mmol), *m*-cresol (30 ml), and pyrophosphoryl chloride (2 ml, 14.4 mmol) were treated as in the case of adenosine. The mixture (29,000 OD_{260} units) was applied to a column (2.5 × 12 cm) of Dowex 1-X8 (formate, 100–200 mesh). The column was washed with water (400 ml) and aristeromycin 6′-phosphate was eluted with 0.1 *N* formic acid (340 ml). The eluate (23,750 OD_{260} units) was evaporated to dryness under reduced pressure. To the residue was added ethanol to give a white powder (545 mg, 75% yield), mp 186–188° uncor. The product was homogeneous on paper electrophoresis [mobility, 0.89 relative to adenosine 5′-phosphate (1.0) in sodium borate (0.05 *M*, pH 9.2)] and on paper chromatography [R_f 0.74 in isobutyric acid–0.5 *N* aqueous ammonia (10:6)]: $\lambda_{max}^{0.1\ N\ HCl}$ 260.5 mμ (ε 14,500), $\lambda_{min}^{0.1\ N\ HCl}$ 234 mμ; $\lambda_{max}^{H_2O}$ 262 mμ (ε 14,800), $\lambda_{min}^{H_2O}$ 232 mμ; $\lambda_{max}^{0.1\ N\ NaOH}$ 263 mμ (ε 14,300), $\lambda_{min}^{0.1\ N\ NaOH}$ 228 mμ; $[\alpha]^{24}D$ −34.6° (*c* 1.0, water).

Anal. Calcd for $C_{11}H_{16}N_5O_6P\cdot H_2O$: C, 36.36; H, 4.99; N, 19.28; P, 8.54. Found: C, 36.30; H, 4.99; N, 18.87; P, 8.48.

9-β-D-Xylofuranosylhypoxanthine 5′-Phosphate and 9-β-D-Xylofuranosylhypoxanthine 3′,5′-Cyclic Phosphate.—To a suspension of 9-β-D-xylofuranosyladenine[35] (361 mg, 1.35 mmol) in acetonitrile (20 ml) was added pyrophosphoryl chloride (1.4 ml, 10 mmol) at 0–5°. The mixture was stirred for 2 hr at this temperature and then was poured into a mixture of ice and water (130 ml). The mixture was adjusted to pH 2 with sodium hydroxide and treated with activated charcoal (5 g) as described above. The eluate containing 5′-phosphate (34%) and 3′,5′-cyclic phosphate (66%) of 9-β-D-xylofuranosyladenine (examined by paper electrophoresis) was concentrated to dryness under reduced pressure. The residue was dissolved in 2 *N* acetic acid (100 ml) and was treated with sodium nitrite (8 g) at 37° for 40 hr. The mixture, after desalting by charcoal treatment (8 g), was concentrated and applied to a Dowex 1-X8 (chloride, 100–200 mesh) column (2 × 41 cm). The column was first washed with water (990 ml) and the nucleotides were then eluted successively with 0.003 *N* hydrochloric acid containing 0.02 *M* sodium chloride and 0.003 *N* hydrochloric acid containing 0.04 *M* sodium chloride.

The first fraction (2100 ml, 3990 OD_{250} units, 28% yield) was worked up as described for uridine. The barium salt of 9-β-D-xylo-furanosylhypoxanthine 5′-phosphate was obtained as a white powder (114 mg, 16% yield) which was homogeneous on paper electrophoresis [mobility, 0.90 relative to inosine 5′-phosphate (1.0) in sodium borate (0.05 *M*, pH 9.2)] and on paper chromatography [relative mobility 1.1 compared to inosine 5′-phosphate (1.0) in isobutyric acid–0.5 *N* aqueous ammonia (10:6)]: $\lambda_{max}^{0.1\ N\ HCl}$ 249 mμ (ε 10,500); $\lambda_{max}^{H_2O}$ 248.5 mμ (ε 11,400); $\lambda_{max}^{0.1\ N\ NaOH}$ 253.5 mμ (ε 11,800); $[\alpha]^{25}D$ −21.0° (*c* 0.5, water).

Anal. Calcd for $C_{10}H_{11}BaN_4O_8P\cdot 2H_2O$: N, 10.78; P, 5.97. Found: N, 10.88; P, 6.23.

The second fraction (3415 ml, 7370 OD_{250} units, 49% yield) was worked up as described above. The barium salt of 9-β-D-xylofuranosylhypoxanthine 3′,5′-cyclic phosphate was isolated as a white powder (180 mg, 31% yield) which was homogeneous on paper electrophoresis [mobility 0.69 relative to inosine 5′-phosphate (1.0) in sodium borate (0.05 *M*, pH 9.2)] and on paper chromatography [relative mobility 1.2 compared to inosine 5′-phosphate (1.0) in isobutyric acid–0.5 *N* aqueous ammonia (10:6)]: $\lambda_{max}^{0.1\ N\ HCl}$ 250 mμ (ε 11,100); $\lambda_{max}^{H_2O}$ 249 mμ (ε 11,100), $\lambda_{min}^{H_2O}$ 223 mμ; $\lambda_{max}^{0.1\ N\ NaOH}$ 254 mμ (ε 12,300), $\lambda_{min}^{0.1\ N\ NaOH}$ 231 mμ; $[\alpha]^{25}D$ −44.3° (*c* 1.0, water).

Anal. Calcd for $C_{10}H_{10}BaN_4O_7P\cdot 2H_2O$: C, 27.67; H, 3.25; N, 12.91; P, 7.15. Found: C, 27.33; H, 3.34; N, 12.63; P, 7.25.

Registry No.—Adenosine 5′-phosphate, 61-19-8; 6-thioinosine 5′-phosphate, 53-83-8; uridine 5′-phosphate, 58-97-9; aristeromycin 6′-phosphate, 19471-36-4; barium salt of 9-β-D-xylofuranosylhypoxanthine 5′-phosphate, 19458-99-2; barium salt of 9-β-D-xylofuranosylhypoxanthine 3′,5′-cyclic phosphate, 19459-00-8.

Acknowledgment.—We are grateful to Drs. Y. Abe, J. Manaka, and K. Tanaka, this division, for their encouragements throughout this work, to Dr. J. J. Fox, Sloan-Kettering Institute for Cancer Research, and to Dr. T. Ueda, Hokkaido University, for reviewing our manuscript. Thanks are also due to Dr. T. Kishi for his supply of aristeromycin, to Mr. M. Kan for elementary analysis, and to Miss K. Mimuro for physicochemical determinations.

(35) B. R. Baker and K. Hewson, *J. Org. Chem.*, **22**, 966 (1957).

Structure and Stereochemistry of Reduction Products of Abietic-Type Resin Acids[1]

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Received January 25, 1967

Products formed by catalytic hydrogenation of abietic, neoabietic, and levopimaric acid are correlated with those obtained by reduction with lithium in liquid ammonia. Structural and stereochemical assignments are presented for all known and several new dihydroabietic acids on the basis of hydroxylation–cleavage reactions, lactonization behavior, results on hydrogenation, and spectral data including nmr, far-uv, ORD, and CD measurements. A marked difference in the equilibrium position of the γ- and δ-lactones derived from 13α- and 13β-dihydroabietic acids is noted and used to define or confirm the configuration at C-13 in these acids. Newly characterized compounds include 9,5-friedoabietan-18:10-olide (**15b**) (13α-dihydroabietic γ-lactone) and the following acids: 7-abieten-18-oic (**7**), 8(14)-abieten-18-oic (**8**), 13-abieten-18-oic (**9**), 8-abieten-18-oic (**14**), 13(15)-abieten-18-oic (**27**), and 8,13(15)-abietadien-18-oic acid (**31**).

In connection with work on the synthesis[4] of the tricyclic diterpene hydrocarbon fichtelite (18-norabietane[5]), and as an extension of earlier studies[6] on the lithium–ethylamine reduction of dehydroabietic acid, we had occasion to investigate the structure and

(1) Based on the Ph.D. Thesis of J. N. M., The University of Kansas, Sept 1965, and revised from the presentation given before the Division of Organic Chemistry at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965 (Abstracts, p 17p; see Abstracts of Second Midwest Regional Meeting of the American Chemical Society, Lawrence, Kan., Oct 1966, p 46). Financial support for earlier portions of this work from the National Science Foundation (G-19936), from the University of Kansas Center for Research in Engineering Science (CRES-40B), and from the Alfred P. Sloan Foundation, is gratefully acknowledged.

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(3) Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

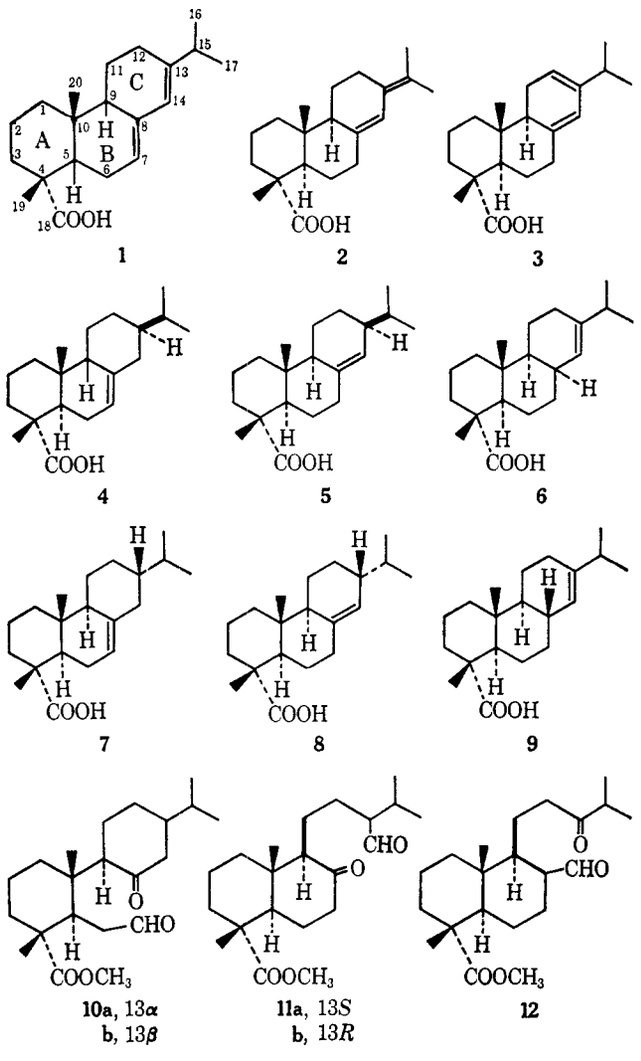
(4) (a) A. W. Burgstahler and J. N. Marx, *Tetrahedron Lett.*, 3333 (1964); *J. Org. Chem.*, **34**, 1562 (1969). (b) *Cf.* N. P. Jensen and W. S. Johnson, *ibid.*, **32**, 2045 (1967).

stereochemistry of products formed by reduction of abietic (**1**), neoabietic (**2**), and levopimaric (**3**) acid (Chart I). Other workers have shown that catalytic hydrogenation of these three resin acids yields various dihydro and tetrahydro acids, some of which are known to be mixtures.[7,8] Lithium–ammonia reduction of abietic acid has also been reported.[4,9]

Under neutral or basic conditions, partial catalytic hydrogenation of abietic acid would be expected to favor approach to the less hindered α side of the molecule to produce dihydro acids **4, 5,** and **6.** In fact, the two known dihydroabietic acids arising directly from such partial hydrogenation are **4** and **5.**[10–13] By contrast, lithium–ammonia reduction, with its preference for axial protonation,[14] would be expected to yield mainly acids **7, 8,** and **9.** In our work we have found that this reduction affords not only these three acids but also acid **5.** The major product is the 13α-8(14)-ene acid **8,** obtained previously in impure form by Royals and coworkers,[9] who, however, had assigned a 7-ene structure to it. As isolated from the reduction mixture by crystallization, **8** is contaminated by *ca.* 15% persistent isomeric impurity, separable by chromatography of the methyl esters on silver nitrate impregnated alumina, analogous to tlc separations of other resin acid esters.[15] The 8α-13-ene structure **6** has been proposed[8] and provisionally accepted[16,17] for this minor component; however, our results indicate that it is actually the previously unknown 8β-13-ene acid **9.**

The second most abundant product of the reduction of abietic acid with lithium in ammonia is the 13β-8(14)-ene acid **5.** The remaining minor product, the 13α-7-ene acid **7,** is a new compound, which was isolated as a cocrystallizing mixture with **9,** readily separable by chromatography on silver nitrate–alumina. The formation of acids **8** and **5** as principal products of the reduction also accords with our additional observation that the action of lithium in ethylamine on a related system, 3,5-cholestadiene, yields mainly 4-cholestene. Likewise, by analogy with the sodium–alcohol reduction of 2,4-cholestadiene to 4-cholestene,[18] lithium–ammonia reduction of levopimaric acid (and also neoabietic acid) was found to give mainly acids **8** and **5.**[19]

CHART I



(5) The numbering and systematic nomenclature follow the recent proposals (third revision, Oct 1968) of a group chaired by Dr. J. W. Rowe, U. S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, Wis. *Cf.* R. McCrindle and K. H. Overton, *Advan. Org. Chem.*, **5,** 50 (1965). The parent abietane skeleton as proposed by E. Fujita, T. Fujita, and H. Katayama [*Chem. Commun.*, 968 (1967)] possesses the *trans-anti-trans* configuration with a 13α-isopropyl group. Inverted configurations are designated by the position number and the correct stereochemistry just before the skeletal name. The order of groups on ring methylene position is determined by the sequence rule [R. S. Cahn, C. K. Ingold, and V. Prelog, *Experientia*, **12,** 81 (1956)].

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

(7) For references to the earlier work, see J. L. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, Cambridge University Press, Cambridge, 1952, Chapter 5.

(8) For a recent, independent assignment of the configurations of the tetrahydroabietic acids, see J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, **31,** 4128 (1966). We thank Professors Huffman and Herz for sending us a copy of their manuscript prior to publication.

