ca.* 6:1. Recrystallization from hexane gave the 2α-acid, **13**, as white crystals: mp 123–125°; ir 5.87, 6.06, and 11.29 μ; nmr δ 0.75 (s, 3 H), 1.27–2.50 (envelope, 13 H), 2.85 (m, 1 H), 4.46 (br s, 1H), 4.76 (br s, 1 H).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.18; H, 9.76.

When the Wittig reaction was carried out as described above utilizing the methyl esters instead of the mixed acids, a similar mixture of compounds was obtained.

4aβ-Methyl-8-methylene-1,2,3,4,4a,5,6,7,8,8aα-decahydronapthalene-2β-carboxylic Acid (12).—An ethereal solution of 0.150 g of the mixture of stereoisomeric methylene acids described above was treated with diazomethane for 15 min. The ether was evaporated and the resulting oil was heated at reflux for 2 hr with 1 ml of methanol containing 0.108 g of sodium methoxide and protected from atmospheric moisture. The methanol was removed under reduced pressure at steam bath temperature, water was added, and the solution was heated on the steam bath under nitrogen for 1 hr. After cooling to room temperature and acidifying to pH 1 with concentrated hydrochloric acid, the reaction mixture was extracted with ether. The extracts were washed once with water, dried, and filtered and the solvent was removed under reduced pressure, leaving 0.135 g (90%) of yellow oil which crystallized on standing. Crystallization of the acid from hexane at −10° afforded 0.067 g of tan crystals, mp 107–114°. Recrystallization from the same solvent gave 0.054 g of off-white crystals, mp change in crystalline from 95–117°, mp 117.5–118.5°; mmp with an authentic sample,[2b,9] change in crystalline from 95–115°, mp 115–117°. The infrared spectrum was identical with that of the authentic sample, as was the glc retention time of the methyl esters: nmr δ 0.75 (s, 3 H), 1.02–2.67 (envelope, 14 H), 4.47 (br s, 1 H), 4.73 (br s, 1 H) [lit. (in CCl_4) δ 0.75, 4.52, 4.78[2b]].

Registry No.—**3**, 32178-64-6; **3** methyl ester 2,4-DNP, 32298-25-2; **4**, 16035-97-5; **5**, 32178-63-5; **6**, 32298-28-5; **7**, 32298-80-9; **7** methyl ester 2,4-DNP, 32298-29-6; **8**, 32367-43-4; **10**, 32298-30-9; **12**, 32298-31-0; **13**, 32179-13-8; *o*-methoxybenzylidenesuccinic acid, 24289-96-1; *o*-methoxybenzylsuccinic acid, 32298-34-3; *o*-methoxybenzylsuccinic anhydride, 32298-35-4.

Studies on Resin Acids. VII. Isomerization of 19-Norabietatetraenes[1]

J. W. HUFFMAN

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

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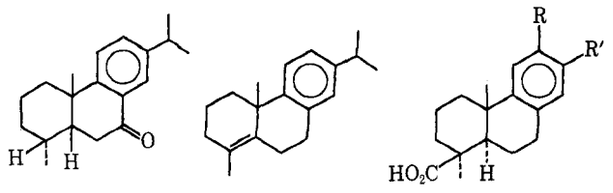
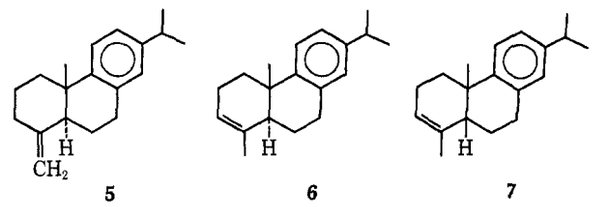
The composition of the mixture of olefins obtained by lead tetraacetate decarboxylation of 4-epidehydroabietic acid (**4**) has been found to be very nearly the same as that obtained from dehydroabietic acid. Acid-catalyzed isomerization of this mixture of olefins leads to a mixture of 19-norabieta-4,8,11,13-tetraene (**2**) and 19-nor-5β-abieta-3,8,11,13-tetraene (**7**), in which the latter predominates. Hydroboration–oxidation of **7** gives 18-nor-5β-abieta-8,11,13-trien-3α-ol (**9**), which on oxidation affords the corresponding ketone **14**. The course of the isomerization of the olefin mixture is discussed.

