dimethyl); n.m.r. signals at 0.82, 0.87, 1.00, and 1.01 p.p.m. (methyl singlets).

Anal. Calcd. for $C_{20}H_{34}$: C, 87.51; H, 12.49. Found: C, 87.54; H, 12.25.

C.—The previous procedure was modified because of the observed volatility of the hydrocarbon. A mixture of 0.175 g. of **22d**, 10 ml. of ethylene glycol, and 0.35 ml. of 95% hydrazine was refluxed for 20 min., concentrated to b.p. 193° (about 10 min.), then allowed to cool for 30 min. Colorless needles (probably hydrazone) separated. Potassium hydroxide (1.15 g.), 0.15 ml. of hydrazine, and 3 ml. of ethylene glycol (3 ml.) were added, and the mixture was refluxed for 3 hr. Working up as for B gave isohibane **22f** as a colorless solid (0.14 g., 84%), identical with the hydrocarbon described above.

Resin Acids. III. 9-Hydroxyabietic Acid and Its Transformation Products*[1,2]

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The structure of the substance produced by selenium dioxide oxidation of abietic acid is revised to 9-hydroxyabietic acid. The assignment is based on spectroscopic evidence and on conversion to $\Delta^{7,9(11)}$-abietadienoic acid which was in turn synthesized from $\Delta^{8(9)}$-abietenoic acid. In the course of this work, an entry into the pseudoabietic acid series has been effected and the stereochemistry of the various lactones belonging to this series has been elucidated.

Oxidation of abietic acid (**1**) with selenium dioxide furnishes dehydroabietic acid and a hydroxyabietic acid which has been assigned formula **2**, 12-hydroxyabietic acid, by Fieser and Campbell[4] because of its oxidation with potassium permanganate to isobutyric acid, its ultraviolet spectrum which reportedly was superimposable on that of abietic acid, and because of its failure to yield a lactone. The allylic nature of the hydroxyl group demanded by **2** was demonstrated by an attempt at hydrogenation with platinum oxide in acetic acid which resulted in hydrogenolysis and formation of a dihydroabietic acid.[5]

A puzzling feature of the chemistry of hydroxyabietic acid is that on heating at 175–200° in an atmosphere of nitrogen it was reported to undergo dehydration to "anhydrohydroxyabietic acid," m.p. 167.5–169.5°, $[\alpha]^{25}\mathrm{D}$ +21°. This substance had an ultraviolet spectrum very similar to that of abietic acid, was oxidized to isobutyric acid with potassium permanganate, was unsaturated toward bromine, gave on nitration the same 12,14-dinitrodehydroabietic acid produced more directly by nitration of dehydroabietic acid, was slowly reduced to a tetrahydroabietic acid under the influence of platinum in acetic acid solution, and was therefore assigned[4] formula **4**. On the other hand, Sandermann[6] claimed to have obtained an acid, m.p. 172°, $[\alpha]\mathrm{D}$ +21, identical with "anhydrohydroxyabietic acid," by pyrolysis of maleopimaric acid (**5**),[7] but assigned to it a different structure. Sandermann named this material "isoabietic acid" and suggested that it was a C-9 stereoisomer of abietic acid, but doubts[5] have been expressed about the homogeneity of "isoabietic acid" and its identity with "anhydrohydroxyabietic acid."

For a number of reasons we had occasion to repeat the selenium dioxide oxidation of abietic acid. Our study of the product whose properties tally with those given in the literature[4] shows that its structure must be revised to 9-hydroxyabietadienoic acid (**6a**). The results are described in this paper, together with relevant material that has led to an entry into the pseudoabietic acid (**7**) series of compounds. Work describing the preparation and proof of structure of authentic 12-hydroxyabietadienoic acid (**2**) will be described in a future publication.

While the infrared and ultraviolet spectrum of the minor selenium dioxide oxidation product[8] indicated the presence of the heteroannular diene chromophore already postulated earlier,[4] the n.m.r. spectrum[9] which had sharp methyl singlets at 0.92 (C-10 methyl) and 1.30 (C-4 methyl), two superimposed methyl doublets centered at 0.94 p.p.m. (J = 7 c.p.s., isopropyl group), and two vinyl resonances very similar to those appearing in the n.m.r. spectrum of abietic acid (broadened signal of H—half-height width 7 c.p.s.—at 5.44, sharp signal of H-14 at 5.73 p.p.m.) immediately showed that revision of the older formula was required. The lack of signals typical of a proton geminal to hydroxyl clearly eliminated C-12 (as originally postulated) and C-6 as the site of the hydroxyl group which must be tertiary. While the signals of the isopropyl methyl groups could be interpreted as arising from two methyl singlets in different magnetic environments, the absence of deshielding suggested that the hydroxyl group was not located at C-18 and that the

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* To Professor Louis F. Fieser.

[1] Previous paper: W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels, *J. Org. Chem.*, **30**, 1873 (1965).

[2] Supported in part by a grant from the National Science Foundation (GP-1492).

[3] Abstracted from a dissertation submitted by H. J. Wahlborg in partial fulfillment of the requirements for the Ph.D. degree, April 1965.

[4] L. Fieser and W. P. Campbell, *J. Am. Chem. Soc.*, **60**, 159 (1938).

[5] For a review of the literature on these and related matters up to 1953, see J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, 2nd Ed., Cambridge University Press, London, 1952, pp. 374–480; Vol. V, 1957, pp. 604–610.