(9) (a) E. E. Royals, W. C. Bailey, and R. M. Kennedy, *ibid.*, **23,** 151 (1958); (b) W. G. Bailey, Ph.D. Thesis, Emory University, 1956; (c) R. M. Kennedy, Ph.D. Thesis, Emory University, 1957. We thank Dr. Royals for additional experimental details concerning this work.

(10) Apart from the bond isomerization product **13** (Chart II), only these two dihydroabietic acids **4** and **5** have been isolated in pure state from the hydrogenation of abietic acid. Lombard[11] had correctly assigned structure **4** to the one with mp 166°, $[\alpha]D$ −26°, which Velluz and coworkers[12] later mistakenly formulated as **9.** The other acid, mp 151°, $[\alpha]D$ +42°, is also formed by hydrogenation of neoabietic and levopimaric acid. Although Velluz[12] assigned structure **6** to this acid, our data indicate that it is **5.** Recently, it has been observed[18] that partial hydrogenation of 12α-hydroxyabietic acid yields dihydro-12α-hydroxy products analogous to **4** and **5.**

(11) R. Lombard, *Bull. Soc. Chim. Fr.*, [V] **9,** 833 (1942); [V] **11,** 526 (1944). R. Lombard and J. Ebelin, *ibid.*, 316 (1951); 438 (1952); 930 (1953).

(12) L. Velluz, G. Muller, A. Petit, and J. Mathieu, *ibid.*, 401 (1954).

(13) W. Herz, H. J. Wahlborg, W. D. Lloyd, W. H. Schuller, and G. W. Hedrick, *J. Org. Chem.*, **30,** 3190 (1965).

(14) (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3; (b) F. Johnson, *Chem. Rev.*, **68,** 375 (1968).

(15) D. F. Zinkel and J. W. Rowe, *J. Chromatog.*, **13,** 74 (1964).

(16) B. E. Cross and P. L. Myers, *J. Chem. Soc., C,* 471 (1968). Evidently the sample of **8** used by these authors was contaminated with **5** as well as **9,** since their products of osmium tetroxide hydroxylation included the 8α,14α-glycol of **5** as well as the 8α,14α-glycol of **8** and the 13β,14β-glycol of **9** (see Experimental Section). We cordially thank Professor Cross for kindly providing samples and making comparisons of our products with theirs. He has also informed us (letter, July 30, 1968) that his more recent evidence agrees with our assignment of structure **9** rather than **6** to the persistent 13-ene contaminant of **8.** See also ref 17.

(17) Although a minor epoxide isolated from the reaction of *m*-chloroperbenzoic acid with impure acid **8** was evidently derived from the 8α-13-ene isomer **6,** as claimed,[8] new work has recently been reported (J. W. Huffman and J. A. Alford, 5th International Symposium on the Chemistry of Natural Products, London, July 8–13, 1968) which confirms our conclusion that the principal contaminant of **8** has structure **9** and not **6.**

(18) H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1,** 575 (1937).

(19) The formation of **5** and **8** by chemical reduction of levopimaric acid (**3**) provides further direct chemical evidence for the 9α configuration in this acid: (a) W. G. Dauben and R. M. Coates, *ibid.*, **28,** 1698 (1963); (b) W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41,** 1113 (1963); (c) A. W. Burgstahler, H. Ziffer, and U. Weiss, *J. Amer. Chem. Soc.*, **83,** 4660 (1961).

Proof of Structure. A. Position of the Double Bond.—Chemical evidence for the location of the double bonds in the foregoing dihydroabietic acids was obtained by hydroxylation of the corresponding methyl esters with osmium tetroxide, followed by lead tetraacetate cleavage of the resulting glycol esters. In each case, these operations gave a ketoaldehyde ester whose nmr spectrum allowed the position of the double bond to be assigned with certainty. Thus the 8β-13-ene acid **9** afforded a ketoaldehyde ester which must have structure **12.** The isopropyl methyl doublet was shifted downfield, in agreement with the formation of an alkyl isopropyl ketone.[20] The C-10 methyl was nonshielded, and the aldehyde proton gave rise to a doublet at τ 0.47, in accord with the presence of an equatorial aldehyde function.[21] That epimerization had not occurred during the cleavage reaction was shown by the fact that no deuterium incorporation was observed when the reaction was conducted in acetic acid-1-*d*. All the data, therefore, are in agreement with the assignment of structure **9** to this acid.[17]

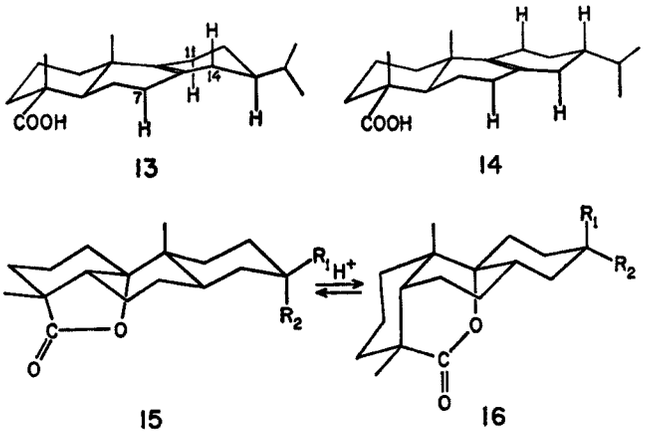
Acids **5** and **8** gave rise to ketoaldehyde esters **11a** and **11b,** respectively, whose nmr spectra showed the isopropyl methyl resonance in the normal position. However, the C-10 methyl signal was shifted upfield by *ca.* 0.2 ppm, owing to the fact that this methyl group lies in the shielding cone of the carbonyl group.[22] In agreement with their formulation as α-disubstituted aldehydes, the nmr spectra of these cleavage products exhibited the aldehyde proton signal as doublets (J = 2 Hz).

Unlike **11a** and **11b,** the ketoaldehyde esters **10a** and **10b** derived from acids **4** and **7,** respectively, displayed normal chemical shifts, both for their isopropyl and for their C-10 methyl resonances. However, the aldehyde proton signal appeared as a triplet with J = 2 Hz. This result requires the presence of two protons on the α carbon and is consistent only with cleavage of a 7-ene structure.

In contrast to the foregoing results, ozonolysis of the acid now known to have structure **8,** has been reported[9] to give a product derived from a 7-ene structure. In our work, we found that ozonization of moderately pure acid **8** gave a mixture of products, only about half of which appeared to be the result of "normal" cleavage of an 8(14)-ene. None of the reported[9] monomeric keto anhydride could be isolated, and any which may have been present would have had to arise by bond rearrangement during ozonolysis[23] or from contamination of **8** by **7** (or **4**).

B. Configuration at C-13.—For determination of the configuration at C-13 in the 7-ene and 8(14)-ene acids, the well-known dihydroabietic acid lactonization reaction proved especially useful. By treatment with HBr in acetic acid, the dihydro acids **4** and **5** formed by partial hydrogenation[11,12] of abietic-type dienoid acids are converted into a common dihydro acid whose previous[12] formulation as the 13β-8-ene acid **13** (Chart II) has been confirmed.[24] Similar treatment of acid **8** has also been reported[9] to give an analogous product, which we have found to be a mixture containing the 13α-7-ene acid **7** (20–25%) and the expected 13α-8-ene acid **14** (75–80%). Apparently the 8-ene structure is less stable in **14** than in **13,** although the reason (evidently conformational in nature[14b]) is not clear.

CHART II



a, R_1 = isopropyl; R_2 = H
b, R_1 = H; R_2 = isopropyl
c, R_1 = R_2 = H

Acid **13** on further treatment with HBr in acetic acid or with cold sulfuric acid gives γ-lactone **15a,**[7] whose structure and stereochemistry have been unequivocally determined.[25] Although it has also been reported[9] that this same compound results from lactonization of acid **8** (impure), but in low yield, we have found that a new γ-lactone, **15b,** is the major direct product. Minor amounts of lactone **15a** apparently arise, at least in part, from 13β contaminants (such as **5**) present in all but the most highly purified preparations of acid **8.** It has also been noted[26] that prolonged treatment of **15a** (or its dihydroabietic acid precursors) with sulfuric acid gives rise to δ-lactone **16a.** Moreover, a different δ-lactone, **16b,** results from further acid treatment[9] of **15b** or its precursors. However, the ratio at equilibrium of γ- to δ-lactone is very different in the two sets of isomers. At 25° it is *ca.* 55:45 of lactones **15a** and **16a,** and *ca.* 1:99 of lactones **15b** and **16b.**

These differences in the equilibrium position of the two sets of lactones can be accounted for by reasoning similar to that presented previously.[24,25b,27] At equilibrium (at 25°), the unknown podocarpane (13-deisopropylabietane) prototype has been estimated[25b] to contain 95.7% δ-lactone **16c** and only 4.3% γ-lactone **15c,** corresponding to a free-energy difference of 1.8 kcal/mol. Since an axial isopropyl group in a cyclohexane ring is *ca.* 2.1 kcal/mol less stable at 25° than an equatorial one,[28] a β-isopropyl group in the present

(20) *Cf.* isopropyl methyl doublet centered at τ 8.95 in 3-methyl-2-butanone (Sadtler Nuclear Magnetic Resonance Spectra, Vol. 3, No. 1885).

(21) *Cf.* 19-norabietan-18-al (equatorial aldehyde), τ 0.37 (J = 3 Hz),[4a] and 18-norabietan-19-al (axial aldehyde), τ −0.20 (J < 1 Hz),[4a] in which there is a similar geometrical relationship to the C-10 methyl.

(22) The C-10 methyl in 6-keto steroids shows an almost identical upfield shift; *cf.* N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry: Illustrations from the Steroid Field," Holden-Day, Inc., San Francisco, Calif., 1964, p 20. See also ref 8 and 30.

(23) An example of such a bond shift during ozonolysis is reported by C. R. Enzell and B. R. Thomas, *Tetrahedron Lett.*, 225 (1965).

(24) W. Herz and H. J. Wahlborg, *J. Org. Chem.*, **30,** 1881 (1965).

(25) (a) L. A. Subleskey and T. F. Sanderson, *J. Amer. Chem. Soc.*, **76,** 3512 (1954); (b) L. J. Gough, T. F. Sanderson, V. I. Stenberg, and E. Wenkert, *J. Org. Chem.*, **25,** 1269 (1960). For additional proof of the configuration at C-8, see ref 24.

(26) Le-Van Thoi, *Bull. Soc. Chim. Fr.*, 761 (1955); *cf.* ref 24.

(27) E. Wenkert and J. W. Chamberlin, *J. Amer. Chem. Soc.*, **81,** 688 (1959).

(28) N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **31,** 894, 4327 (1966).

TABLE I

PROTON CHEMICAL-SHIFT VALUES FOR ABIETIC-TYPE RESIN ACIDS[a,b]

Acid	C-4 Methyl	C-10 Methyl	Isopropyl methyls (J = 5–7 Hz)	Olefinic protons
Abietadien-18-oic				
Abietic (1)	8.71	9.13	8.97	4.22, 4.66
Neoabietic (2)	8.77	9.16	8.26[c]	3.71
Levopimaric (3)	8.80	9.05[d]	8.98	4.39, 4.78
Palustric (8,13-diene)	8.77	8.92	8.96	4.58
8,13(15)-diene (31)	8.83	9.00	8.34[c]	
Abieten-18-oic				
13β-7-ene (4)	8.75	9.15	9.09, 9.14[e,f]	4.74
13α-7-ene (7)	8.75	9.17	9.14[e]	4.73
13β-8(14)-ene (5)	8.86	9.21	9.11, 9.16[e,f]	4.56
13α-8(14)-ene (8)[g]	8.86	9.22	9.12, 9.16[e,f]	4.67
8β-13-ene (9)	8.82	9.15	9.03	4.91
13β-8-ene (13)[h]	8.79	9.02	9.11	
13α-8-ene (14)	8.81	9.01	9.12	
8β-13(15)-ene (27)	8.83	9.14	8.35[c]	
Abietan-18-oic[g]				
8α,13β (17)	8.80	8.90	9.10	
8β,13β (18)	8.84	9.17	9.13[e]	
8β,13α (19)	8.83	9.19	9.14[e]	

[a] Determined in carbon tetrachloride solution on Varian A-60 and HA-100 nmr spectrometers at 250-sec sweep time/500-Hz sweep width with internal tetramethylsilane as reference. [b] *Cf.* ref 24, 29, and 30. [c] Isopropylidene singlet. [d] Reflects folded B/C conformation (*cf.* ref 19c). [e] Assignment verified by double-resonance decoupling of the C-15 proton on the HA-100 instrument by irradiation at *ca.* τ 8.5. [f] Pair of doublets (resolved only in the 100-MHz spectrum). [g] *Cf.* ref 8. [h] *Cf.* ref 24.

TABLE II

FAR-ULTRAVIOLET ABSORPTION OF METHYL ABIETEN-18-OATES[a]

Parent abieten-18-oic acid	λ_{max}, nm (ϵ_{max})	λ_{min}, nm (ϵ_{min})
13β-7-ene (4)	204.0 (6,500)	195 (5,600)
13α-7-ene (7)	203.5 (6,800)	194 (6,200)
13β-8(14)-ene (5)[b]	200.5 (10,700)	
13α-8(14)-ene (8)	206.5 (8,700)	197 (7,700)
13β-8-ene (13)[c]	195.0 (9,400)	
13α-8-ene (14)	196.5 (7,800)	
8β-13-ene (9)	190.5 (9,500)	
8β-13(15)-ene (27)	197.0 (12,300)	

[a] Measured in Phillips Petroleum Co. Spectro Grade isooctane in 0.1-cm quartz cells from 220 to 186 nm on a Cary Model 14 recording spectrophotometer with continuous nitrogen purge; scan speed 30 nm/min; optical density range 0–1.0. All readings are corrected for solvent blank. Our values for two previously published reference compounds follow: 4-cholestene, λ_{max} 193.3 nm (ε 10,200) [lit.[31] λ_{max} 193 nm (ε 10,000)]; 5α-lanost-8-en-3β-yl acetate, λ_{max} 200 nm (ε 8200) [lit.[31] λ_{max} 200 nm (ε 8330)]. [b] For methyl 8(14)-pimaren-18-oate, λ_{max} 201.4 nm (ε 9880). [c] For methyl 8-pimaren-18-oate, λ_{max} 193.5 nm (ε 8860).

system helps to favor the otherwise less stable γ-lactone by 2.1 minus 1.8, or 0.3 kcal/mol. This gives a calculated equilibrium composition of 62% **15a** and 38% **16a.** On the other hand, an α-isopropyl group increases the stability of the ring-C inverted δ-lactone by 2.1 plus 1.8, or 3.9 kcal/mol, which corresponds to 99.8% **16b** in equilibrium with 0.2% **15b.** In both cases, the predicted values lie close to those observed experimentally.