In the course of the hydroboration–oxidation of the mixture of olefins obtained by lead tetraacetate decarboxylation of dehydroabietic acid, there was obtained, among other products, 19-norabieta-8,11,13-trien-7-one (**1**).[2] It was suggested that this ketone was probably derived from 19-norabieta-4,8,11,13-tetraene (**2**), but this was not confirmed[2] and in an effort to gain additional information concerning the origin of **1**, a convenient source of olefin **2** was sought. Although **2** has been isolated from the decarboxylation mixture by chromatography,[3] this substance constitutes less than 30% of that mixture.[2,3] Since it had been reported that lead tetraacetate decarboxylation of podocarpic acid methyl ether (**3**) gives a mixture of olefins which contains 63% of the analog of **2**,[4] this reaction was carried out on 4-epidehydroabietic acid (**4**).[1] This procedure gave, however, a mixture of 32% of **2**, 41% of 19-norabieta-4(18),8,11,13-tetraene (**5**), and 27% of 19-norabieta-3,8,11,13-tetraene (**6**). Repetition of the decarboxylation in the podocarpic acid series gave, in contrast to the original report,[4,5] a mixture containing 32% of the analog of **2** and 38 and 25% of the analogs of **5**

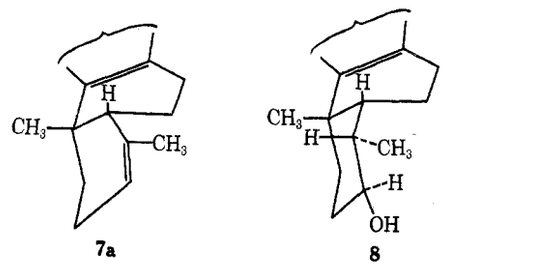
(1) Part VI: J. W. Huffman, *J. Org. Chem.*, **35**, 3154 (1970).
(2) J. W. Huffman, *ibid.*, **35**, 478 (1970).
(3) C. R. Bennett, R. C. Cambie, R. A. Franich, and T. J. Fullerton, *Aust. J. Chem.*, **22**, 1711 (1969).
(4) C. R. Bennett and R. C. Cambie, *Tetrahedron*, **23**, 927 (1967).
(5) R. C. Cambie and W. A. Denny, *Aust. J. Chem.*, **22**, 1699 (1969), subsequently reported similar data, correcting their original report (ref 4).



1 2 3, R = OCH_3; R′ = H
4, R = H; R′ = $CH(CH_3)_2$



5 6 7

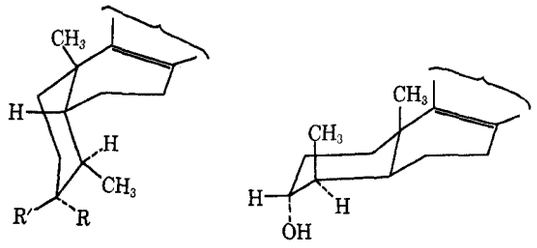


7a 8

and **6**, respectively. The decarboxylation of dehydroabietic acid gives a mixture of **2**, **5**, and **6** in relative percentages of 27, 40, and 33,[2] and on the basis of Cambie's original data[4] and the obvious difference between them and these results, it was suggested that the lead tetraacetate decarboxylations proceed *via* a hot carbonium ion.[2] However, since it is apparent that very nearly the same percentages of isomeric olefins are obtained in these decarboxylations regardless of the stereochemistry at C-4, it seems probable that the reactions are proceeding by way of a classical, open carbonium ion.