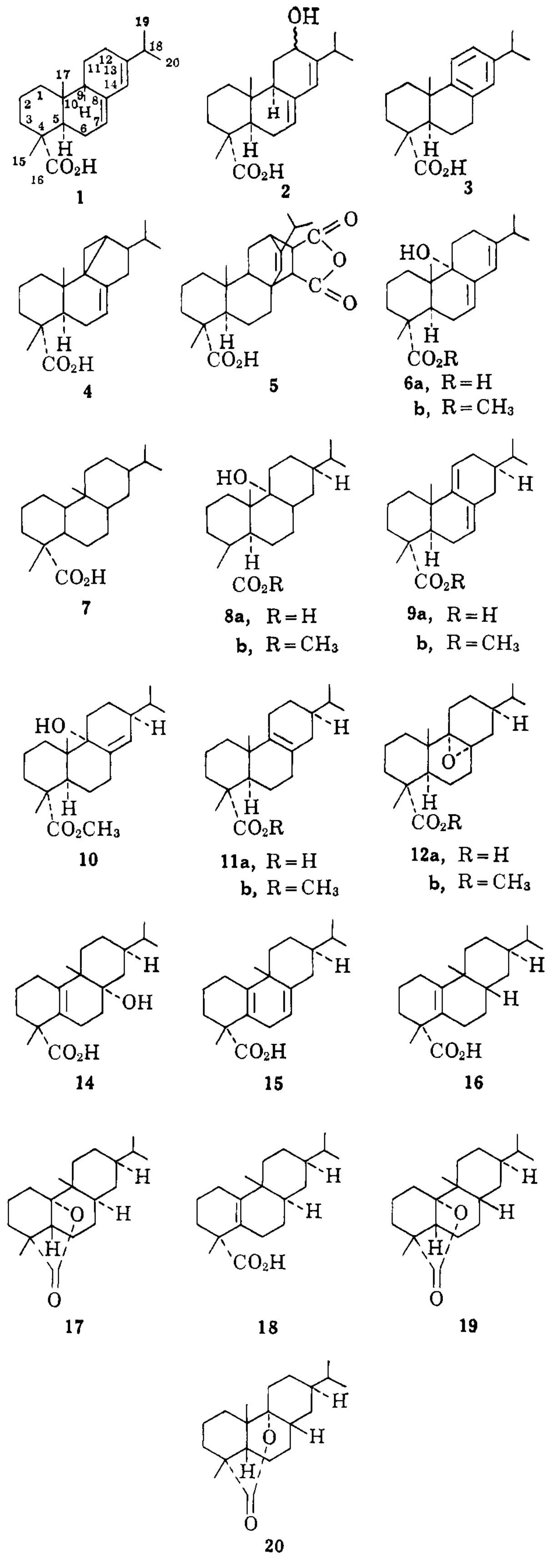
[6] W. Sandermann, *Ber.*, **76**, 1261 (1943).

[7] The stereochemistry of maleopimaric acid shown in formula **5** is as deduced recently by W. D. Lloyd and G. W. Hedrick, *J. Org. Chem.*, **26**, 2029 (1961); L. H. Zalkow, R. A. Ford, and J. P. Kutney, *ibid.*, **27**, 3535 (1962); W. A. Ayer, C. E. McDonald, and J. B. Stothers, *Can. J. Chem.*, **41**, 1113 (1963).

[8] Respectable yields (15%) were realized only when particular attention was paid to washing the crude salt thoroughly to remove residual sulfuric acid.

[9] N.m.r. spectra were run in deuteriochloroform, unless otherwise specified, on a Varian A-60 spectrometer purchased within the aid of a grant from the National Science Foundation. Frequencies are given in parts per million with tetramethylsilane serving as the internal standard.

CHART I



selenium dioxide oxidation product should be represented by **6a** (see Chart I).

The extreme instability of the hydroxy acid which underwent more or less spontaneous dehydration to dehydroabietic acid interfered with several schemes aimed at structure elucidation.[10] Recourse was therefore had to hydrogenation for obtaining derivatives which could lead to proof of structure since the driving force for dehydration to dehydroabietic acid would be eliminated.

Hydrogenation of **6b** with platinum oxide in ethanol avoided hydrogenolysis observed by Fieser and Campbell and resulted in the isolation of two dihydro derivatives which were separated chromatographically.[11] The less polar material, m.p. 89–90°, exhibited n.m.r. signals at 0.82 and 0.90 (isopropyl), 0.97 (C-10 methyl), 1.28 (C-4 methyl), 3.62 (methoxyl), and 5.38 p.p.m. (vinyl proton, probably H-7) and was subsequently identified as **8b**. The more polar material which had n.m.r. signals at 0.85 and 0.92 (two separate methyl doublets, J = 7 c.p.s.), 0.93 (C-10 methyl), 1.17 (C-4 methyl), 2.73 (quartet, J = 6.4 c.p.s., one allylic proton?), 3.70 (methoxyl), and 5.60 p.p.m. (vinyl proton) appeared to be an isomeric methyl hydroxyabietenoate which could not be crystallized or converted to a crystalline acid.

Treatment of the less polar ester with warm acetic acid effected dehydration and conversion to a liquid ester **9b**, $\lambda_{\max}$ 236, 241, and 250 mμ ($\epsilon_{\max}^{241}$ 8000), n.m.r. signals at 0.83 and 0.93 (isopropyl), 0.97 (C-10 methyl), 1.23 (C-4 methyl), 3.67 (methoxyl), and 5.40 p.p.m. (two vinyl protons), which could be hydrolyzed to a crystalline acid, m.p. 169–171°, $[\alpha]_D$ −76°, $\lambda_{\max}$ 236, 241, and 250 mμ ($\epsilon_{\max}^{241}$ 10,300). This substance differed in all respects from abietic acid and other previously known abietic-type resin acids and, because of the ultraviolet spectrum which is typical of a transoid $\Delta^{7,9(11)}$-diene system,[12] must be assigned formula **9a**.