Thus, the lactonization causes little or no epimerization at C-13, and its application to the various dihydroabietic acids proved to be a convenient method of determining or verifying the configuration at this center. In each case the result was consistent with the assignments shown in Chart I. As would be expected, the reaction proceeded more slowly with the 8β-13-ene acid **9** than with the other dihydro acids and, interestingly, gave almost exclusively the 13α-isopropyl lactones **15b** and **16b.**

C. Spectral Evidence.—The nmr spectra of the acids (Table I) are consistent with the positions assigned to the double bonds. In acid **9** the 13,14 double bond (*cf.* abietic, levopimaric, and palustric acid) causes the isopropyl methyl doublet to be shifted downfield from where it appears in the other isomers. In the 7-ene acids **4** and **7,** the C-4 methyl resonance is likewise shifted downfield from its position in the spectra of the other isomers. This effect evidently arises from conformational changes introduced into ring B by a 7,8 double bond. In any event, it is also present in the spectrum of abietic acid (**1**),[29] 9-hydroxyabietic acid,[24] 9-hydroxy-13β-abiet-7-en-18-oic acid,[24] isopimaric acid,[30] and the 14-keto-7-ene acid derived from acid **8** by dehydrochlorination and hydrolysis of its nitrosyl chloride addition product[9] (see Experimental Section). Acids **5** and **8** with an 8,14 double bond, would be expected to have "normal" [30] C-10 methyl shifts. The appearance of the isopropyl

(29) As determined by us (Table I). J. C. W. Chien [*J. Amer. Chem. Soc.*, **82,** 4762 (1960)] does not report this shift, but his values, determined under different conditions, are difficult to correlate. This has also been noted by by J. D. McChesney, Ph.D. Thesis, Indiana University, 1965, p 24 (see also ref 30a below).

(30) (a) E. Wenkert, A. Afonso, P. Beak, R. W. J. Carney, P. W. Jeffs, and J. D. McChesney, *J. Org. Chem.*, **30,** 713 (1965). (b) J. W. ApSimon, W. G. Craig, P. V. Demarco, W. D. Mathieson, and W. B. Whalley, *Tetrahedron*, **23,** 2375 (1967).

signals as a pair of doublets in the 100-MHz spectra of these two isomers indicates a nonequivalent magnetic environment which molecular models suggest would probably be associated with an 8,14 double bond.

Further spectral support for the assignments of the positions of the double bonds in the dihydroabietic acids is seen in the far-ultraviolet (far-uv) absorption of the methyl esters (Table II). In all cases, the absorption characteristics are comparable with those of appropriate steroid or terpene analogs.[31] The λ_{max} of the methyl ester of acid **5** is perhaps a little lower than expected, but a conformation of ring C allowing the isopropyl group to become pseudoequatorial could possibly account for it. This might also explain the close similarity of the nmr spectrum of **5** with that of acid **8**, in which a pseudoequatorial isopropyl group is almost certainly present.

The ORD (Figure 1) and CD curves of the dihydroabietic acids also support the assigned structures. Thus, in agreement with predictions based on chirality considerations,[32] and by analogy with the sign of the Cotton effect of 17β-hydroxy-4-estrene (+) and 17β-hydroxy-5-estrene (−),[32] acids **5** and **8** exhibit positive Cotton effects, while acids **4** and **7** display negative ones.[33] The curve of acid **9** might at first sight appear to indicate a positive Cotton effect, similar to that of 17β-acetoxy-5β-androst-3-ene[32] and 5β-cholest-3-ene,[34] thereby implying a B/C-*cis* ring junction (formula **6**) rather than a *trans* one (formula **9**). Actually, however, the circular dichroism of this acid shows that the sign of the Cotton effect is negative, like that of 5α-cholest-3-ene,[32] which also has a positive rotation at 230 nm before dipping to the first extremum of a negative Cotton effect (*cf.* positive background in the ORD curves of the saturated acids **17, 18,** and **19**[35]). Molecular models also indicate that the strong positive Cotton effect of acid **5** is best accounted for[32] with ring C in a conformation requiring the 13β-isopropyl group to be pseudoequatorial. The marked difference in the ORD curves of **13** and **14** can be rationalized if the 13β-isopropyl group in **13** is allowed to become equatorial. Then all of the three allylic pseudoaxial hydrogens (7α, 11α, and 14β) form right-handed helices with the double bond and therefore contribute toward a positive Cotton effect.[32] In **14,** with an equatorial 13α-isopropyl group, only the 7α hydrogen exerts a positive contribution, while the now pseudoaxial 11β and 14α hydrogens make a negative one, thus causing the Cotton effect to be weakly negative.

Relation to Tetrahydroabietic Acids.—The structural and stereochemical assignments of the various dihydroabietic acids are also consistent with the results of catalytic hydrogenation of these acids over platinum in acetic acid (Table III). The products are the three known tetrahydroabietic acids, mp 168, 182, and 202°,[7,8,12] which are readily identified by the glpc

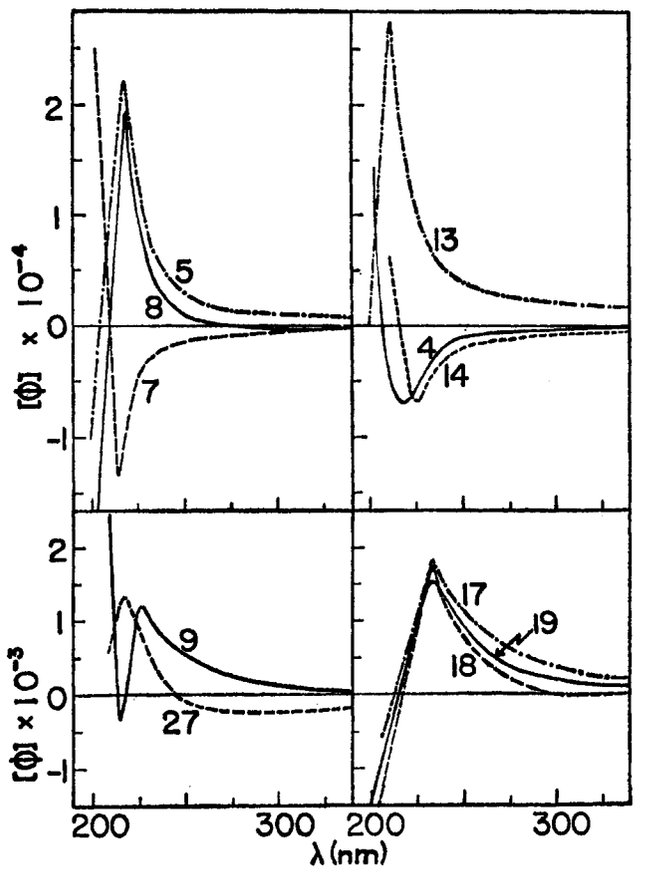


Figure 1.—Optical rotatory dispersion (in *n*-hexane) of reduced abietic-type resin acids. (For circular dichroism data, see Experimental Section.)

TABLE III
TETRAHYDRO ACIDS FROM HYDROGENATION OF ABIETIC-TYPE RESIN ACIDS[a]

Starting acid	Percent of tetrahydroabietic acid formed[b] 17 (mp 168°)	18 (mp 202°)	19 (mp 182°)
1	25	33	35[c]
2	25	34	40[c]
3	28	34	34[c]
4	66	28	6
5	34	62	4
7	0	0	100
8	0	10	90
9	0	6	94
13	39	55	6
14	2	5	93[d]
27	4	16	80
31	25	27	48

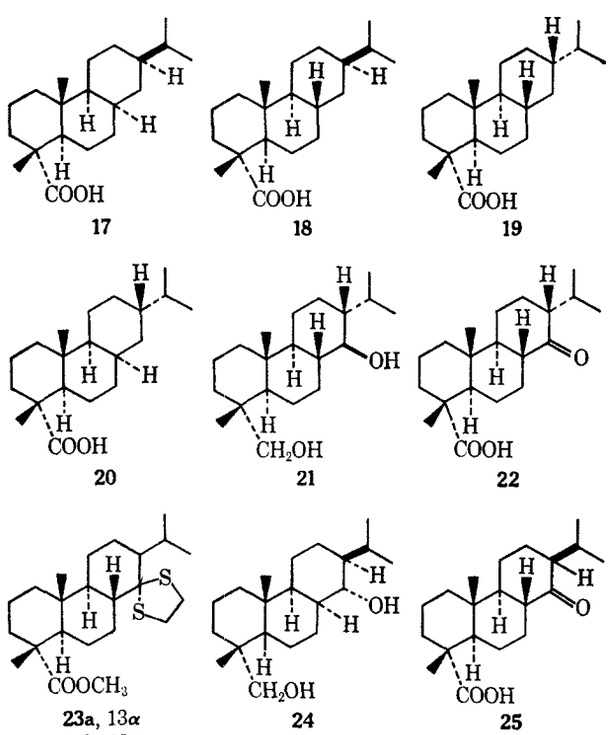
[a] Microscale (3–5 mg) hydrogenations were conducted at 25° (1 atm) over prereduced platinum oxide (30 mg) in glacial acetic acid (10 ml) and were complete in 3–20 min. [b] Determined by glpc of the methyl esters on 20% DEGS as described in ref 36. Peak area calculations were verified with a Du Pont 310 curve resolver. [c] Dehydroabietic (8,11,13-abietatrien-18-oic) acid constituted most of the remainder of the product. Acids **1, 2,** and **3** were at least 95–98% pure according to glpc of their methyl esters. The other starting acids were chromatographically homogeneous. [d] A similar product composition resulted from hydrogenation of a 4:1 mixture of **14** and **7** over 5% rhodium on alumina at 150° in ethanol at 2000 psi.

(31) R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, **27,** 345 (1962).
(32) A. Yogev, D. Amar, and Y. Mazur, *Chem. Commun.*, 339 (1967).
(33) Although the plain (longer wavelength) portions of the ORD curves of 4- and 5-cholestene [C. Djerassi, W. Clossen, and A. E. Lippman, *J. Amer. Chem. Soc.*, **78,** 3163 (1956)] have been cited in connection with those of analogous dihydropimaric and dihydroisopimaric acids [A. J. Bose, *Chem. Ind.* (London), 1628 (1959); 1104 (1960)], the signs of the Cotton effects[32] of these steroids are actually opposite to those of the more apposite 19-nor steroids mentioned above [*cf.* M. Legrand and R. Viennet, *C. R. Acad. Sci., Paris, Ser. C,* **262,** 1290 (1965)].
(34) Determined by us on a sample kindly supplied by Dr. Ruth Lack from Professor C. W. Shoppee's collection [C. W. Shoppee, D. E. Evans, and G. H. R. Summers, *J. Chem. Soc.*, 97 (1957)].
(35) J. D. Renwick and P. M. Scopes, *ibid., C,* 1949 (1968).

retention values[36] of their methyl esters and in part by their nmr spectra.[8] From Table III it is seen that, although minor amounts of epimerization occurred at C-13, hydrogenation of acids **7, 8,** and **14** with a 13α-isopropyl group afforded mainly the tetrahydro acid of mp 182°, in accord with the 13α-isopropyl configuration that has been proposed[4a,8] for the latter. Hydrogenation of acids **4, 5,** and **13,** on the other hand, gave mainly the 168 and 202° acids, in agreement with previous findings of Velluz and coworkers[12] and the assignment of a 13β-isopropyl configuration to these two tetrahydro acids.[1,8] The hydrogenation of the 8β-13-ene acid **9** to a mixture containing essentially only the 182 and 202° acids further indicates that the latter two acids belong to the B/C-*trans* series and shows that the 168° acid is the 13β-B/C-*cis* isomer **17.**

This last conclusion is confirmed by the significant downfield shift of the C-10 methyl resonance in the nmr spectrum (Table I) of the 168° acid compared with the corresponding shifts in the other two tetrahydro acids.[8] Such steric deshielding in **17** is caused by the axial 12β and 14β hydrogens. The comparatively low melting point is also in agreement with the folded structure required by **17.** The formation of this acid as the major product from high pressure hydrogenation of abietic acid over Raney nickel[11] is likewise expected (α side, all-*cis* reduction). Hence the 202° acid has the 8β,13β structure **18,** and the 182° acid has the 8β,13α structure **19.** The latter assignment was made in our preliminary report,[4a] while the other two were later made independently by Huffman, *et al.*,[8] and by two of us.[1]

CHART III



Several unsuccessful attempts were made to obtain the as yet unknown fourth 9α isomer, 8α-abietan-18-oic acid (**20**), the least stable member of the series (B/C-*cis* fusion and axial isopropyl group). It was hoped that, under some conditions, hydrogenation of either **7** or **14** would occur from the α side, as in the case of **4** and **13,** but evidently the blocking effect of the α-isopropyl group as it becomes axial in **20** is sufficient to prevent this. Even high pressure hydrogenation of a mixture of **7** and **14** over rhodium on alumina[37] failed to give detectable amounts of a new tetrahydro acid.