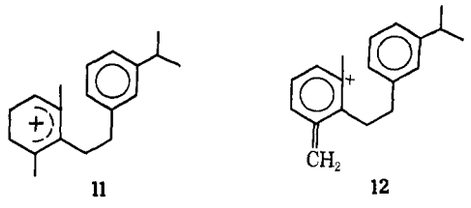
It has been reported that the acid-catalyzed isomerization of the 19-norpodocarpatetraene mixture gives a 2:1 mixture of the 4- and 3-enes[5] and by analogy it was assumed that similar treatment of the norabietatetraenes[2,6a] would give a mixture rich in **2**, which would be amenable to either chemical or chromatographic separation techniques. The use of Cambie's conditions (*p*-toluenesulfonic acid–dioxane) gave little evidence of isomerization, and repetition of Cambie's isomerization of the norpodocarpatetraenes failed to give the reported results.[5] When the mixture of olefins from dehydroabietic acid was heated with *p*-toluenesulfonic acid in toluene there was obtained a mixture which contained from 30 to 50% of **2** with the balance of the mixture being an olefin which was different from either **5** or **6**. Attempted separation by silver nitrate–silica gel chromatography failed; however, selective epoxidation of **2**[5] or preparative glc gave a pure sample of the new compound. The mass spectrum of this material indicated that it was isomeric with **2**, **5**, and **6** (M^+ 254),[6b] and the nmr spectrum showed a vinyl proton signal at δ 5.33, a broadened singlet due to a vinyl methyl at δ 1.71, and an angular methyl signal at δ 1.27. The only structure consistent with these data is 19-nor-5β-abieta-3,8,11,13-tetraene (**7**), in which A and B rings have adopted a nonsteroidal conformation (**7a**).[7] Treatment of the norpodocarpatetraene mixture under similar conditions gives similar results.

In order to gain additional insight into the structure of **7**, and in particular its mode of formation, a mixture of **2** and **7** which was rich in **7** was subjected to hydroboration–oxidation. The principal product was a secondary alcohol, $C_{19}H_{28}O$, which showed a moderately shielded C-10 methyl singlet in the nmr at δ 1.17 and a carbinol proton as a multiplet at δ 3.12. Since the signals for the benzylic protons partially overlapped that of the carbinol proton, the acetate was prepared and this showed a very broad signal ($W_{1/2}$ = 23 Hz) at δ 4.50. The width of this signal indicates that proton is axial, and the vicinal coupling constant for the secondary methyl is 5 Hz, indicating that H-4 is also axial, with the secondary methyl group equatorial.[8a] Although both the nonsteroidal conformer of 19-nor-5β-abieta-8,11,13-trien-3β-ol (**8**) and the steroidal conformer of 18-nor-5β-abieta-8,11,13-trien-3α-ol (**9**) would have the hydroxyl and secondary methyl group equatorial, the angular methyl signal is at the same frequency as that of 18-norabieta-8,11,13-trien-3α-ol (**10**).[2] This indicates that the methyl group in both compounds has the same spatial relationship to the aromatic ring and that the hydroboration product of olefin is the 3α-ol (**9**), resulting from α attack of diborane on **7**. Examination of a model of **7** indicates that in the nonsteroidal conformation β attack is hindered by the angular methyl group. In the steroidal conformer the convex β face of ring A is relatively unhindered while the concave α side of the olefin is shielded by rings B and C. The



9, R = OH; R′ = H
13, R = R′ = H
14, R = R′ = O

10



11 12

(6) (a) J. W. Huffman and P. G. Arapakos, *J. Org. Chem.*, **30**, 1604 (1965). (b) We would like to thank the Research Triangle Institute for Mass Spectrometry, Research Triangle Park, N. C., for carrying out this determination.

(7) In the 5α isomer of **7** (**6**), the angular methyl signal appears at δ 1.05 (ref 2). The only way to explain the rather profound deshielding of the angular methyl in **7** is by some change in the spatial relationship between the angular methyl group and the aromatic ring. The steroidal conformation of **7** would have the angular methyl and the aromatic ring in nearly the same relationship as in **6**, and consequently the angular methyl signal would not be expected to be significantly different from that of **6**.