The formation of **9b** and **9a** can come about only if dehydration of the precursor is accompanied by removal of a hydroxyl group from C-9, the n.m.r. spectrum eliminating C-11 as the locus of the hydroxyl group. Hence the precursor is methyl Δ^7-9-hydroxyabietenoate (**8b**) and the acid of Fieser and Campbell is 9-hydroxyabietic acid (**6a**).[13]

It might be argued that there are two other tertiary sites in abietic acid, C-5 and C-18, and that dehydration of a precursor with a hydroxyl group at C-5 or C-18 could be accompanied by double-bond isomerization of **9b**. However, the introduction of a hydroxyl group at a nonallylic site by selenium dioxide oxidation of abietic acid is mechanistically not admissible, even if this were not contraindicated by other evidence, and C-18 is ruled out as a site for the hydroxyl group be-

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[10] The methyl ester was somewhat more stable (absence of autocatalysis) but also underwent partial dehydration easily and presented additional difficulties in purification and recovery because of its low melting point.

[11] The crude hydrogenation product also contained variable amounts of dehydroabietic acid (formed by spontaneous dehydration of **6b**) which was eluted first.

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

[13] A possible alternative structure for **8b** which cannot be ruled out completely is methyl $\Delta^{8(14)}$-9-hydroxyabietenoate (**10**), a substance which could have been formed by 1,4 addition of hydrogen to the diene system of **6b**. Such 1,4 additions have been observed in related work (unpublished experiments of H. J. Wahlborg). Since the H-14 resonance of authentic $\Delta^{8(14)}$-abietenoic acids is not a sharp doublet but is rendered diffuse by long-range coupling to H-12 and perhaps other allylic protons, differentiation between structures **8b** and **10**, which could conceivably be converted to **9b** on treatment with acetic acid, is difficult. However, the shape of the vinyl proton multiplet is reminiscent of H-7 of abietic acid so that **8b** seems more plausible. In any event, this uncertainty does not affect the argument leading to formula **9a**.

cause of the n.m.r. spectrum of **8a**. Moreover, C-5 and C-18 are improbable sites because the relatively mild conditions of the dehydration should not be sufficient to cause double bond isomerization. Thus the other resin acids isomerize only slowly in acetic acid[14] and, more specifically, an acid **9a** has not previously been encountered during attempts to isomerize neoabietic, levopimaric, or abietic acid which would be expected as primary dehydration products if the precursor were a methyl 5- or 18-hydroxyabietenoate.[15]

While the spectroscopic evidence for the structure of **9a** appeared conclusive, chemical proof was considered desirable. The obvious starting material for the synthesis of **9a** was $\Delta^{8(9)}$-abietenoic acid (**11a**) but attempts to convert this to a $\Delta^{7,9(11)}$-diene by oxidation with selenium dioxide in acetic acid or treatment with N-bromosuccinimide[16] led only to the formation of dehydroabietic acid and Δ^{6}-dehydroabietic acid. Epoxidation of **11b** with *m*-chloroperbenzoic acid resulted in a homogeneous but noncrystalline epoxide ester **12b**; ample analogy exists for the assumption that attack occurs from the α side. The epoxide **12a** was crystalline and was used in subsequent work, although separation from *m*-chlorobenzoic acid was difficult at this stage.

Treatment of **12a** with Lewis or mineral acids, the usual reagents for the generation of the $\Delta^{7,9(11)}$-diene system from an 8,9-epoxide,[17] resulted in intractable tars or difficultly separable mixtures of **9a** and another component later shown to be **15** (*vide infra*). However, in an effort to convert the noncrystalline ester **12b** to the acid **12a**, it was subjected to the action of lithium iodide in collidine, a reagent which has previously been found suitable for the selective hydrolysis of esters of hindered acids.[18] To our pleasant surprise, hydrolysis was accompanied by epoxide ring opening and elimination in the desired direction, **9a** being formed in 60% yield. The acid **12a** also underwent epoxide cleavage with lithium iodide and collidine to give **9a**.

Since the sample of **9a** prepared in this manner was identical in all respects with the material derived from the selenium dioxide oxidation product, the structure of the latter is conclusively established as 9-hydroxyabietic acid (**6a**). Although the assignment is tentative, the hydroxyl group probably is α oriented, whatever the mechanism of its introduction,[19] because approach from the β side would be greatly hindered by the axial C-10 methyl group. Support for this conclusion is found in the observation that a small amount of 7-α-hydroxydehydroabietic acid (**13**)[20,21] is also formed during the oxidation of **1**.[22]

The structure of Fieser and Campbell's hydroxyabietic acid having been solved, the problem of "anhydrohydroxyabietic acid" still remained. Dehydration of **6a** by the published procedure[4] gave a crude product whose infrared spectrum was essentially identical with a spectrum of pure dehydroabietic acid (**3**). Ultraviolet peaks at 267 and 276 mμ indicated the presence of **3** (approximately 90% of total), peaks at 241 and 250 mμ the presence of about 5% of starting material, and a peak at 290 mμ the presence of a third component (less than 3%), undoubtedly a conjugated triene. Several recrystallizations furnished a sample of dehydroabietic acid, m.p. 170–171°, $[\alpha]_D$ +56°, whose n.m.r. and infrared spectra coincided with those of authentic material and gave no mixture melting point depression, but whose ultraviolet spectrum still exhibited a weak peak at 241 mμ. It is evident that "anhydrohydroxyabietic acid" was **3** contaminated with **1** which accounts for the lowered rotation and the chemical behavior which are reported in the literature.

Reference has been made earlier to the difficulty of separating **12a** from the by-product *m*-chlorobenzoic acid. When an attempt was made to effect purification by chromatography over silicic acid, **12a** was partially converted to an isomeric substance of greater polarity which could be prepared more conveniently by treatment of **12a** with acetic acid at 90°.