As a further chemical confirmation of its formulation as **19** and in connection with its use in the synthesis of fichtelite,[4a] a multistep, stereoselective preparation of the 182° tetrahydro acid was also carried out. Reduction–hydroboration[38] of acid **8** gave diol **21,** whose stereochemistry was assigned on the basis of the C-14 proton signal, which appeared as a triplet, J = 9–10 Hz, characteristic of an axial proton coupled to two adjacent axial protons.[39] Oxidation of diol **21** with Jones reagent gave the corresponding keto acid **22,** an alternative route to which has been reported by Huffman, *et al.*[8] This acid is stable to base and therefore has the all-*trans* configuration shown.[4a,8] Interestingly, it is extremely reluctant[4a,16] to form a 2,4-dinitrophenylhydrazone, evidently for steric reasons. Removal of the keto function of **22** to give the tetrahydro acid **19** was accomplished *via* esterification with diazomethane, thioketal formation to give **23,** and Raney nickel desulfurization, followed by hydrolysis. Some epimerization at C-13 occurred during the thioketal formation,[8] although under mild conditions most of the product retained the original configuration, as would be expected.[40] The desulfurization reaction was also not completely specific, since 5–10% of the C-13 epimeric acid **18** and up to 20% of the 13α-8-ene acid **14** could be detected by glpc of the reaction mixture. In contrast to this stereoselective route to **19,** Wolff–Kishner reduction of keto acid **22** caused complete epimerization at C-13 to give **18,** as has been independently observed by Huffman, *et al.*[8] Similar isomerization has been noted in the Wolff–Kishner reduction of even less hindered ketones, such as 9,10-diketoperhydroanthracene.[41]

For comparison purposes, a similar sequence of reactions was carried out on acid **5.** Reduction–hydroboration gave mainly diol **24,** whose nmr spectrum shows a deshielded C-10 methyl resonance as well as the expected *trans*-diaxial coupling (triplet, J = 10 Hz) of the C-14 proton. The β-side attack of diborane on acid **8** and the α-side attack on acid **5** is evidently controlled by the configuration at C-13 in the respective compounds. Jones oxidation of diol **24** was attended by clean epimerization at C-8 but not at C-13, to yield **25,** which corresponds to recent independent findings of Huffman and Alford.[17] The structure of **25** follows from the negative ORD curve of its methyl ester (like

(36) F. H. M. Nestler and D. F. Zinkel, *Anal. Chem.*, **39,** 1118 (1967).

(37) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 979–982.

(38) M. Nussim, Y. Mazur, and F. Sondheimer, *J. Org. Chem.*, **29,** 1120 (1964); *cf.* ref 16.

(39) A. I. Scott, D. W. Young, S. A. Hutchinson, and N. S. Bhacca, *Tetrahedron Lett.*, 849 (1964); E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Amer. Chem. Soc.*, **86,** 2218 (1964); W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwells, *J. Org. Chem.*, **30,** 1873 (1965).

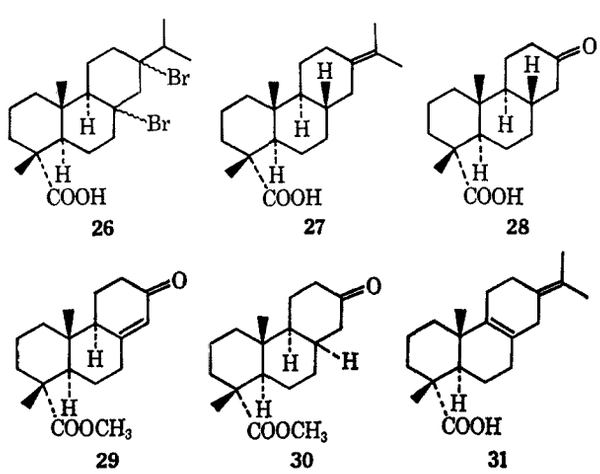
(40) R. E. Ireland and J. A. Marshall, *ibid.*, **27,** 1620 (1962).

(41) R. K. Hill, J. G. Martin, and W. H. Stouch, *J. Amer. Chem. Soc.*, **83,** 4006 (1961); R. L. Clarke, *ibid.*, **83,** 965 (1961); N. S. Crossley and H. B. Henbest, *J. Chem. Soc.*, 4413 (1960); C. Djerassi, T. T. Grosnickle, and L. B. High, *J. Amer. Chem. Soc.*, **78,** 3166 (1956); see also ref 14b.

that of **22**[8]), the unhindered nature of the carbonyl group as judged by its ready formation of a 2,4-dinitrophenylhydrazone, the incorporation of one deuterium atom when diol **24** was oxidized with deuterated Jones reagent, and its conversion in good yield into tetrahydro acid **18** by the thioketal–desulfurization sequence.

Further Correlations. Acids 27 and 31.—Independent chemical evidence for the 8β configuration of **19** was obtained from a determination of the structure of the dihydroabietic acid formed by the action of sodium in cold ethanol[42] on abietic acid dihydrobromide (**26,** Chart IV). On the basis of the following evidence, this product of reductive elimination is the 8β-13(15)-ene acid **27.** The nmr spectrum (Table I) indicates the presence of an isopropylidene group (*cf.* neoabietic acid). Catalytic hydrogenation (Table III) afforded mainly acid **19,** implying a common stereochemistry at C-8 in the two compounds. Ozonolysis gave acetone and the tricyclic keto acid **28.** This keto acid was also obtained from the methyl ester of neoabietic acid (**2**) by partial ozonolysis[6,43] to **29,** followed by reduction with lithium in ammonia and oxidation of the resulting diol.[44] The B/C-*trans* ring junction in **28,** and hence in **27** and **19,** follows from the well-established stereochemical course of the metal–ammonia reduction of analogous 3-keto steroidal 4-enes and related compounds[14] and by the fact that the methyl ester of **28** exhibits a strong positive Cotton effect in its ORD, like that of 5α-cholestan-3-one.[45] Catalytic hydrogenation of **29** over palladium in ether furnished a mixture containing a 4:7 ratio of the methyl ester of **28** and the 8α epimer **30** (*cf.* related reduction of 4-cholesten-3-one to 5β-cholestan-3-one[46]).

CHART IV



Finally, from the mother liquors of the preparation of acid **27,** we were able to isolate a new isomer of abietic acid having the 8,13(15)-diene structure **31.** Readily purified as the methyl ester, this acid is the principal product if the sodium–alcohol reduction is conducted at elevated temperatures or if only sodium ethoxide in ethanol is used.[47] The structure follows from the nmr spectrum (Table I), which indicates the presence of an isopropylidene group and a downfield shift of the C-10 methyl signal, suggestive of the presence of unsaturation in the 8,9 position (*cf.* the C-10 methyl signal in the spectra of acids **13** and **14**). The absence of an olefinic proton signal and the presence of strong absorption at τ 8.06 (secondary allylic protons) and 7.40 (doubly allylic protons), coupled with the lack of conjugated diene absorption in the uv, allow only the 8,13(15)-diene structure **31** for this compound.

In accord with this assignment, hydrogenation of **31** over platinum in acetic acid resulted in the absorption of 2 mol of hydrogen with the formation of a mixture (Table III) of acids **17, 18,** and **19,** thereby proving that the original carbon skeleton was still intact. Isomerization with hydrochloric acid in ethanol[48] converted **31** in high yield into abietic acid (**1**). It is of interest that, in the formation of **31** by bisdehydrobromination of abietic acid dihydrobromide with base, no appreciable amount of conjugated dienic product could be detected.

Experimental Section[49]

Lithium–Ammonia Reduction of Abietic Acid. A. 8(14)-Abieten-18-oic Acid (8) and 13-Abieten-18-oic Acid (9).—By the method of Royals and coworkers,[9] reduction of 200 g (0.445 mol) of the diamylamine salt (mp 136–137.5°, $[\alpha]_D$ −60°) of abietic acid (**1**)[50] with 15 g (2.16 g-atoms) of lithium shot[51] was conducted at −35° in 2 l. of distilled anhydrous liquid ammonia. The blue color was allowed to persist for 4 hr before addition of ethanol. Isolation of the acidic product afforded, after four recrystallizations from acetone, 38 g (28%) of impure **8**: mp 190–195°; $[\alpha]_D$ −26° (lit. mp 197–198°, $[\alpha]_D$ −24°;[4b] mp 197–197.5°, $[\alpha]_D$ −24.7°[9]). Fractional crystallization of the mother liquors gave an additional 10 g of product with the same melting point and rotation (total yield 35%). Integration of the olefinic peaks in the nmr spectrum (*cf.* Table I) indicated the presence of *ca.* 85% **8** together with 15% **9.** This proportion of isomers was confirmed by glpc of the methyl esters (diazomethane). Four additional crystallizations from acetone gave material of mp 195–197.5°, $[\alpha]_D$ −25°, with little change in the nmr spectrum and glpc behavior. Efforts to achieve purification through the diamylamine salt, mp 116–117°, were unsuccessful; however, column chromatography of the methyl esters (1-g scale) on silver

(42) T. Hasselstrom and J. D. McPherson, *J. Amer. Chem. Soc.*, **61,** 1228 (1939).

(43) G. C. Harris and T. F. Sanderson, *ibid.*, **70,** 339 (1948); *cf.* S. W. Pelletier, K. N. Iyer, C. W. J. Chang, and A. Ogiso, *Tetrahedron Lett.*, 3819 (1968).

(44) This transformation of **29** to **28** has also been carried out by Dr. A. Afonso in the laboratories of Professor Ernest Wenkert. We thank Professor Wenkert for communicating his results to us for inclusion in this paper (see Experimental Section).

(45) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 43.

(46) H. Grasshof, *Hoppe-Seyler's Z. Physiol. Chem.*, **223,** 249 (1934).

(47) For possibly related results, see T. Hasselstrom and J. D. McPherson, *J. Amer. Chem. Soc.*, **61,** 2247 (1939); also p 426 of ref 7.

(48) V. M. Loeblich, D. E. Baldwin, and R. V. Lawrence, *ibid.*, **77,** 2823 (1955); see also ref 6 and 24.

(49) Melting points were determined in open capillaries with a Hershberg melting point apparatus calibrated against standard substances. Thin layer chromatography (tlc) was performed on microscope slides covered with silica gel G (Merck). Gas–liquid partition chromatography (glpc) was conducted at 200° on DEGS and SE-30/EGiP columns as described in ref 36, which also gives retention data for the methyl esters of the various dihydro- and tetrahydroabietic acids described herein. Sodium D-line rotations were measured on 1–2% solutions in ethanol at 25° with a Perkin-Elmer Model 141 polarimeter. Except where noted, optical rotatory dispersion (ORD) and circular dichroism (CD) curves were determined at 28° in *n*-hexane (1.0-cm cell) on a Cary Model 60 recording spectropolarimeter. Ultraviolet spectra were recorded in ethanol (or isooctane for the data in Table II) on a Cary Model 14 spectrophotometer. Infrared spectra were taken in carbon tetrachloride solution with a Perkin-Elmer Model 137 Infracord. Nmr spectra were determined in carbon tetrachloride solution on a Varian A-60 or HA-100 instrument with tetramethylsilane as internal reference. Ether solutions were dried over anhydrous magnesium sulfate. Petroleum ether refers to the fraction with bp 35–45°. Combusion analyses were performed by the Weiler and Strauss Microanalytical Laboratory, Oxford, England.

(50) Obtained from WW gum resin by the procedure of G. C. Harris and T. F. Sanderson, "Organic Syntheses," Col. Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1963, p 1.

(51) P. D. Bartlett and E. B. Lefferts, *J. Amer. Chem. Soc.*, **77,** 2804 (1955); *cf.* L. R. Worden and A. W. Burgstahler, *J. Chem. Educ.*, **45,** 425 (1968).

nitrate impregnated alumina (gradient elution with ether–petroleum ether), similar to the tlc method of Zinkel and Rowe,[15] was effective. The oily ester, $[\alpha]_D$ −34°, of **8** was eluted first, and on hydrolysis with refluxing 15% potassium hydroxide it afforded pure **8**: mp 199–200° (from acetone); $[\alpha]_D$ −32°; ORD (*c* 0.10) $[\Phi]_{400}$ −205°, $[\Phi]_{315}$ −270°, $[\Phi]_{275}$ ±0°, $[\Phi]_{250}$ +1050°; ORD (*c* 0.010) $[\Phi]_{230}$ +6000°, $[\Phi]_{218}$ +19,500°, $[\Phi]_{210}$ ±0°, $[\Phi]_{203}$ −16,000°; CD (*c* 0.00435) $[\Theta]_{245}$ ±0, $[\Theta]_{210}$ +37,000, $[\Theta]_{197}$ ±0.

The second component from the chromatographic separation was the methyl ester, $[\alpha]_D$ +5.5°, of **9** (*cf.* part C below). Hydrolysis with alcoholic base gave pure **9**, which, after recrystallization from ligroin, had mp 146–147°; $[\alpha]_D$ +6°; ORD (*c* 0.10) $[\Phi]_{400}$ +30°, $[\Phi]_{300}$ +105°, $[\Phi]_{250}$ +525°; ORD (*c* 0.010) $[\Phi]_{227}$ +1200°, $[\Phi]_{215}$ −300°, $[\Phi]_{210}$ +2500°; CD (*c* 0.0135) $[\Theta]_{260}$ ±0, $[\Theta]_{221}$ +2200, $[\Theta]_{208}$ −4900, $[\Theta]_{197}$ ±0.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.74; H, 10.65.