(8) (a) F. Johnson, N. A. Starkousky, and W. D. Gurowitz, *J. Amer. Chem. Soc.*, **87**, 3492 (1965). (b) S. P. Acharya and H. C. Brown, *J. Org. Chem.*, **35**, 3874 (1970), have used a similar argument in discussing the conformation of thujopsene. These authors discuss in some detail the theoretical justification for this approach in probing the conformational preferences of mobile systems.

stereochemical course of the hydroboration reaction provides confirmatory evidence for the nonsteroidal conformation of **7**.[8b]

In contrast to the highly stereoselective hydroboration of **7**, catalytic hydrogenation gave a mixture of two hydrocarbons. The nmr spectrum of the major product showed the high-field methyl singlet (δ 1.18) associated with a steroidal conformation[8b] while the C-10 methyl signal for the minor component of the mixture appeared at δ 1.40, indicating a nonsteroidal conformation for rings A and B. On the basis of these data the major isomer is 18-nor-5β-abieta-8,11,13-triene (**13**), with an equatorial secondary methyl group, while the minor product is the C-4 epimer with an equatorial methyl and nonsteroidal conformation.

Although the isomerization of the mixture of **2**, **5**, and **6** is *a priori* a straightforward acid-catalyzed olefin isomerization proceeding through a carbonium ion at C-4, an alternative path involving rupture of the 9-10 bond, followed by the recyclization in a manner similar to that suggested by Wenkert for the dehydroabietonitrile–isodeoxypodocarponitrile reaction could not be excluded.[9] It should be noted, however, that if this mechanism were operative, the intermediate would be either a symmetrical allylic carbonium ion (**11**) or a tertiary homoallylic carbonium ion (**12**, or the isomeric ion corresponding to **6**). If the former course correctly represented the reaction path, the product olefins would be a racemic mixture and if the latter mechanism were operative, the products would be enantiomeric with the natural resin acids. Consequently, alcohol **9** was oxidized to the corresponding ketone (**13**) under conditions which preclude isomerization at C-4.[10] The ketone thus obtained showed a C-10 methyl signal in the nmr at relatively high field (δ 1.26) indicating a steroidal conformation for the molecule, and the relatively small value of the vicinal coupling constant for the secondary methyl protons (J = 6 Hz) indicates that this methyl group is equatorial.[7] The rotatory dispersion curve of **13** showed a negative Cotton effect curve (amplitude −12.7) as predicted by the octant rule for the steroidal conformer of 18-nor-5β-abieta-8,11,13-tetraen-3-one (**14**). The structure of **14** would thus seem to exclude a breaking of the 9–10 bond during the isomerization and tends to support a simple carbonium ion mechanism.

During the course of several different isomerizations of the mixture of olefins from dehydroabietic acid, it was found that the relative percentages of **2** and **7** were somewhat variable. In an effort to follow the course of the reaction one run was carried out and the composition of the reaction mixture was monitored at various intervals. Initially there is a rapid conversion of **5** and a somewhat less rapid conversion of **6** to **2**, followed by a rather slow conversion of **2** to a mixture of **2** and **7**. Although no effort was made to carry this reaction to completion, after 25 hr the isomerization mixture contains 61% of **7**, 37% of **2**, 2% of **6**, and a trace of **5** and traces of three other compounds. Following the completion of this work Whitlock reported isomerization data for the deisopropyl analog of **2**, using *p*-toluenesulfonic acid–acetic acid.[11] These authors observed nearly the same ratio of **2** to **7** that we observe; however, they also obtained nearly 20% of three other isomeric olefins. These differences in product composition can probably be attributed to solvent differences, which would ultimately amount to a counterion effect.[12] Whitlock has attempted to explain the differences in his solvolysis results and olefin isomerizations in terms of conformational effects;[11] however, our results seem to favor the alternative explanation.