The infrared spectrum of the new compound indicated the presence of a hydroxyl group. The ultraviolet spectrum had the strong end absorption characteristic of a highly substituted double bond. In the n.m.r. spectrum the lack of signals characteristic of vinyl protons and proton geminal to hydroxyl groups demonstrated that the double bond was tetrasubstituted and the hydroxyl group tertiary. A formula in accord with these properties is $\Delta^{5(10)}$-8α-hydroxypseudoabietenoic acid (**14**)[23] which would have resulted from a Wagner–Meerwein rearrangement analogous to the one involved in the formation of the γ-lactone **17** from **11a** under the influence of sulfuric acid at 0°.[25,26] If the oxirane ring of **12a** is α, the hydroxyl group of **14** must be α as well.

Support for the postulated structure was furnished by the following transformations. Treatment of **14** with boiling ethanol containing a few drops of hydrochloric acid resulted in dehydration and conversion to a substance, m.p. 159–162°, $[\alpha]_D$ +29°, which was identical with the minor product obtained by similar

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[14] D. Baldwin, V. Loeblich, and R. V. Lawrence, *J. Am. Chem. Soc.*, **78**, 2015 (1956).

[15] $\Delta^{7,9(11)}$-abietadienoic acid (**9a**) appears to be the most stable of the abietic-type resin acids. When **9a** was refluxed for 10 hr. with ethanolic hydrogen chloride, the n.m.r. spectrum of recovered crude material was superimposable on that of starting material. Under these conditions, the other resin acids undergo extensive isomerization.[14]

[16] C. Doree, J. McGhie, and F. Kurzer, *J. Chem. Soc.*, 570 (1949).

[17] M. J. Birchenaugh and J. F. McGhie, *ibid.*, 2038 (1949).

[18] F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, **43**, 113 (1960); E. Wenkert, P. Beak, R. W. J. Carney, J. W. Chamberlin, D. B. R. Johnston, C. D. Roth, and A. Tahara, *Can. J. Chem.*, **41**, 1924 (1963).

[19] J. P. Schaefer and B. Horrath, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p. 41N.

[20] P. F. Ritchie, T. F. Sanderson, and L. F. McBurney, *J. Am. Chem. Soc.*, **75**, 2610 (1953).

[21] G. Dupont, R. Dulou, G. Ourisson, and C. Thibault, *Bull. soc. chim. France*, 708 (1955).

[22] **13** in the form of its methyl ester was isolated by chromatographing a sample of crude **6b** prepared by acidification and methylation of unrecrystallized sodium salt of **6a** and was identified further by conversion to methyl Δ^{6}-dehydroabietate.[21] Since **13** contains an α-hydroxy group, it may be argued that the hydroxyl group of its companion **6** should likewise be α. While the material balance from the selenium dioxide oxidation is by no means 100% and the formation of some 7-β-hydroxydehydroabietic acid would nullify the above argument, careful scrutiny of all fractions failed to reveal the presence of the latter.

[23] Following a terminology apparently introduced by Velluz[24] we propose to name **14** and similar substances as derivatives of the parent compound, pseudoabietane (9β-methyl-10-nor-α-5β,8α-abietane).

[24] L. Velluz, G. Muller, A. Petit, and J. Mathieu, *Bull. soc. chim. France*, 401 (1954).

[25] D. H. R. Barton, *Chem. Ind.* (London), 638 (1948).

[26] L. A. Subluskey and T. F. Sanderson, *J. Am. Chem. Soc.*, **76**, 3517 (1954). Mechanistic considerations define the stereochemistry of this lactone at C-9 and C-10 (for a chemical proof *vide infra*) from which it follows that, since the isopropyl side chain is equatorial,[27] it must be β.

[27] L. J. Gough, T. F. Sanderson, V. I. Stenberg, and E. Wenkert, *J. Org. Chem.*, **25**, 1269 (1960).

treatment of **12** (*vide supra*). The ultraviolet spectrum had strong end absorption, but no peak in the range 210–400 mμ, thus indicating the absence of conjugation. The n.m.r. spectrum exhibited the usual methyl resonances (two superimposed doublets and two singlets) and a broadened singlet at 2.53 p.p.m., half-width 8 c.p.s., indicative of two doubly deshielded allylic protons. These were spin coupled to one vinyl proton whose signal appeared as a somewhat broadened triplet or superimposed doublet of doublets ($J = 3$ c.p.s.) centered at 5.30 p.p.m.

The only structure consonant with this spectrum is $\Delta^{5(10),7}$-pseudoabietadienoic acid (**15**). The surprisingly specific preference for elimination toward C-7 may be due to the possibility of partial overlap with the π-electron system of the 5,10 double bond.

The particular arrangement of double bonds in **15** requires that ring B be very nearly planar. In a Dreiding model of **15**, the C-9 methyl group projects above the plane only as far as the C-9–C-11 bond projects below the plane of the B ring. In the same way the C-4 carboxyl and methyl groups neutralize each other. The net effect is that ring C is below the plane of ring B and, since it is far bulkier than the other substituents, should determine the direction from which reagents approach the molecule, *i.e.*, from the β side, a situation which would be fairly unusual in resin acid chemistry. Models of other structures which could conceivably represent the dehydration product (for example, $\Delta^{5(10),8(14)}$-pseudoabietadienoic acid) do not exhibit such planarity and would be expected to undergo the usual rearside attack.

As will be demonstrated in the sequel, hydrogenation proceeds with the uptake of 1 mole equiv. of hydrogen from the β side, thus establishing the validity of the arguments in terms of **14** and **15**. The product A, m.p. 186–188°, $[\alpha]_D$ +86°, isolated in 76% yield, had a tetrasubstituted double bond (ultraviolet end absorption, no vinyl proton resonance, strong n.m.r peak at 1.95 p.p.m. characteristic of allylic protons) and must be formulated as either **16** or **18**.