B. 13β-Abiet-8(14)-en-18-oic Acid (5).—The combined mother liquors from the reduction were diluted to 200 ml with hot acetone and mixed with 50 ml of diamylamine. After the solution had been cooled to −20°, the resulting mixture of salts was collected and the filtrate was concentrated to provide an additional crop. The solid product after recrystallization from acetone melted at 105–110°. Acidification of the mother liquors with cold 3 *N* hydrochloric acid and extraction with ether furnished a solid whose nmr spectrum showed only the one olefinic proton peak (τ 4.56) present in **5** (*cf.* Table I). Three crystallizations of this product from acetone–water furnished 15 g (11% from abietic acid diamylamine salt) of **5** as prisms: mp 144–147°; $[\alpha]_D$ +40° (lit. mp 143–145°, $[\alpha]_D$ +43.9°;[11] mp 151°, $[\alpha]_D$ +42°;[12] mp 146°, $[\alpha]_D$ +43°;[52] mp 149°, $[\alpha]_D$ +43°[53]). After further purification through the cyclohexylamine salt, mp 205–206°, a sample had mp 148.5–150°; $[\alpha]_D$ +42°; ORD (*c* 0.10) $[\Phi]_{400}$ +355°, $[\Phi]_{300}$ +1050°; ORD (*c* 0.010) $[\Phi]_{230}$ +8500°, $[\Phi]_{217}$ +22,000°, $[\Phi]_{205}$ ±0°, $[\Phi]_{200}$ −10,000°; CD (*c* 0.00525) $[\Theta]_{260}$ ±0, $[\Theta]_{209}$ +17,000, $[\Theta]_{195}$ ±0. The methyl ester had mp 84–85°, $[\alpha]_D$ +33°, as reported.[11]

In the preparation (1-g scale) of **5** by low pressure hydrogenation[11,29,53] of neoabietic acid (**2**)[54] over 10% palladium on carbon in ethanol, nmr analysis indicated that at least two other isomers were formed. Acid **5** with mp 140–144° was isolated in 15% yield after three crystallizations from acetone–water. In the similar preparation of **5** by partial hydrogenation[11,29] of levopimaric acid (**3**)[55] over the same catalyst in ethanol, considerable disproportionation to dehydroabietic acid occurred unless the reduction was conducted at −10 to −15° (ice–salt bath). The nmr spectrum of the crude product obtained under these conditions indicated that **5** was formed almost exclusively, but the yield of product with mp 141–144° (after three crystallizations) was only 25%.

C. 7-Abieten-18-oic Acid (7).—Regeneration of the free acids from the solid diamylamine salt mixture (mp 105–110°) of part B above, followed by recrystallization from acetone, gave a mixture of **7** **8**, and **9** (nmr analysis). The mother liquors contained much abietic acid and were discarded. Four crystallizations of the solid acid mixture from acetone afforded 10 g of impure **8**, mp 190–195°. Fractional crystallization of the residues, with nmr analysis as a guide for combining fractions, gave 4.5 g of crystalline product, mp 161–162°, $[\alpha]_D$ −8°, containing **7** and **9** in the ratio 9:11, according to glpc of their methyl esters. By column chromatography on silver nitrate–alumina, the methyl ester, mp 39.5–40°, $[\alpha]_D$ −26°, of **7** was eluted first, followed closely by the methyl ester, $[\alpha]_D$ +3.5°, of **9** (*cf.* part A above). Hydrolysis of its crystalline methyl ester furnished pure acid **7**: mp 180–182°; $[\alpha]_D$ −24°; ORD (*c* 0.10) $[\Phi]_{400}$ −170°, $[\Phi]_{300}$ −480°, $[\Phi]_{250}$ −1400°; ORD (*c* 0.010) $[\Phi]_{230}$ −3100°, $[\Phi]_{214}$ −13,500°, $[\Phi]_{205}$ ±0°, $[\Phi]_{202}$ +25,000°; CD (*c* 0.0042) $[\Theta]_{260}$ ±0, $[\Theta]_{224}$ +5700, $[\Theta]_{205}$ −33,000, $[\Theta]_{192}$ ±0.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 79.02; H, 10.54.

For comparison and spectral purposes, an authentic sample of the C-13 epimer of **7** [**13β-abiet-7-en-18-oic acid** (**4**)] was kindly supplied by Professor Leon Velluz.[12] This sample had mp 162.5–164°; $[\alpha]_D$ −14.5° (lit. mp 166°, $[\alpha]_D$ −26°;[11] mp 164°, $[\alpha]_D$ −16°[12]); ORD (*c* 0.10) $[\Phi]_{400}$ −160°, $[\Phi]_{300}$ −400°, $[\Phi]_{250}$ −980°; ORD (*c* 0.015) $[\Phi]_{230}$ −4500°, $[\Phi]_{217}$ −6800°, $[\Phi]_{205}$ ±0°, $[\Phi]_{202}$ +14,000°; CD (*c* 0.0075) $[\Theta]_{260}$ ±0, $[\Theta]_{227}$ +1100, $[\Theta]_{207}$ −17,500, $[\Theta]_{191}$ ±0.

Lithium–Ammonia Reduction of Levopimaric and Neoabietic Acid.—To a stirred solution of 1.0 g (3.3 mmol) of levopimaric acid (**3**)[55] in 60 ml of 1:1 ether–ammonia was added 0.2 g of lithium shot.[51] After 3 hr, 5 ml of methanol was added, and the ammonia was allowed to evaporate. Acidification of the residue with cold 3 *N* hydrochloric acid and extraction with ether gave a product whose nmr spectrum resembled that of the one derived from abietic acid except for the lack of a peak at τ 8.75, thus showing the absence of **7**. Olefinic proton peaks at τ 4.56, 4.67, and 4.91 indicated the presence of **5**, **8**, and **9** (*cf.* Table I). After precipitation of the diamylamine salts (two crops), followed by regeneration of the free acids in the filtrate, there was obtained 0.16 g of **5**, identified by its nmr spectrum and melting point (140–144°, after two crystallizations from acetone–water). Regeneration of the acids from the crude mixture of solid diamylamine salts, followed by four recrystallizations from acetone, furnished 0.30 g of the acid **8**–**9** mixture, mp 190–195°. The material in the mother liquors was not examined further.

Reduction of neoabietic acid (**2**)[54] by the same procedure afforded a mixture whose nmr spectrum was similar to that of the crude reduction product of levopimaric acid. Acids **5** and **8**–**9** were isolated in approximately the same yields as above. Glpc of the methyl esters of the total product mixture of all three reductions indicated that the acids isolated were the only ones present, in addition to recovered starting material. Any peak corresponding to the methyl ester of **6**, if present, was very minor or was obscured by one of the other peaks.

Lithium–Ethylamine Reduction of 3,5-Cholestadiene.—A stirred solution of 0.50 g (1.35 mmol) of 3,5-cholestadiene, mp 79–80°, $[\alpha]_D$ −120°,[56] in 40 ml of ethylamine was treated with small amounts of lithium shot[51] until the blue color persisted for several minutes. A few drops of *t*-amyl alcohol were introduced to discharge the color, and then more lithium was added to restore it. This operation was repeated three times. The neutral product recovered by evaporation, dilution with water, and extraction with petroleum ether crystallized from acetone in fine needles: mp 79–81°; $[\alpha]_D$ +69° ($CHCl_3$); yield 0.41 g (82%). The recorded values[57] for 4-cholestene are mp 83°; $[\alpha]_D$ +76°. Treatment with bromine in ethyl acetate, followed by crystallization of the product from cold ethyl acetate–methanol, afforded a dibromide with mp 116–117°; $[\alpha]_D$ +37° (lit.[57] mp 117°; $[\alpha]_D$ +39° for 4-cholestene dibromide).

A similar reduction of 2,4-cholestadiene,[58] mp 67–68°, $[\alpha]_D$ +165°, furnished a comparable yield of hydrocarbon whose melting point and spectral properties indicated that it also was mainly 4-cholestene.

Hydroxylation–Cleavage Experiments. A. Ketoaldehyde Esters 11a and 11b from Acids 5 and 8.—A solution of 210 mg (0.66 mmol) of the methyl ester, mp 84–85°, of **5** and 180 mg (0.71 mmol) of osmium tetroxide in 10 ml of dry pyridine was allowed to stand overnight at 25°. The brown solution was then diluted with water and extracted with ether. After removal of the ether, the osmate ester was dissolved in 10 ml of dioxane and treated with hydrogen sulfide,[59] and the mixture was concentrated under reduced pressure. Chromatography of the residue of 8 g of silica gel and elution with ether furnished 200 mg (90%) of glycol ester formulated as **methyl 8α,14α-dihydroxy-13β-abietan-18-oate,**[17] which crystallized from methanol–petroleum ether in fine needles: mp 165–166°; $[\alpha]_D$ −12°; nmr (pyridine) τ 6.17 (d, J = 10 Hz, C-14 H), 6.36 (methoxyl), 8.76 (C-4 methyl), 8.98 (deshielded C-10 methyl), and 9.06 (d, J = 7 Hz, isopropyl); nmr ($CDCl_3$) τ 6.28 (methoxyl), 6.42 ($W_{1/2}$ = 10 Hz, C-14 H), 8.79 (C-4 methyl), 8.97 (deshielded C-10 methyl), and 9.05 and 9.14 (overlapping isopropyl doublets, J = 6 Hz). Except for the melting point, these properties correspond closely with those recorded by Cross and Myers for the glycol ester mistakenly identified as "IXb" in their paper.[16]

(52) G. Brus, P. Legendre, and J. Grainier, *Bull. Soc. Chim. Fr.*, 955 (1947).
(53) O. E. Edwards and R. Howe, *Can. J. Chem.*, **37**, 760 (1959).
(54) Isolated from WW gum resin by the procedure of V. M. Loeblich and R. V. Lawrence, *J. Org. Chem.*, **21**, 610 (1956).
(55) Isolated from pine oleoresin by the procedure of V. M. Loeblich, D. E. Baldwin, R. T. O'Connor, and R. V. Lawrence, *J. Amer. Chem. Soc.*, **77**, 6311 (1955); *cf.* W. D. Lloyd and G. W. Hedrick, *Org. Syn.*, **45**, 64 (1965).
(56) J. C. Eck, R. L. Van Peursem, and E. W. Hollingsworth, *J. Amer. Chem. Soc.*, **61**, 171 (1939).
(57) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 253.
(58) E. L. Skau and W. Bergmann, *J. Org. Chem.*, **3**, 166 (1938).
(59) D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2085 (1956).

Anal. Calcd for $C_{21}H_{36}O_4$: C, 71.55; H, 10.29. Found: C, 71.49; H, 10.33.

Hydrolysis of the ester with refluxing alcoholic potassium hydroxide furnished the corresponding acid, **8α,14α-dihydroxy-13β-abietan-18-oic acid,** which crystallized from ethanol–ethyl acetate–petroleum ether in fine needle clusters: mp 234–235°; $[\alpha]D$ −15° (*cf.* mp 229–232°, $[\alpha]D$ −17°, recorded by Cross and Myers[16] for their glycol acid derived from the above ester).

A solution of 80 mg of the ester and 100 mg of lead tetraacetate in 3 ml of acetic acid was stirred at 25° for 2 hr. One drop of ethylene glycol was added, and after 10 min the product was isolated by dilution of the mixture with water and extraction with ether. The resulting oily ketoaldehyde ester **11a** (**methyl 8,14-dioxo-8,14-seco-13*S*-abietan-18-oate**) was homogeneous by tlc and showed ir absorption at 3.7 and 5.8–5.9 μ and nmr peaks at τ 0.22 (d, J = 2 Hz, aldehyde H), 6.28 (methoxyl), 8.82 (C-4 methyl), 9.04 (d, J = 5.5 Hz, isopropyl), and 9.25 (shielded C-10 methyl).

By the same procedure, the methyl esters of 157 mg (0.52 mmol) of the **8–9** mixture, mp 194–197°, furnished 125 mg (74%) of glycol ester formulated as **methyl 8α,14α-dihydroxyabietan-18-oate,**[16] which likewise crystallized from methanol–petroleum ether in fine needles: mp 147–148° (lit.[16] mp 148–149°); $[\alpha]D$ −45°; nmr (in pyridine) peaks at τ 6.28 (d, J = 3 Hz, C-14 H), 6.40 (methoxyl), 8.69 (C-4 methyl), 8.94 and 9.02 (overlapping isopropyl doublets, J = 6.5 Hz), and 9.10 (C-10 methyl); nmr in $CDCl_3$ as recorded by Cross and Myers.[16] Melting point and ir comparison through the courtesy of Professor Cross confirmed the identity with glycol ester "Xc" in his paper.[16]

Anal. Calcd for $C_{21}H_{36}O_4$: C, 71.55; H, 10.29. Found: C, 71.37; H, 10.42.

Hydrolysis of the ester with refluxing alcoholic potassium hydroxide furnished the corresponding acid, **8α,14α-dihydroxy-abietan-18-oic acid,** which crystallized from ether–petroleum ether in fine needles: mp 162–164°; $[\alpha]D$ −42° (lit.[16] mp 151–154°, $[\alpha]D$ −39.5°).

Cleavage of the ester with lead tetraacetate gave the corresponding ketoaldehyde ester **11b** (**methyl 8,14-dioxo-8,14-seco-abietan-18-oate**) as an oil: ir 3.7 and 5.8–5.9 μ; nmr τ 0.43 (d, J = 2 Hz, aldehyde H), 6.28 (methoxyl), 8.83 (C-4 methyl), 9.04 (d, J = 5.5 Hz, isopropyl), and 9.25 (shielded C-10 methyl).

Ozonolysis of 0.30 g (1.0 mmol) of the **8–9** mixture, mp 194–197°, in the manner described by Kennedy,[9c] gave a mixture of keto acids whose nmr spectrum displayed a peak at τ 9.25 (C-10 methyl) with *ca.* half the area of the peak at 8.83 (C-4 methyl). Treatment of the crude product with refluxing acetic anhydride for 2 hr gave a mixture of anhydrides whose ir spectrum exhibited bands at 5.53, 5.70 (shoulder), 5.77, and 5.85 μ. Efforts to isolate a pure product by chromatography on silica gel led to extensive loss of material.