A priori it appears rather unusual that the major product of the isomerization of **2**, **5**, and **6** should be a cis-fused, trisubstituted olefin (**7**); however, examination of models indicates that in **2**, **5**, and **6** there are rather severe steric interactions between C-18 and C-6, which are relieved by isomerization to **7**.

Experimental Section[13]

Decarboxylation of Dehydroabietic Acid.—This reaction was carried out as described previously.[2,6] Analysis by nmr and glc gave the following results: **5**, 40%; **6**, 33%; **2**, 27%. Canonica, *et al.*, report 37, 34, and 29%, respectively.[14]

Decarboxylation of 4-Epidehydroabietic Acid (**4**).—This reaction was carried out in the same manner as that of dehydroabietic acid; analysis by nmr showed 41% 19-norabieta-4(18),8,11,13-tetraene (**5**), 27% 19-norabieta-3,8,11,13-tetraene (**6**), and 32% 19-norabieta-4,8,11,13-tetraene (**2**). The olefins were isolated as described earlier.[2,6]

Decarboxylation of *o*-Methylpodocarpic Acid (**3**).—Decarboxylation of *o*-methylpodocarpic acid and the isolation of the olefins were carried out as described previously.[2,6] Analysis by nmr and glc gave the following results: 38% 12-methoxy-19-norpodocarpa-4(18),8,11,13-tetraene; 26% 12-methoxy-19-norpodocarpa-3,8,-11,13-tetraene, and 32% 12-methoxy-4,8,11,13-tetraene. Cambie reports 39, 33, and 28%, respectively, from this reaction.[5]

Isomerization of 19-Norabietatetraenes.—To a solution of 5.24 g of the mixture of **2**, **5**, and **6** obtained from the lead tetraacetate decarboxylation of dehydroabietic acid in 250 ml of toluene was added 0.45 g of *p*-toluenesulfonic acid and the mixture was heated at reflux 5 hr and then allowed to stand for 24 hr at room temperature. The precipitated toluenesulfonic acid was filtered off, the toluene was removed at reduced pressure, and the residue was taken up in hexane. The hexane solution was washed with 5% aqueous sodium hydroxide and water, dried, concentrated to a small volume, and filtered through a column of Merck acid-washed alumina. Elution with hexane gave 4.85 g (93%) of a mixture containing 63% of 19-norabieta-4,8,11,13-tetraene (**2**) and 37% of 19-nor-5β-abieta-3,8,11,13-tetraene (**7**), plus traces of other isomers. Attempted separation by chromatography on silver nitrate–silica gel[15] was unsuccessful, and the mixture was finally resolved by preparative glc to give pure (glc) **7** [nmr 1.27 (s, C-10 methyl), 1.71 (br s, C-4 methyl), 5.33 (m, H-3)] and pure (glc) **2**.

In one run, carried out as described above, aliquots were withdrawn at intervals and the course of the reaction was monitored by glc (Table I).

Isomerization of 12-Methoxy-19-norpodocarpatetraenes. A.—A solution of 1.00 g of the mixture of olefins from *o*-methylpodocarpic acid in 50 ml of toluene containing 0.10 g of *p*-toluenesulfonic acid was heated at reflux for 4 hr and allowed to stand at room temperature for 18 hr. The product was isolated as de-

(9) E. Wenkert and B. G. Jackson, *J. Amer. Chem. Soc.*, **80**, 211 (1958).

(10) (a) E. J. Corey and R. A. Sneen, *ibid.*, **78**, 6269 (1969); (b) J. W. Huffman, J. A. Alford, and R. R. Sobti, *J. Org. Chem.*, **35**, 473 (1970).

(11) H. W. Whitlock, Jr., and L. E. Overman, *J. Amer. Chem. Soc.*, **93**, 2247 (1971).

(12) D. J. Cram and M. R. V. Sahyun, *ibid.*, **85**, 1257 (1963).