Now cleavage of the γ-lactone **17** is reported[24,26,28] to result in an unsaturated acid (B), m.p. 191°, $[\alpha]_D$ −37°, which has been assigned formula **18** (H-8 α) because of its derivation from **17** whose stereochemistry at C-8 and C-9 is implied in its mode of formation. Comparison of A and B clearly shows that they are different. They cannot differ at C-13 since they are both derived from the same precursor **11a** and all subsequent transformations would not be expected to affect this center. Therefore they must differ at C-8. If the γ-lactone has the stereochemistry **17** (H-8 α), substance A is **16** (H-8 β) as was predicted on the basis of structure **15** for its precursor.

The above reasoning is not without flaw since it is based on a mechanistic, though highly plausible, argument for the C-8 stereochemistry of lactone **17**.[25–27] However, the results to be discussed now definitely show that the assignments are correct and that substance A is properly represented by **16**.

γ-Lactone **17**, m.p. 311°, $[\alpha]_D$ −6°,[29] is formed exclusively when **11a** is subjected to the action of mineral acid at 0°, but treatment of **17** with concentrated sulfuric acid leads to a 1:1 equilibrium of **17** and the δ-lactone **20**,[25–30] m.p. 149°, $[\alpha]_D$ +43°,[29,30] thus proving that **17** is the initially formed product and that **20** arises only from the isomerization of **17**. In a quite analogous manner, substance A was exposed to the action of concentrated sulfuric acid at 0°. Analysis of the product indicated the presence of approximately 70% of a δ-lactone, identified as **20** by recrystallization and comparison with an authentic sample and 30% of a γ-lactone which could not be separated satisfactorily and initially was thought to be **17**. However, the ratio of lactones formed from A was so at variance with the ratio present in the equilibrium mixture from **11a**, that two possibilities had to be considered. Either the δ-lactone **20** was formed initially from its precursor A, which would require a revision in the structure of the latter, and was then partially converted to **17**, equilibration not being complete under the reaction conditions. Alternatively, the γ-lactone present in the mixture produced from A was not **17**, but the second possible isomer which can be constructed with Dreiding models, *i.e.*, **19**. Lactone **19** would be unstable owing to the B/C ring *cis* fusion, but would be expected to form rapidly from A if the latter were correctly represented by **16**, since no migrations or epimerizations would have to intervene in its production.

The lactonization of A was therefore carried out under conditions which would allow the isolation of a fast-forming, unstable lactone. This was accomplished by dissolving A in chloroform and rapidly adding the solution to sulfuric acid at 0°. After 30 sec., the reaction was quenched and gave a 90% yield of a crude γ-lactone. Chromatography and recrystallization gave a γ-lactone in 70% yield, which had m.p. 97°, $[\alpha]_D$ +23°, and which, because it was clearly different from **17**, was assigned formula **19**.

To determine more explicitly the nature of the new lactone and its relationship to the previously known lactones, it was again dissolved in the sulfuric acid–chloroform mixture and its transformation was followed spectrophotometrically. As anticipated, the γ-lactone peak due to **19** disappeared rapidly as the δ-lactone peak of **20** emerged. When a 15:85 ratio of γ- to δ-lactone had been reached, the temperature was raised to 25°, whereupon the γ peak re-emerged with a concomitant decrease in the δ-lactone peak. At length the ratio of γ- to δ-lactone remained constant at 1:1 which agrees with the ratio previously observed[27] for the equilibrium between **17** and **20**. Moreover, the infrared spectrum of this mixture was superimposable on the spectrum of an artificial mixture of **17** and **20** and differed from the spectrum of an artificial mixture of **19** and **20**.

These results confirm that γ-lactone **19** is unstable and is quickly isomerized to δ-lactone **20** which then yields the equilibrium mixture of **17** and **20**. This requires that the configuration of **19**, and of its precursor **16**, at C-8 be H-8 β and in turn provides unequivocal chemical evidence for the previously[25] assigned configurations at C-8 in **17** (H-8 α) and **20** (H-8 β).

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[28] R. F. B. Cox, *J. Am. Chem. Soc.*, **66**, 865 (1944).

[29] Le-Van-Thoi, *Bull. soc. chim. France*, 760 (1955).

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

Experimental[31]

9-Hydroxyabietic Acid (6a).—Oxidation of 40 g. of abietic acid in 500 ml. of ethanol with 15 g. of selenium dioxide in 20 ml. of water and 80 ml. of ethanol by the method of Fieser and Campbell[4] gave 11.5 g. of recrystallized partial sodium salt of **6a**, but only when the crude salt was washed thoroughly with water to remove all traces of sulfuric acid which is retained stubbornly. The free acid was recrystallized from ethanol–water or ether–petroleum ether. The melting point varied because of water of hydration, but was generally about 157–160°, $[\alpha]^{24}\text{D}$ −127°; lit.[4] m.p. 153–155°, $[\alpha]\text{D}$ −125°. The ultraviolet spectrum had the same shape as that of abietic acid with the same peak positions [main peak 242 mμ ($\epsilon_{\max}$ 21,700)]. The n.m.r. spectrum was discussed earlier.

The methyl ester **6b** was prepared by mixing an ethereal solution of **6a** with ethereal diazomethane. After evaporation of the ether, the residue was recrystallized from a small amount of petroleum ether and then melted at 74–75°; lit.[4] m.p. 75–77.5°, $[\alpha]\text{D}$ −96°. The n.m.r. spectrum exhibited signals at 0.92 (C-10 methyl), 0.98 and 1.10 (superimposed isopropyl doublets), 1.31 (C-4 methyl), 3.74 (H-14), and 5.48 p.p.m. (broadened triplet, H-7).