Oxidation of **11b** with Jones reagent[60] gave a comparison sample of the monomethyl ester of the keto diacid resulting from "normal" cleavage at C-8–C-14. The material was characterized by an nmr spectrum which was essentially the same as that of **11b** except for the disappearance of the aldehyde proton signal at τ 0.43. Treatment with acetic anhydride as above gave what appeared to be the expected dimeric keto ester anhydride, characterized by ir absorption at 5.55, 5.78, and 5.85 μ, and an essentially unchanged nmr spectrum.

B. Ketoaldehyde Esters 10a and 10b from Acids 4 and 7.—Hydroxylation as in A above of the methyl ester prepared from 76 mg (0.25 mmol) of **4** (sample kindly supplied by Professor Leon Velluz[12]) afforded 60 mg (76%) of the corresponding glycol ester formulated as **methyl 7α,8α-dihydroxy-13α-abietan-18-oate**: nmr at τ 6.34 (methoxyl), 6.53 ($W_{1/2}$ = 7 Hz, C-7 H), 7.11 (OH), 8.83 (C-4 methyl), 8.96 (deshielded C-10 methyl), and 9.12 (d, 6.5 Hz, isopropyl). This product was not characterized further but was oxidized directly with lead tetraacetate to give ketoaldehyde ester **10a** (**methyl 7,8-dioxo-7,8-seco-13β-abietan-18-oate**): nmr τ 0.37 (t, J = 2 Hz, aldehyde H), 6.34 (methoxyl), 8.80 (C-4 methyl), 9.00 (d, J = 6 Hz, isopropyl), and 9.10 (C-10 methyl) (last two assignments tentative).

A similar hydroxylation-cleavage of 30 mg (0.1 mmol) of the methyl ester, mp 39.5–40°, of **7** gave 15 mg of ketoaldehyde ester **10b** (**methyl 7,8-dioxo-7,8-secoabietan-18-oate**): τ 0.33 (t, J = 2 Hz, aldehyde H), 6.33 (methoxyl), 8.83 (C-4 methyl), 9.08 (d, J = 6 Hz, isopropyl), and 9.10 (C-10 methyl) (last two assignments tentative).

C. Ketoaldehyde Ester 12 from Acid 9.—From the osmium tetroxide hydroxylation of 100 mg (0.3 mmol) of the methyl ester of chromatographically pure **9**, mp 146–147°, there was obtained 40 mg of recovered starting material and 28 mg of crystalline glycol ester, mp 93–98°, which, although homogeneous by tlc, could not be recrystallized from any solvent. This ester was identical by ir and nmr comparison with that derived from the 188° glycol acid mistakenly identified as "XIIb" in the paper by Cross and Myers[16] and is formulated as predominantly **methyl 13,14β-dihydroxyabietan-18 oate** on the basis of the nmr spectrum: τ 6.33 (methoxyl), 6.82 (d, J = 9 Hz, C-14 H), 8.81 (C-4 methyl), 9.07 and 9.12 (pair of doublets, J = 7 Hz, isopropyl), and 9.10 (C-10 methyl). Cleavage of 25 mg of this product with 32 mg of lead tetraacetate was conducted in 1 ml of acetic acid-1-*d* for 2.5 hr at 25°. The mixture was then evaporated to dryness *in vacuo*, triturated with carbon tetrachloride, and filtered, and the solvent was removed, giving 18 mg of oily ketoaldehyde ester **12** (**methyl 13,14-dioxo-13,14-seco-abietan-18-oate**), homogeneous by tlc, whose nmr spectrum indicated that it was essentially deuterium free, with peaks at τ 0.47 (d, J = 3.5 Hz, aldehyde H), 6.35 (methoxyl), 8.86 (C-4 methyl), 8.95 (d, J = 7 Hz, isopropyl attached to carbonyl[20]), and 9.09 (nondeshielded C-10 methyl).

14-Oxo-7-abieten-18-oic Acid from the Nitrosyl Chloride Addition Product of Acid 8.—By reaction with nitrosyl chloride in acetic acid–ethyl acetate at 5°, acid mixture **8–9,** mp 194–197°, was converted in 30% yield into the reported α-chloro oxime, mp 176–177°.[9] Heating this product with pyridine at 90° for 30 min afforded the α,β-unsaturated oxime, as described.[9] After purification through the cyclohexylamine salt, mp 193–194°, this had mp 191–192°; λ_{max} 239 nm (ε 5500) [lit.[9] mp 192.5–193°, λ_{max} 239 nm (ε 6600)]; nmr signals at τ 3.90 (broad, oxime H), 4.70 (olefinic H), 8.73 (C-4 methyl), 9.12 (C-10 methyl), and 9.15 (d, J = 6 Hz, isopropyl). These data indicate that this product is the oxime of 14-oxo-7-abieten-18-oic acid.

Hydrolysis of the unsaturated oxime with 3 *N* sulfuric acid in refluxing 80% ethanol gave a difficultly purified keto acid whose spectral properties suggested that it contained increasing amounts of the isomeric 8-ene acid as the reaction proceeded. After hydrolysis for 2 hr the keto acid isolated as the cyclohexylamine salt (mp 192–195°) had λ_{max} 243 nm (ε 4400); nmr τ 4.70 (olefinic H) and 8.73 (C-4 methyl); ORD[61] (*c* 0.20, in methanol) $[\Phi]_{500}$ +180°, $[\Phi]_{330}$ +750°, $[\Phi]_{315}$ +700°; ORD (*c* 0.0055, in hexane) $[\Phi]_{265}$ +8500°, $[\Phi]_{247}$ ±0°, $[\Phi]_{230}$ −7800°, $[\Phi]_{220}$ −3000°. After hydrolysis for 4 hr the product (as the cyclohexylamine salt) had λ_{max} 248 nm (ε 4800) [lit.[9] λ_{max} 249 nm (ε 6400)], and the nmr spectrum showed considerable diminution of the peaks at τ 4.70 and 8.73, suggesting extensive isomerization of the double bond from the 7,8 to 8,9 position (*cf.* acid isomerization of **8** to a mixture of **7** and **14**).

Epoxidation of Methyl 13-Abieten-18-oate.—A solution of 106 mg (0.33 mmol) of the oily methyl ester of chromatographically pure **9** and 110 mg (0.64 mmol) of *m*-chloroperbenzoic acid in 5 ml of chloroform was stirred at 25° for 0.5 hr. Recovery of the neutral fraction afforded 108 mg of solid epoxide which, although homogeneous by tlc, recrystallized from methanol to give a product with mp 93–100°. The nmr spectrum exhibited signals at τ 6.34 (methoxyl), 7.64 (C-14 H, slightly broadened), 8.86 (C-4 methyl), 9.16 (C-10 methyl), and a pair of doublets centered at 9.07 and 9.11 (J = 6.5 Hz, isopropyl). (These values differ from those reported by Huffman, *et al.*,[8,17] for an epoxide apparently derived from the 8α-13-ene acid **6** present in a preparation of **8** melting at 187–194°.) A sample recrystallized from ether for analysis had mp 87–94°.

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25. Found: C, 75.55; H, 10.33.

Isomerization of Acids 5 and 8. A. 13β-Abiet-8-en-18-oic Acid (13).—As an alternative to the reported[12] isomerization of **5** to **13** with hydrogen bromide in acetic acid (which we found to yield bromine-containing products), a modification of the procedure of Edwards and Howe,[53] suggested to us by Professor Ernest Wenkert from work of Dr. A. Afonso,[44] was employed. A solu-

(60) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin. *J. Chem. Soc.*, 2548 (1953).

(61) We thank Dr. Ulrich Weiss and Mr. David W. Hudson, NIAMD, National Institutes of Health, Bethesda, Md., for this determination.

tion of 1.0 g (3.3 mmol) of **5** (mp 144–147°) and 0.1 g of *p*-toluenesulfonic acid in 30 ml of benzene was refluxed for 1 hr. After the solution had been washed with water, the product was recovered by evaporation of the solvent and crystallization from acetone to yield 0.84 g (84%) of **13** as platelets: mp 181–183°; $[\alpha]_D$ +120° (lit. mp 175°, $[\alpha]_D$ +125°;[11] mp 185°, $[\alpha]_D$ +125°;[12] mp 185–187°[62]). The nmr spectrum was devoid of olefinic proton absorption, and the methyl ester was homogeneous by glpc. A recrystallized sample had mp 183–185°; $[\alpha]_D$ +124°; ORD (*c* 0.10) $[\Phi]_{400}$ +860°, $[\Phi]_{300}$ +2100°; ORD (*c* 0.0050) $[\Phi]_{230}$ +8500°, $[\Phi]_{210}$ +27,000°, $[\Phi]_{200}$ ±0°; CD (*c* 0.0027) $[\Theta]_{235}$ ±0, $[\Theta]_{199}$ +26,500, $[\Theta]_{188}$ +17,000. The diamylamine salt crystallized from acetone in flattened needles, mp 117–118°.

B. 8-Abieten-18-oic Acid (14).—Application of the above procedure to the **8–9** mixture, mp 194–197°, afforded a similar yield (80%) of isomerized product which, after two crystallizations from acetone, had mp 173–176°; $[\alpha]_D$ +6° (lit.[9c] mp 174.5–176°, $[\alpha]_D$ +8°). However, the nmr spectrum and glpc of the methyl ester showed that this product contained *ca.* 20–25% **7** and only 75–80% desired 8-ene acid **14**. Separation was effected by chromatography of the methyl esters on silver nitrate impregnated alumina,[15] with the ester of **14** being eluted before that of **7**. Hydrolysis of the purified ester furnished pure **14** which crystallized from acetone as short needles: mp 164–166° with resolidification and remelting at 172–174°; $[\alpha]_D$ +6°; ORD (*c* 0.10) $[\Phi]_{400}$ −380°, $[\Phi]_{300}$ −780°, $[\Phi]_{250}$ −2000°; ORD (*c* 0.0125) $[\Phi]_{225}$ −6700°, $[\Phi]_{217}$ ±0°, $[\Phi]_{210}$ +6900°; CD (*c* 0.0125) $[\Theta]_{245}$ ±0, $[\Theta]_{215}$ −7300, $[\Theta]_{200}$ −2500.

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.53; H, 10.64.

The diamylamine salt crystallized from acetone in long thin needles, mp 124–125.5°.

C-13 Epimeric Dihydroabietic γ- and δ-Lactones 15 and 16.—Treatment of 0.10 g of **13** with 3 ml of a saturated solution of hydrogen bromide in glacial acetic acid for 18 hr at 25°, or with 2 ml of 18 *M* sulfuric acid (*d* 1.84) for 1 hr at 0°, gave a mixture showing a strong ir band at 5.65 μ (γ-lactone) and lesser peaks at 5.80 (δ-lactone) and 5.90 μ (acid). Two recrystallizations of the neutral fraction from acetone furnished 45 mg (45%) of 13β-dihydroabietic γ-lactone **15a** (**9,5-friedo-13β-abietan-18:10-olide**): mp 129.5–131°; $[\alpha]_D$ −3° (lit.[7,12] mp 130–131°; $[\alpha]_D$ −2°, −6°); nmr signals at τ 8.95 (C-4 methyl), 9.11 (d, J = 6 Hz, isopropyl), and 9.15 (C-9 methyl). When allowed to stand in concentrated sulfuric acid for 24 hr at 25°, **15a** was converted into a mixture of γ- and δ-lactones in a ratio of *ca.* 55:45, determined by the relative ir absorption at 5.65 and 5.80 μ[24,27] and confirmed by glpc (see below). Hydrolysis of this mixture with potassium hydroxide in refluxing *n*-butyl alcohol[9] furnished 13β-dihydroabietic δ-lactone **16a** (**5β,13β-abietan-18:9-olide**) in 35% yield. When crystallized from methanol this formed small plates: mp 147–149°; $[\alpha]_D$ +42° (lit. mp 151–152°, $[\alpha]_D$ +42.6°;[24] mp 149°, $[\alpha]_D$ +43°[26]); ir 5.80 μ; nmr as recorded by Herz and Wahlborg.[24] When allowed to stand in concentrated sulfuric acid for 24 hr at 25°, **16a** gave the same 55:45 ratio of γ- and δ-lactones obtained from **15a**.

For preparation of γ-lactone **15b**, a solution of 1.0 g (3.3 mmol) of acid **14** (containing 25% acid **7**) in 20 ml of chloroform, was stirred with 0.6 ml of 18 *M* sulfuric acid for 10 min at 0°. The ir spectrum of the product indicated the presence of 20% γ-lactone and 80% unchanged acid. With longer reaction times a δ-lactone band at 5.80 μ began to appear in the spectrum. Crystallization from acetone–water separated the bulk of unchanged acid. Chromatography of the mother liquor residues on 15 g of neutral alumina (activity grade II) afforded, by elution with ether, 0.16 g (16%) of 13α-dihydroabietic γ-lactone **15b** (**9,5-friedoabietan-18:10-olide**), which crystallized from methanol in needles: mp 101–102°; $[\alpha]_D$ −45°; ir 5.65 μ; nmr τ 8.93 (C-4 methyl), 9.05 (C-9 methyl), and 9.08 (d, J = 6 Hz, isopropyl).

Anal. Calcd for $C_{20}H_{32}O_2$: C, 78.90; H, 10.59. Found: C, 78.60; H, 10.52.

When allowed to stand in 5 ml of 18 *M* sulfuric acid for 24 hr at 25°, 0.50 g of **15b** gave a mixture of γ- and δ-lactones in a ratio of *ca.* 1:99, whereas contact with sulfuric acid for 1 hr at 0° produced a 40:60 ratio, as reported.[9] Selective removal of residual γ-lactone by saponification as above in the isolation of **16a** gave 13α-dihydroabietic δ-lactone **16b** (**5β-abietan-18:9-olide**), which showed carbonyl absorption only at 5.80 μ. Further purification by chromatography on 10 g of neutral alumina and elution with ether afforded 0.38 g (76%) of **16b** as a colorless oil, $[\alpha]_D$ −38° (lit.[9] $[\alpha]_D$ −43°), which could not be induced to crystallize. The principal nmr peaks appeared at τ 8.80 (C-4 methyl), 8.92 (C-10 methyl), and 9.06 (d, J = 5.5 Hz, isopropyl). Sulfuric acid equilibration of this product for 24 hr at 25° produced the 1:99 mixture of γ- and δ-lactones obtained from **15b**.