(13) Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were taken as films or potasium bromide pellets on a Perkin-Elmer Model 137 spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian Associates Model A-60 spectrometer using deuteriochloroform as a solvent and tetramethylsilane as an internal standard. Signals are reported in parts per million relative to this standard (δ). Optical rotatory dispersion curves were determined in methanol using a Jasco ORD/UV-5 spectropolarimeter. Analytical glc data were obtained using an F and M Model 810 chormatograph with 8 ft × 0.125 in. SE-30 on Chromosorb W or 10 ft × 0.125 in. OV-17 on Chromosorb W columns at temperatures of 225–240°.

(14) L. Canonica, B. Danieli, P. Manitto, and G. Russo, *Gazz. Chim. Ital.*, **98**, 699 (1968).

(15) T. Norin and L. Westfelt, *Acta Chem. Scand.*, **17**, 1828 (1963).

TABLE I
COURSE OF THE ISOMERIZATION OF 19-NORABIETATETRAENES

Time, hr	Compd, %			
	2	5	6	7
0	27	40	33	0
1	74	1	13	12
2	67	Trace	5	28
3	57	Trace	3	40
4	51	Trace	3	46
6	48	Trace	2	50
8	46	Trace	2	52
25	37	Trace	2	61

scribed above to give 0.493 g of a mixture which contained 54% 12-methoxy-19-nor-5β-podocarpa-3,8,11,13-tetraene [nmr δ 5.35 (m, H-4), 3.72 (OCH_3) (d, J = 1 Hz, C-4 methyl), and 1.28 (s, C-10 methyl)] and 46% 12-methoxy-19-norpodocarpa-4,8,11,13-tetraene [nmr δ 3.72 (s, OCH_3), 1.67 (br s, C-4 methyl), 1.37 (s, C-10 methyl)]. Cambie[4] reports signals at δ 3.68, 1.64, and 1.33 for this compound.

B.—The norpodocarpatetraene mixture was treated and the product was isolated as described by Cambie[5] to give a mixture which contained 36% 12-methoxy-19-norpodocarpa-4(18),8,11,-13-tetraene, 24% 12-methoxy-19-norpodocarpa-3,8,11,13-tetraene, and 40% 12-methoxy-4,8,11,13-tetraene.

Epoxidation of Isomerized Abietatetraenes.—To a solution of 2.84 g of a mixture of **2** (54%) and **7** (46%) in 125 ml of methylene chloride was added 1.41 g of *m*-chloroperbenzoic acid. The mixture was stirred at room temperature for 0.75 hr and then excess 10% aqueous sodium bisulfite was added. The organic layer was drawn off and washed with bisulfite solution and two portions of 10% aqueous sodium carbonate. After drying the solvent was removed to give 1.73 g of oil which was taken up in hexane and chromatographed on 80 g of Bio-Rad activity I neutral alumina. Elution with hexane gave 0.255 g of **7**, homogeneous by glc. Elution with hexane–benzene mixtures gave 0.599 g of a mixture of epoxides, which was not investigated further.

Hydroboration of Isomerized Abietatraenes.—To a solution of 2.89 g of the mixture of **2** and **7**, obtained as described above, in 25 ml of dry ether containing 1.00 g of lithium aluminum hydride and maintained at 0° was added dropwise a solution of 3.75 ml of boron trifluoride in 60 ml of ether. The reaction mixture was stirred for 2 hr at ambient temperature and sufficient ice was added to decompose the excess diborane. Saturated brine was added, the ethereal solution was decanted, and the aqueous phase was slurried with two portions of ether which were combined with the original organic phase. The ethereal solution was dried and the solvent was removed at reduced pressure with gentle warming. The residual alkylboranes were taken up in 120 ml of tetrahydrofuran to which was added 60 ml of 10% aqueous sodium hydroxide followed by 50 ml of 30% hydrogen peroxide. The reaction mixture was stirred at room temperature for 18 hr, and the aqueous layer was drawn off and extracted with two portions of ether. The combined organic layers were washed with water and dried and the solvent was removed to give 2.40 g of pale amber oil. Tlc (silica gel G, benzene–ethyl acetate, 8:1) indicated that the product was a mixture of at least three compounds with one predominating. On standing the oil partially crystallized and trituration with hexane gave 0.451 g of 18-nor-5β-abieta-8,11,13-trien-3α-ol (**9**). Recrystallization from hexane gave 0.350 g: mp 135–136°; nmr δ 1.11 (d, J = 5 Hz, C-4 methyl), 1.17 (s, C-10 methyl), and 3.12 (m, H-3).