An attempt to prepare an adduct of **6a** and tetracyanoethylene resulted in formation of dehydroabietic acid and unidentifiable products. Reaction of **6a** with ketene–boron trifluoride at −78° gave noncrystalline material from which no homogeneous fraction could be isolated.

Methyl Δ^7-9α-Hydroxyabietenoate (8b).—A solution of 2.0 g. of **6b** in ethanol was hydrogenated with prereduced platinum oxide at atmospheric pressure for 1.5 hr., filtered, and concentrated at reduced pressure. The residue was chromatographed over 60 g. of neutral alumina. Benzene–petroleum ether (1:2) eluted 0.35 g. of methyl dehydroabietate; benzene–petroleum ether (3:2) gave 0.5 g. of crystalline **8b**. Further elution with this solvent mixture and with benzene–petroleum ether (7:3) gave 0.4 g. of a mixture of isomers, and elution with benzene gave 0.05 g. of a second methyl 9-hydroxyabietenoate which could not be crystallized: infrared bands at 3700 and 1720 cm.$^{-1}$; ultraviolet end absorption. The n.m.r. spectrum of this fraction was discussed previously. Hydrogenation of **6a** under the same conditions furnished a crude acid whose infrared and n.m.r. spectra indicated that one double bond had been hydrogenated and that the hydroxyl group was still present, but chromatography over silicic acid resulted in dehydration and formation of mixtures.

Recrystallization of **8b** furnished material, m.p. 89–90°, whose n.m.r. spectrum has been discussed previously; ultraviolet end absorption; infrared bands at 3700 and 1720 cm.$^{-1}$.

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25; O, 14.35. Found: C, 75.74; H, 10.20; O, 13.98.

$\Delta^{7,9(11)}$-Abietadienoic Acid (9a). **A.**—A solution of 0.075 g. of **8b** in 30 ml. of acetic acid was concentrated to 5 ml., diluted with benzene, washed thoroughly with water, dried, and evaporated. The n.m.r. spectrum of the noncrystalline residue was identical with the n.m.r. spectrum of an authentic sample of **9b** prepared from $\Delta^{7,9}$-abietadienoic acid with diazomethane and the infrared spectra were superimposable.

A solution of 0.2 g. of **9b**, 1.5 g. of lithium iodide, and 15 ml. of collidine was refluxed in a nitrogen atmosphere for 18 hr., cooled, acidified, and thoroughly extracted with ether. The ether solution was filtered, washed, dried, and evaporated, and the residue was chromatographed over 10 g. of neutral alumina. Ether–benzene (1:4) yielded a trace of impurities; ether–benzene (1:3) yielded after one recrystallization from methanol–water 0.095 g. of **9a**, m.p. 164–168°. Another recrystallization raised the melting point to 167–170°; $[\alpha]^{24}\text{D}$ −74°; $\epsilon_{\max}^{241}$ 10,250; n.m.r. signals at 0.83 and 0.93 (slightly broadened, almost superimposed doublets of isopropyl group), 0.97 (C-10 methyl), 1.23 (C-4 methyl), and 5.40 p.p.m. (m, H-7 and H-11).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; O, 10.58. Found: C, 78.92; H, 10.04, O, 10.99.

B.—A solution of 1.2 g. of **12b**, 35 ml. of freshly distilled collidine, and 5 g. of lithium iodide was refluxed and worked up as in A. The residue was chromatographed over 45 g. of alumina. Elution with benzene–ether (4:1) gave yellow impurities; elution with benzene–ether (7:3) gave 0.7 g. of crude **9a** which was recrystallized from methanol–water: m.p. 169–171°, $[\alpha]^{24}\text{D}$ −76.6° (*c* 1.16), $\epsilon_{\max}^{241}$ 10,330. The infrared and n.m.r. spectra were superimposable on the material prepared as in A.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; O, 10.58. Found: C, 79.34; H, 10.09; O, 10.62.

8,9-Epoxyabietanoic Acid (12a).—$\Delta^{8(9)}$-Abietenoic acid (**11a**), m.p. 179–181°, $[\alpha]^{23}\text{D}$ +115°, was prepared by hydrogenation of abietic acid and subsequent isomerization of the crude product.[24] The n.m.r. spectrum exhibited signals at 0.82 and 0.92 (slightly broadened, almost superimposed doublets of isopropyl group), 0.97 (C-10 methyl), and 1.20 p.p.m. (C-4 methyl); the allylic protons gave rise to one broadened peak centered at 1.90 p.p.m. Oxidation of **11a** with selenium dioxide in acetic acid solution gave rise to dehydroabietic acid (n.m.r. spectrum) only. To a solution of 1.0 g. of **11a** in 8 ml. of chloroform was added 0.6 g. of *m*-chloroperbenzoic acid. After 2 days at room temperature, the mixture was filtered from *m*-chlorobenzoic acid, 0.2 g., and diluted with chloroform; excess oxidizing agent was decomposed with potassium iodide. The solution was acidified, shaken with dilute potassium thiosulfate solution, washed, dried, concentrated to 5 ml., and filtered from 0.1 g. of *m*-chloroperbenzoic acid. The filtrate was evaporated at reduced pressure, taken up in hot benzene–petroleum ether, and allowed to cool. The precipitate, m.p. 183–185°, still contained *m*-chloroperbenzoic acid (n.m.r. spectrum). Several crystallizations from ether–petroleum ether furnished pure **12a**: m.p. 190–192°; n.m.r. signals at 0.92 and 1.00 (slightly broadened, almost superimposed isopropyl doublets), 1.17 (C-10 methyl), and 1.28 p.p.m. (C-4 methyl).

Anal. Calcd. for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06; O, 14.98. Found: C, 75.20; H, 9.98; O, 14.62.