The percentage equilibrium ratios (by ir analysis[24]) of γ-lactone to δ-lactone from sulfuric acid treatment at 25° of some of the other dihydroabietic acids investigated in this study were as follows: acid **4**, 55:45; acid **7–9** mixture (mp 161–162°), 5:95; acid **8–9** mixture (mp 194–197°), 5:95; acid **27** (see later), 10:90. By glpc at 200° on DEGS, **15a**, **15b**, **16a**, and **16b** were separated cleanly and exhibited the following retention times relative to methyl pimarate: 4.78, 2.39, 3.35, and 3.51, respectively. On SE-30/EGiP, the values relative to the same standard were 1.97, 1.23, 1.47, and 1.58.

Reduction–Hydroboration of Acids 8 and 5. A. Abietane-14β,18-diol (21).—To an ice-cold solution of 0.4 g of lithium aluminum hydride and 1.0 g (3.3 mmol) of acid **8–9** mixture, mp 190–195°, in 30 ml of dry ether was added 2.0 ml of boron trifluoride etherate in 30 ml of ether over a period of 3 hr.[38] The mixture was allowed to warm to 25° and was then stirred for 6 hr. Saturated sodium sulfate solution was slowly added until hydrolysis was complete and the mixture had turned white. Solid sodium sulfate was then added, and the coagulated salts were separated by filtration. The ether filtrate was evaporated, and the solid residue was dissolved in 70 ml of 80% ethanol containing 1.0 g of sodium hydroxide. To this was added slowly, with stirring, 6.0 ml of 30% hydrogen peroxide, and the mixture was refluxed overnight. The oily product obtained on extraction with chloroform was dissolved in hot benzene, causing crystallization to occur. After completion of crystallization at room temperature (further cooling led to the formation of very stable gels with the solvent), there was obtained 0.65 g (65%) of diol **21** as prisms, mp 172–174°. A recrystallized sample had mp 173–175°; $[\alpha]_D$ +11°; nmr spectrum (pyridine) τ 6.51 (AB quartet, J = 11 Hz, C-4 hydroxymethyl[63]), 6.87 (t, J = 9 Hz, C-4 H), 9.00 and 9.12 (overlapping isopropyl doublets, J = 6.5 Hz), 9.09 (C-4 methyl), and 9.15 (C-10 methyl).

Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 78.08; H, 11.72.

In agreement with the proposed structure and configuration, the nmr spectrum of the oily diacetate of **21**, prepared by acetylation with acetic anhydride in pyridine, showed signals at τ 5.50 (t, J = 10 Hz, C-4 H), 6.31 (AB quartet, J = 11 Hz, C-4 acetoxymethyl[63]), 8.03 and 8.05 (acetate methyls), 9.12 (C-4 methyl), 9.15 (d, J = 7 Hz, isopropyl), and 9.17 (C-10 methyl).

B. 13β-Abietane-14α,18-diol (24).—Application of the foregoing reduction–hydroboration procedure to 1.0 g (3.3 mmol) of **5**, mp 144–147°, furnished 0.60 g (60%) of a diol which formed stable gels with most crystallization solvents. Partial purification by chromatography on 20 g of silica gel and elution with ether, followed by crystallization from ether, afforded **24** as a microcrystalline solid which softened at 115° and melted at 155–157°: nmr signals at τ 6.27 (t, J = 6.5 Hz, C-14 H), 6.71 (AB quartet, J = 10 Hz, C-4 hydroxymethyl[63]), 8.96 (deshielded C-10 methyl), 9.06 and 9.12 (overlapping isopropyl doublets, J = 6.5 Hz), and 9.18 (C-4 methyl).

Anal. Calcd for $C_{20}H_{36}O_2$: C, 77.87; H, 11.76. Found: C, 77.94; H, 11.89.

The nmr spectrum of the oily diacetate of **24** showed peaks at τ 4.85 (t, J = 9 Hz, C-14 H), 6.30 (AB quartet, J = 11 Hz, C-4 acetoxymethyl[63]), 8.05 and 8.07 (acetate methyls), 8.93 (deshielded C-10 methyl), 9.05 and 9.11 (overlapping isopropyl doublets, J = 6 Hz), and 9.19 (C-4 methyl).

A later minor fraction from chromatography of the mother liquors from the hydroboration reaction had mp 125–127°, but this was not examined further.

Oxidation of Diols 21 and 24. A. 14-Oxoabietan-18-oic Acid (22).—To a stirred solution of 1.0 g (3.3 mmol) of **21** in 60 ml of acetone at 0° was added 6.0 ml of Jones reagent.[60] A green

(62) C. Tabacik-Wlotzka, M. Mousseron, and A. Chafaï, *Bull. Soc. Chim. Fr.*, 2299 (1963).

(63) A. Gaudemer, J. Polonsky, and E. Wenkert, *ibid.*, 407 (1964), and references cited therein.

precipitate formed rapidly and gradually coagulated to a hard mass. After 8 hr at 25°, the mixture was treated with 5 ml of methanol and then with 100 ml of water, with stirring and heating, to digest the precipitate. The crude keto acid **22**, collected by filtration, weighed 0.87 g (81%): mp 251–254°. Recrystallization from methanol gave colorless rectangular platelets: mp 257–259°; $[\alpha]D$ +19°. Huffman, *et al.*,[8] record mp 256–257°, $[\alpha]D$ +21°, for a sample prepared from the β-epoxide[9] of **8**.

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 74.98; H, 10.06.

Esterification with diazomethane gave the methyl ester of **22**, which crystallized from methanol in needles: mp 80–81°; $[\alpha]D$ +14°; nmr as recorded by Huffman, *et al.*[8]

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25. Found: C, 75.19; H, 10.11.

Neither acid **22** nor its methyl ester formed a semicarbazone or 2,4-dinitrophenylhydrazone under the usual conditions. (Cross and Myers[16] report formation of the latter derivative from the ester after reaction for 14 days.) Neither the acid nor ester was epimerized by sodium methoxide in refluxing methanol or 5% hydrochloric acid in diglyme at 100°. The ORD[61] of **22** in methanol was the same as that recorded by Huffman, *et al.*,[8] for an ethanol solution.

B. 14-Oxo-13β-abietan-18-oic Acid (25).—Application of the foregoing oxidation to 0.40 g of **24** furnished 0.35 g of crude **25**, which partially solidified but could not be obtained crystalline. The nmr spectrum showed peaks at τ 8.84 (C-4 methyl), 9.09 and 9.15 (overlapping isopropyl doublets, J = 7 Hz), and 9.13 (C-10 methyl). The 2,4-dinitrophenylhydrazone of the methyl ester (diazomethane) formed readily but melted over the range 100–112°. When seeded with a sample prepared as described below, the methyl ester of **25** crystallized from methanol–water in fine needles: mp 79–79.5°; $[\alpha]D$ −92°; nmr τ 6.35 (methoxyl), 8.83 (C-4 methyl), 9.09 and 9.14 (overlapping isopropyl doublets, J = 7 Hz), and 9.16 (C-10 methyl); ORD (*c* 0.0435) $[\Phi]_{400}$ −690°, $[\Phi]_{319}$ −2300°, $[\Phi]_{313}$ −1650°, $[\Phi]_{309}$ −1850°, $[\Phi]_{283}$ +230°; CD (*c* 0.0435) $[\Theta]_{330}$ ±0, $[\Theta]_{297}$ −1550, $[\Theta]_{220}$ +1850.

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25. Found: C, 75.15; H, 10.42.

As an alternative route to the methyl ester of **25**, 1 ml of boron trifluoride etherate was added dropwise to a stirred solution of 0.44 g (1.47 mmol) of the methyl ester (mp 83–85°) of **5** and 0.2 g of sodium borohydride in 10 ml of dry diglyme cooled to 0°. The mixture was stirred for 3 hr at 25°, and 5 ml of 10% sodium hydroxide and 5 ml of 30% hydrogen peroxide were added. Stirring was continued for an additional 3 hr, water was added, and the neutral product was isolated by extraction with chloroform. Crystallization from methanol gave 0.28 g (57%) of **methyl 14α-hydroxy-8α,13β-abietan-18-oate** as fine needles: mp 137–137.5°; nmr ($CDCl_3$) τ 6.35 (methoxyl), 6.54 (hydroxyl), 8.82 (C-4 methyl), 9.00 (deshielded C-10 methyl), and 9.10 and 9.20 (pair of doublets, isopropyl, J = 7 Hz).

Anal. Calcd for $C_{21}H_{36}O_3$: C, 74.95; H, 10.78. Found: C, 74.72; H, 10.85.

Oxidation of 0.23 g (0.97 mmol) of the foregoing product in 10 ml of acetone at 0° by dropwise addition of Jones reagent[60] until the orange color persisted for 5 min afforded 0.15 g (65%) of recrystallized methyl ester of **25**, mp 79–79.5° (see above). When conducted with Jones reagent prepared with D_2SO_4 and D_2O (with precautions to exclude moisture in the work-up with D_2O), the oxidation yielded a keto ester containing one deuterium atom, as was determined by comparison of the mass spectrum with that of a nondeuterated sample.

Methyl 14-Oxoabietan-18-oate Ethylenethioketal (23a).—A solution of 0.50 g (1.5 mmol) of the methyl ester of **22** in 2.0 ml of ethanedithiol and 0.6 ml of boron trifluoride etherate was prepared at 0° and allowed to stand overnight at 20°. Extraction of the solidified mixture with benzene, repeated washing with 5% sodium hydroxide solution, and recrystallization of the product from methanol–benzene gave 0.56 g (91%) of thioketal **23a** as feathery needles: mp 205.5–206.5°; $[\alpha]D$ −33° ($CHCl_3$); nmr (*cf.* Huffman, *et al.*[8]) τ 6.33 (methoxyl), 6.79 (ethylenethioketal protons), 8.84 (C-4 methyl), 9.15 (C-10 methyl), and a pair of doublets centered at 9.01 and 9.08 (J = 6.5 Hz, isopropyl).

Anal. Calcd for $C_{23}H_{38}O_2S_2$: C, 67.27; H, 9.33; S, 15.62. Found: C, 67.31; H, 9.25; S, 15.48.

In larger batches, the formation of **23a** was attended by considerable epimerization[8] (mainly at C-13 to give **23b**), as shown by the lower melting point (195–202°) of the product and by its subsequent conversion into samples of **19** containing significant amounts of the C-13 epimer **18** (see below).

Methyl 14-Oxo-13β-abietan-18-oate Ethylenethioketal (23b).—By the procedure used to prepare **23a**, 0.11 g of the methyl ester of **25** (mp 77–79°) was converted in comparable yield into **23b**, which crystallized from benzene in needle clusters: mp 192–195° (lit.[8] mp 192–193°); nmr spectrum as recorded by Huffman, *et al.*,[8] for a sample isolated from the mother liquors of **23a**.

Anal. Calcd for $C_{23}H_{38}O_2S_2$: C, 67.27; H, 9.33. Found: C, 67.45; H, 9.61.

Abietan-18-oic Acid (19). A. From Thioketal 23a.—A stirred suspension of *ca.* 25 g of Raney nickel catalyst (W-2) and 1.30 g (3.15 mmol) of **23a**, mp 205.5–206.5°, in 300 ml of absolute ethanol was refluxed overnight. The neutral product was purified by chromatography on 25 g of neutral alumina (elution with 1:1 ether–petroleum ether). There was obtained 0.86 g (85%) of an oil which when seeded with a sample of the methyl ester of **19**, prepared as described below, crystallized slowly from methanol at −10 to −20°: mp 45–46°; $[\alpha]D$ +7° (lit. mp 44–45°;[64] $[\alpha]D$ +7.2°[11]). Glpc showed the crystalline ester (0.55 g, 55%) to be homogeneous, but the crude material averaged about 5–10% methyl ester of **18** and up to 20% methyl ester of **14**, depending on the activity of the Raney nickel. Saponification of the crystalline ester gave 0.47 g (90%) of **19** as prisms from acetone: mp 180–182°; $[\alpha]D$ +6° (lit. mp 180–181°, $[\alpha]D$ +10°;[8] mp 185.5–186°, $[\alpha]D$ −2.3°;[9] mp 185–186°, $[\alpha]D$ +12.4°;[11] mp 183–184°, $[\alpha]D$ +6°;[64] mp 179–181°, $[\alpha]D$ +6.2°[65]); ORD (*c* 0.288) $[\Phi]_{400}$ +60°, $[\Phi]_{300}$ +205°, $[\Phi]_{233}$ +1550°, $[\Phi]_{217}$ ±0°, $[\Phi]_{200}$ −1500°; CD (*c* 0.288) $[\Theta]_{250}$ ±0, $[\Theta]_{217}$ +3100, $[\Theta]_{190}$ ±0.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.51; H, 10.99.

B. From Acid 8 by Hydrogenation.—A solution of 1.0 g (3.3 mmol) of acid mixture **8–9**, mp 194–197°, in 30 ml of acetic acid–ethyl acetate (1:1) was hydrogenated over 0.2 g of platinum oxide during 30 min. The resulting solid gave a negative test with tetranitromethane, and the nmr spectrum showed no detectable signal at τ 8.90 (absence of **17**; see Table I). Glpc of the methyl ester of the crude product from several runs or from hydrogenation of pure **8**, mp 199–200°, indicated the presence of *ca.* 90% **19** and 10% **18** but no **17** (Table III). Crystallization of the crude acid from acetone gave 0.81 g (80%) of **19** as prisms: mp 179.5–181°, raised to 180–181.5° by recrystallization; $[\alpha]D$ +6°. Further purification by means of the diamylamine salt, mp 127–127.5°, gave material with mp 181.5–182°, $[\alpha]D$ +6°. The methyl ester (mp 45–46°, $[\alpha]D$ +7°) crystallized from methanol at −10 to −20°.