The analytical sample, mp 138–139°, was crystallized from aqueous methanol.

Anal. Calcd for $C_{19}H_{28}O$: C, 83.77; H, 10.36. Found: C, 83.88; H, 10.25.

The acetate was prepared from 0.10 g of **9**. This material would not crystallize: mass spectrum M^+ 314; nmr δ 0.93 (d, J = 5 Hz, C-4 methyl), 1.18 (s, C-10 methyl), 1.95 (s, CH_3CO), 4.50 (m, $W_{1/2}$ = 23 Hz, H-3).

The hexane solution remaining from the isolation of **9** was chromatographed on 90 g of Merck acid-washed alumina. Elution with hexane gave 0.102 g of a mixture of hydrocarbons while benzene–methylene chloride mixtures gave 0.443 g of oil. Later benzene–methylene chloride fractions afforded an additional 0.954 g of **9**.

Hydrogenation of 19-Nor-5β-abieta-3,8,11,13-tetraene.—A solution of 0.152 g of **7** in 10 ml of ethanol containing 0.030 g of Adam's catalyst was hydrogenated at 50 psig. After filtering off the catalyst and removing the solvent there was obtained 0.108 g (71%) of nearly colorless oil. For characterization the product was taken up in hexane and filtered through a column of Bio-Rad neutral alumina. Glc indicated that the mixture contained 66% 18-nor-5β-abieta-8,11,13-triene (**13**) [nmr δ 0.92 (d, J = 5 Hz, C-4 methyl), 1.18 (s, C-10 methyl)] and 34% 19-nor-5β-abieta-8,11,13-triene [nmr δ 0.96 (d, J = 7 Hz, C-4 methyl), 1.40 (s, C-10 methyl)]; mass spectrum, M^+ 256.

18-Nor-5β-abieta-8,11,13-tetraen-3-one (14).—A solution of 0.20 g of **9** in 6 ml of benzene was added slowly with vigorous stirring to a chilled (5°) solution of 0.150 g of chromic acid and 1.50 g of sodium dichromate in 25 ml of acetic acid and 2 ml of water. The reaction was stirred at room temperature for 18 hr, the aqueous layer drawn off, the benzene solution washed thoroughly with water and dried, and the solvent removed to give 0.125 g (65%) of nearly colorless oil, which was homogeneous to tlc (silica gel G, benzene–hexane, 1:1): nmr δ 1.09 (d, J = 6 Hz, C-4 methyl), 1.26 (s, C-10 methyl); ORD $[\phi]_{400}$ +350°, $[\phi]_{302}$ −447°, $[\phi]_{294}$ 0°, $[\phi]_{282}$ +825°. For analysis **14** was converted to the 2,4-dinitrophenylhydrazone, mp 165–166°, from ethanol–ethyl acetate.

Anal. Calcd for $C_{25}H_{30}N_4O_4$: C, 66.65; H, 6.71; N, 12.44. Found: C, 66.86; H, 6.76; N, 12.58.

Registry No.—**2**, 23963-77-1; **5**, 22478-62-2; **6**, 22478-63-3; **7**, 32298-72-9; **9**, 32298-73-0; **9** acetate, 32298-74-1; **13**, 32298-75-2; **14**, 32298-76-3; **14** 2,4-dinitrophenylhydrazone, 32298-77-4; 12-methoxy-19-nor-5β-podocarpa-3,8,11,13-tetraene, 32298-78-5; 12-methoxy-19-nor-5β-podocarpa-4,8,11,13-tetraene, 32298-79-6; 19-nor-5β-abieta-8,11,13-triene, 32367-41-2.

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