Epoxidation of **11b** by the same procedure followed by filtration, decomposition with potassium iodide, washing with thiosulfate and water, and evaporation of chloroform gave a residue which was chromatographed over neutral alumina. Elution with benzene–petroleum ether (1:3) gave **12b** which, although it could not be induced to crystallize, was more convenient to use because of the ease with which it was separated from *m*-chlorobenzoic acid. The n.m.r. spectrum was identical with that of **12a** except for the presence of an additional resonance at 3.66 p.p.m. (methoxyl). A middle fraction from the chromatography was thoroughly dried and used for analysis, but the carbon content was somewhat low.[32]

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 74.76; H, 10.02.

Isolation and Identification of Methyl 7α-Hydroxydehydroabietate (13).—Five grams of the crude partial sodium salt[4] of 9-hydroxyabietic acid was acidified, taken up in ether, and treated with diazomethane. The solvent was removed and the residue was chromatographed over neutral alumina. Elution with benzene–petroleum ether (1:1) first gave 3 g. of **6b** and then several homogeneous fractions of another component (**13**) which were combined (0.3 g.) and recrystallized from ether–petroleum ether and from methanol–water, m.p. 105–107°, $[\alpha]^{25}\text{D}$ +15° (*c* 1.04) (lit.[20,21] m.p. 104 and 112°, $[\alpha]^{25}\text{D}$ +17°), thus contrasting with the properties[20] of methyl 7β-hydroxyabietate, m.p. 92–93°, $[\alpha]^{25}\text{D}$ +56°. The n.m.r. spectrum exhibited signals at 1.22 and 131 (2 sharp singlets, four methyl groups), 3.67 (methoxyl), 4.53 br (H-7), and three aromatic protons at 7.03–7.25 p.p.m.

A solution of 0.1 g. of **13** in 5 ml. of ethanol containing a few drops of concentrated hydrochloric acid was refluxed for 8 hr. and evaporated at reduced pressure, and the residue was extracted with ether. The extract was concentrated and chromatographed over alumina. The apparently homogeneous product had the ultraviolet spectrum ($\lambda_{\max}$ 260 mμ) of Δ^6-dehydroabietic acid[21] and its n.m.r. spectrum confirmed the assumed structure, signals at 1.17 and 1.28 (two superimposed doublets of isopropyl group), 1.09 (C-10 methyl), 1.40 (C-4 methyl), 3.65 (methoxyl), 6.96, 7.15 (total of three aromatic protons), and an ABX pattern with the AB portion centered at 6.15 p.p.m. (J_{AB} = 10 c.p.s., J_{AX} = J_{BX} 4 c.p.s., δ_{AB} = 49 c.p.s.).

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(31) Melting points are uncorrected. Analyses were carried out by Dr. F. Pascher, Bonn, Germany. Infrared spectra were determined in chloroform solution, ultraviolet spectra and rotations in 95% ethanol. Petroleum ether boiled at 30–60°; chromatograms were run with Alcoa F-20 alumina neutralized with ethyl acetate or Mallinckrodt 100-mesh silicic acid. We are indebted to Dr. G. W. Hedrick for generous supplies of long-leaf yellow pine oleoresin for the preparation of starting material.

(32) C. Tabacik-Wlotzka, M. Mousseron, and A. Chafai [*Bull. soc. chim. France*, 2301 (1963)] reported the preparation of this ester as an oil, without further detail. The n.m.r. assignments given in this paper for **11b** and other substances are obviously in error.

"Anhydrohydroxyabietic Acid."—Two grams of **6a** was heated at 175–200° in a nitrogen atmosphere for 30 min.[4] The infrared spectrum of the crude product was essentially superimposable on that of dehydroabietic acid (**3**) as was the ultraviolet spectrum which had peaks at 241, 250 (intensity indicative of 5% **6a**), 267, 276 (indicative of more than 90% of **3**), and 290 mμ. The n.m.r. spectrum of the crude product was that of **3**, with very weak peaks in the vinyl proton region corresponding to those of **1**. Several recrystallizations from ethanol furnished 0.9 g. of dehydroabietic acid, m.p. 170–171°, $[\alpha]_D$ 56°, identical in all respects with authentic **3**. The ultraviolet spectrum still exhibited a weak peak at 241 mμ representative of contamination by a very small amount of **1**.

$\Delta^{5(10)}$-8α-Hydroxy-9β-methyl-10-norabietenoic Acid (**14**).—In an effort to effect purification of **12a**, 5 g. of crude **12a** containing *m*-chlorobenzoic acid was placed on a column of 200 g. of silicic acid and eluted very gradually with solvent of increasing polarity. This required more than a week during which period **12a** partially isomerized. Elution with benzene–ether (9:1) gave, in order, 1.0 g. of **12a**, 1.5 g. of *m*-chlorobenzoic acid, and 1.9 g. of **14** which was recrystallized from ether–petroleum ether and then methanol–water. The product melted at 186–188°: $[\alpha]_D$ −43°; infrared bonds at 3570 and 1700 cm.$^{-1}$; end absorption in the ultraviolet (ϵ^{215} 2400); n.m.r. signals at 0.82 and 0.92 (slightly broadened, almost superimposed doublets of isopropyl group), 1.02 (C-10 methyl), 1.26 (C-4 methyl), 1.90 (broad, four allylic protons), and 7.17 p.p.m. (2 protons, hydroxyl and carboxyl −OH).

Anal. Calcd. for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06; O, 14.98. Found: C, 74.88; H, 9.80; O, 14.96.

B.—A solution of 0.15 g. of crude **12a** in 12 ml. of acetic acid was stirred at 90° for 1.5 hr., cooled, diluted with water, and extracted with ether. The ether extract was washed, dried, evaporated, and chromatographed over alumina; yield 0.05 g. of **14**.