For spectral and comparison purposes, an authentic sample of **8α,13β-abietan-18-oic acid** (**17**) was prepared as follows. A solution of 3.0 g (0.01 mol) of abietic acid (**1**)[50] in 30 ml of absolute ethanol was hydrogenated over 10 g of W-2 Raney nickel catalyst at 200° and 3000 psi for 8 hr.[11] The nmr spectrum (Table I) of the total reduction product and glpc of its methyl ester on DEGS indicated that **17** was the predominant product. Three crystallizations from methanol furnished 1.05 g (35%) of **17** as needles: mp 165–167°; $[\alpha]D$ +17° (lit. mp 164°, $[\alpha]D$ +21°;[8] mp 165–166°, $[\alpha]D$ +28.3°;[11] mp 168°, $[\alpha]D$ +23°;[12] mp 163–164.5°, $[\alpha]D$ +26°;[66] mp 168–170°, $[\alpha]D$ +19°[67]); ORD (*c* 0.237) $[\Phi]_{400}$ +175°, $[\Phi]_{300}$ +370°, $[\Phi]_{233}$ +1840°, $[\Phi]_{215}$ ±0°, $[\Phi]_{205}$ −750°; CD (*c* 0.237) $[\Theta]_{250}$ ±0, $[\Theta]_{215}$ +1900, $[\Theta]_{190}$ ±0. The methyl ester crystallized from methanol in stout needles: mp 95–97°; $[\alpha]D$ +13° (lit. mp 97–98°, $[\alpha]D$ +11°;[8] mp 99°, $[\alpha]D$ +21.3°;[11] mp 96°, $[\alpha]D$ +15°;[12] mp 99°, $[\alpha]D$ +20°[66]).

For preparation of an authentic sample of **13β-abietan-18-oic acid** (**18**), a solution of 1.0 g (3.3 mmol) of **5**, mp 144–147°, in 25 ml of acetic acid was hydrogenated over prereduced platinum oxide as reported previously.[12] The nmr spectrum of the crude product and glpc of its methyl esters (Table III) indicated that **18** and **17** were present in the ratio of 2:1, along with minor amounts of **19**. After six recrystallizations from acetone, there was obtained 0.28 g (27%) of pure **18** as prisms: mp 200–201°; $[\alpha]D$ +8° (lit. mp 201–201.5°, $[\alpha]D$ +8°;[8] mp 202°, $[\alpha]D$ +7°[12]); ORD (*c* 0.201) $[\Phi]_{400}$ −8°, $[\Phi]_{300}$ ±0°, $[\Phi]_{233}$ +1800°, $[\Phi]_{215}$ ±0°, $[\Phi]_{205}$ −1500°; CD (0.201) $[\Theta]_{245}$ ±0, $[\Theta]_{216}$ +2200, $[\Theta]_{195}$ ±0. The methyl ester after crystallization from wet methanol had

(64) E. E. Fleck and S. Palkin, *J. Amer. Chem. Soc.*, **60**, 921 (1938).

(65) L. Ruzicka and St. Kaufmann, *Helv. Chim. Acta*, **24**, 1389 (1941). See also other references cited on p 384 in ref 7.

(66) L. F. Fieser and W. P. Campbell, *J. Amer. Chem. Soc.*, **60**, 159 (1938).

(67) L. Ruzicka and H. Schinz, *Helv. Chim. Acta*, **6**, 662 (1923).

mp 74–76° (lit. mp 75–77°,[8] 77°[12]). Application of the Huang-Minlon modification[68] of the Wolff–Kishner reduction to the methyl ester of **22** gave this same tetrahydro acid, as also observed by Huffman, *et al.*[8]

Desulfurization of ethylenethioketal **23b** (mp 190–192°) furnished the methyl ester of **18** with a purity greater than 90% according to analysis by glpc (ester of **19** apparent major impurity).

13(15)-Abieten-18-oic Acid (27).—Abietic acid dihydrobromide (**26**), mp 172–174°, was prepared by the method of Hasselstrom and McPherson.[42] The product (**27**) of mild sodium–alcohol reduction was obtained by the following modification of the published procedure.[42] To an ice-cold solution of 15 g of sodium dissolved in 600 ml of absolute ethanol, 10.0 g (0.022 mol) of abietic acid dihydrobromide was added (insoluble), followed by 15 g of sodium in 0.1-g pieces, with cooling and stirring. After 2 hr the ice bath was removed and the mixture was allowed to stir overnight at 20°. After dilution with 3 l. of water the mixture was extracted with two 200-ml portions of petroleum ether (discarded) and acidified to pH 2 with 6 *N* hydrochloric acid. Further extraction with three 200-ml portions of ether, followed by drying over anhydrous sodium sulfate, treatment with Norit, filtration, and evaporation of the solvent, furnished impure **27** as colorless plates from acetone: mp 180–205°; yield 1.165 g (18%). Three crystallizations gave material with mp 210–216°; $[\alpha]_D$ −15° (changed by further crystallization to mp 218–220°; $[\alpha]_D$ −18°) (lit.[42] mp 217.5–218.5°; $[\alpha]_D$ −23°); ORD (*c* 0.20) $[\Phi]_{400}$ −140°, $[\Phi]_{300}$ −250°, $[\Phi]_{245}$ ±0°, $[\Phi]_{230}$ +650°; ORD (*c* 0.040) $[\Phi]_{317}$ +1350°, $[\Phi]_{210}$ +650°; CD (0.00735) $[\Theta]_{250}$ ±0, $[\Theta]_{208}$ +5500, $[\Theta]_{200}$ ±0. The methyl ester had mp 129.5–130.5° (lit.[42] mp 131.5–132.5°).

13-Oxopodocarpan-18-oic Acid (28). A. From Acid 27.—Ozone (5% in dry oxygen) was bubbled slowly through a solution of 200 mg (0.66 mmol) of **27** in 40 ml of ethyl acetate at −78° until the solution turned blue. The solution was then flushed with nitrogen, allowed to warm to room temperature, and stirred under hydrogen over 10% palladium on carbon. Three crystallizations of the resulting solid from methanol gave 85 mg (46%) of **28** as needles: mp 158–159°; $[\alpha]_D$ +16°; nmr τ 8.82 (C-4 methyl) and 9.08 (C-10 methyl).

Anal. Calcd for $C_{17}H_{26}O_3$: C, 73.35; H, 9.41. Found: C, 73.43; H, 9.36.

Ozonolysis of the methyl ester of **27** gave the methyl ester of acid **28** (see part B below), whose yellow 2,4-dinitrophenylhydrazone crystallized from methanol–water: mp 192–194°.

Hydroxylation with osmium tetroxide in the manner described for the methyl ester of **5** converted 96 mg (0.3 mmol) of the methyl ester of **27** into 57 mg (54%) of the corresponding glycol ester, characterized by nmr signals at τ 6.38 (methoxyl), 7.60 (OH), 8.82 (C-4 methyl), 8.87 (C-15 methyls), and 9.16 (C-10 methyl). Cleavage with lead tetraacetate gave the methyl ester of **28**, with identical infrared and nmr spectra. The 2,4-dinitrophenylhydrazone had mp and mmp 192–194°.

B. From Neoabietic Acid (2).—To a solution of 200 mg (0.69 mmol) of **29** (mp 123–125°, prepared by partial ozonolysis of methyl neoabietate[6,43]) in 40 ml of dry ether and 50 ml of liquid ammonia was added 0.5 g of lithium shot[51] in portions with stirring. After 15 min, 10 ml of ethanol was added to discharge the blue color. The product recovered after evaporation of the ammonia and extraction from water with ether and then chloroform was apparently mostly diol in nature (ir absorption at 2.8 and 3.0 μ but none in the 5.7–6.2-μ region). This material was stirred with 0.5 ml of Jones reagent[50] in 10 ml of acetone for 3 hr. Isolation of the acidic product by dilution with water, extraction with ether, and crystallization from methanol gave 65 mg (34%) of needles of acid **28**, mp 158–159°, undepressed on admixture with the preparation obtained above. The ir and nmr spectra of the acid as prepared by the two routes were also indistinguishable. Treatment of the mother liquors from the crystallization of the oxidation product with diazomethane and then with 2,4-dinitrophenylhydrazine reagent gave the yellow 2,4-dinitrophenylhydrazone, mp and mmp 192–194° (after three recrystallizations), of the methyl ester of **28**, as described above.

In an alternative procedure (by Dr. A. Afonso[44]), the crude acid from application of the above sequence to 370 mg (1.28 mmol) of **29** was esterified with diazomethane and chromatographed on 12 g of neutral alumina (activity grade II). Elution with benzene–hexane (1:1) gave 230 mg (62%) of the methyl ester of acid **28**, which crystallized from aqueous methanol: mp 98–104°; $[\alpha]_D$ +18°; ORD (0.10) $[\Phi]_{400}$ +85°, $[\Phi]_{312}$ +3300°, $[\Phi]_{280}$ +900°; ORD (*c* 0.010) $[\Phi]_{285}$ +18,000°, $[\Phi]_{220}$ ±0°, $[\Phi]_{210}$ −23,000°; CD (*c* 0.010) $[\Theta]_{330}$ ±0, $[\Theta]_{298}$ +1550, $[\Theta]_{265}$ +1200, $[\Theta]_{216}$ +16,500, $[\Theta]_{196}$ ±0.

Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found: C, 73.59; H, 9.51.

Hydrogenation of 0.1 g (0.35 mmol) of **29** over 50 mg of 10% palladium on carbon in 15 ml of ether[46] at 30° (1 atm) was complete in 20 min and furnished a solid, mp 65–75°, whose nmr spectrum indicated the presence of predominantly B/C-*cis* product **30** (deshielded C-10 methyl resonance at τ 8.92) along with the methyl ester of **28**. Glpc on SE-30/EGiP showed that **30** and the methyl ester of **28** were present in the ratio of 7:4, with retention times of 1.64 and 1.40, respectively, relative to methyl pimarate.

8,13(15)-Abietadien-18-oic Acid (31).—The acids remaining in the mother liquors from the preparation of **27** were converted into the methyl esters with diazomethane. After three crystallizations of the very impure product from methanol, well-formed needles were deposited, which, after two further crystallizations, had mp 104.5–106°; $[\alpha]_D$ +161°; yield 0.60 g (9% from **26**). The nmr spectrum indicated that no olefinic protons were present, thus showing that the substance was the methyl ester of the nonconjugated diene acid **31**. The uv spectrum showed λ_{max} 194.5 nm (ϵ 30,800).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.38; H, 9.95.

Saponification of the ester with 10% potassium hydroxide in ethylene glycol at 180° gave the corresponding acid, **31**, which crystallized from acetone–water in small needles: mp 162–165°; $[\alpha]_D$ +165°; ORD (*c* 0.30) $[\Phi]_{400}$ +1250°, $[\Phi]_{300}$ +3200°; ORD (*c* 0.010) $[\Phi]_{250}$ +7300°, $[\Phi]_{230}$ +18,000°, $[\Phi]_{215}$ ±0°; CD (0.010) $[\Theta]_{250}$ ±0, $[\Theta]_{222}$ +18,500, $[\Theta]_{200}$ ±0.

Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00. Found: C, 79.58; H, 10.13.

By nmr analysis **31** was the major product when the reaction was conducted at elevated temperatures or if the addition of sodium to the sodium ethoxide suspension of **26** was omitted. For isomerization to abietic acid (**1**), a solution of 20 mg of **31** in 5 ml of 5% hydrochloric acid in ethanol was refluxed overnight under nitrogen. This led to the characteristic uv absorption spectrum of abietic acid:[6,48] λ_{max} 235 nm (ϵ 21,100), 241.5 (22,500), and 250 (15,100).

Registry No.—**4,** 19407-36-4; **5,** 19407-37-5; **7,** 19407-38-6; **8,** 19407-39-7; **9,** 19402-25-6; **11a,** 19402-26-7; **11b,** 19402-27-8; **14,** 19402-28-9; **15b,** 19402-29-0; **19,** 19402-30-3; **21,** 19426-92-7; **22,** 19426-93-8; **22** methyl ester, 19426-94-9; **23a,** 19426-95-0; **23b,** 14519-73-4; **24,** 19426-97-2; **25** methyl ester, 19426-98-3; **25** methyl ester (2,4-dinitrophenylhydrazone), 19427-03-3; **27,** 19402-31-4; **28,** 19402-32-5; **31,** 19402-33-6; **31** methyl ester, 19402-34-7; methyl 8α,14α-dihydroxy-13β-abietan-18-oate, 19426-99-4; methyl 8α,14α-dihydrohyabietan-18-oate, 19427-00-0; methyl 14α-hydroxy-8α,13β-abietan-18-oate, 19427-01-1; epoxide of mp 87–94° ($C_{21}H_{34}O_3$), 19427-02-2.

Acknowledgment.—We are indebted to Mr. Ray V. Lawrence and Dr. G. W. Hedrick for generous gifts of WW-gum rosin, levopimaric acid, and specimen samples of abietic, neoabietic, and palustric acid. We also thank Dr. Robert A. Micheli for several steroid samples; Mr. Martin Wesolowski for the far-uv data; Mr. Rodney C. Barkhurst for assistance with some of the ORD and CD measurements; Mr. Roger C. Briden for the HA-100 nmr spectra; Dr. J. C. W. Chien and Dr. James N. Shoolery for earlier nmr spectra of the acid **8–9** mixture; and Rev. George F. Gould, S. J., Mrs. James W. Hayden, Dr. Michael L. Trollope, and Dr. John S. Swenton for their help with some of the initial stages of the work.

(68) Huang-Minlon, *J. Amer. Chem. Soc.*, **68**, 2487 (1946).