$\Delta^{5(10),7}$-9β-Methyl-10-norabietadienoic Acid (**15**).—A solution of 0.4 g. of **14** in ethanol containing a few drops of concentrated hydrochloric acid was refluxed for 5 hr. and evaporated, and the residue was extracted with ether. The ether extract was washed, dried, and evaporated, and the residue was chromatographed over 16 g. of silicic acid. Elution with benzene–petroleum ether (1:1) first gave a yellow gum and then 0.32 g. of colorless material which was crystallized from petroleum ether, acetone–water, and methanol–water: m.p. 159–161°, $[\alpha]^{24}_D$ +29° (*c* 1.00), ultraviolet end absorption. The n.m.r. spectrum has been discussed previously.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 10.00; O, 10.58. Found: C, 79.02; H, 10.22; O, 11.11.

This substance was also encountered when a solution of **12a** in ethanol containing a few drops of concentrated sulfuric acid was refluxed for 36 hr. N.m.r. analysis of the product indicated that it contained 60% of **9a** and 50% of **15**. Further refluxing did not appear to alter this ratio.

$\Delta^{5(10)}$-9β-Methyl-10-nor-8β-abietenoic Acid (**16**).—A solution of 0.05 g. of **15** in 150 ml. of ethanol was reduced with 0.05 g. of prereduced platinum oxide in a semimicro hydrogenator at atmospheric pressure. After 3 hr. 1 mole equiv. of hydrogen had been taken up. The solution was filtered and evaporated, and the residue was recrystallized from ethanol–water: yield 0.038 g., m.p. 184–186°. Recrystallization from methanol–water raised the melting point to 186–188°; $[\alpha]^{24}_D$ +86° (*c* 0.98); n.m.r. signals at 0.82 and 0.90 (slightly broadened, almost superimposed doublets of isopropyl group), 1.03 (C-10 methyl), 1.17 (C-4 methyl), and 1.94 p.p.m. (broad, four allylic protons).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59; O, 10.51. Found: C, 78.88; H, 10.37; O, 10.39.

Lactonization of 16. A.—To a solution of concentrated sulfuric acid chilled to −5° there was added 0.13 g. of **16**. After 15 min., the solution was poured onto ice, and the product was extracted with ether. The ether extract was washed, dried, and evaporated, and the residue was chromatographed over 7 g. of alumina. Elution with benzene–petroleum ether (1:1) gave 0.095 g. of a mixture of a δ- and γ-lactone (infrared bands at 1710 and 1765 cm.$^{-1}$; ratio 7:3). Recrystallization from ethanol–water gave the δ-lactone (**20**): m.p. 151–152°; $[\alpha]^{23}_D$ +42.6° (*c* 1.06); n.m.r. signals at 0.87 and 0.98 (broadened, doublets of isopropyl group), 1.08 (C-10 methyl), and 1.23 p.p.m. (C-4 methyl).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59; O, 10.51. Found: C, 79.02; H, 10.36; O, 10.70.

An authentic sample of **20** was prepared by stirring a solution of **11a** and concentrated sulfuric acid for 4 hr. at room temperature. After quenching with water, the crude product was chromatographed over 100 g. of alumina. Elution with petroleum ether yielded the γ-lactone (**17**), m.p. 131° after recrystallization from petroleum ether and methanol–water. Elution with ether–petroleum ether yielded 1.5 g. of **20** which after recrystallization from petroleum ether melted at 149–151°, melting point undepressed on admixture of material prepared from **16**. The infrared and n.m.r. spectra were superimposable.

B.—A solution of 0.1 g. of **16** in 7 ml. of chloroform chilled to 0° was rapidly added to a chilled mixture of 2 ml. of sulfuric acid and 2 ml. of chloroform. The two-phase mixture was swirled for 30 sec. in an ice bath, then quenched with water, dried, and evaporated. The residual gum was estimated to contain 10% of δ-lactone and 90% of γ-lactone because of the relative strengths of the infrared bands at 1710 and 1765 cm.$^{-1}$. Chromatography over 14 g. of neutral alumina and elution with petroleum ether first gave a small amount of unidentifiable oil and then 0.07 g. of γ-lactone as a gum which was crystallized by triturating with a few drops of petroleum ether, chilling, and scratching. Two recrystallizations from ethanol–water furnished **19**, m.p. 97°, $[\alpha]^{24}_D$ +23° (*c* 1.00). The infrared spectrum was rich in detail and differed from that of **17**. The n.m.r. spectrum exhibited peaks at 0.83 and 0.93 (slightly broadened isopropyl doublet), 1.26 (C-10 methyl), and 1.32 p.p.m. (C-4 methyl).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.51. Found: C, 78.98; H, 10.32.

Isomerization of 19.—The results of Table I were obtained in the following manner. A solution of 13 mg. of **19** in 3 ml. of chloroform was added to a mixture of 1 ml. of chloroform and 1 ml. of concentrated sulfuric acid. The mixture was stirred and quenched with water, and the product was extracted with ether. The ether solution was washed, dried, and evaporated, and the residue was analyzed by infrared spectroscopy. The further course of the isomerization was followed by repeating the reaction with the product from the previous run and fresh sulfuric acid. Reactions times and results are noted in Table I. The first two runs were made at 0°, the last three at 25°.

TABLE I

Reaction time,[a] min.	γ-Lactone,[b] %	δ-Lactone,[b] %
0	100	0
12	23	77
21	18	82
35	28	72
67	47	53
158	51	49

[a] All times relative to time zero. [b] Values accurate to ±3% by comparison with mixtures of known composition.

All lactone percentages are relative to each other and were obtained by measuring the strength of the carbonyl peaks in the infrared spectrum. The assumption that the molar extinction coefficients of the lactone carbonyls are approximately the same was verified by comparison of the infrared spectra of the pure samples with artificial mixtures of known concentration.