reduction step. Reaction time was limited to 21 hr to minimize reduction of the carbomethoxy group. Tlc analysis of the crude product indicated that some reduction of the carbomethoxy group had taken place but chromatography over alumina gave **32** in 35% yield. It was recrystallized from methanol–water and had mp 88–89°; $[\alpha]^{25}D$ −11 ($CHCl_3$, *c* 1.81); ir 3600 (hydroxyl) and 1719, 1250 cm^{-1} (ester); nmr 3.72 br ($w_{1/2}$ = 6, βH-7), 3.61 (methoxyl), 2.53 (hydroxyl), 2.30 br d (*J* = 12.5, αH-5), 1.18 (C-4 methyl), 1.05 (C-10 methyl), and 0.86 d (*J* = 5.8, isopropyl).

Anal. Calcd for $C_{21}H_{36}O_3$: C, 74.95; H, 10.78; O, 14.26. Found: C, 74.89; H, 10.87; O, 14.25.

Methyl 7-Oxo-13β-abietanoate (34).—Oxidation of 0.3 g of **32** in acetone with excess Jones reagent at 0° for 10 min followed by the usual work-up yielded 0.26 g of a mixture of **33** (80%) and **34** (20%) as determined by the nmr spectrum. Preparative tlc did not effect any purification of **33** which had ir bands at 1720, 1250 (ester), and 1706 cm^{-1} (ketone); nmr 3.61 (methoxyl), 1.22 (C-4 methyl), 1.03 (C-10 methyl), and 0.86 d (*J* = 5.9, isopropyl); ORD curve (*c* 0.22, contaminated with 20% of **34**), $[\alpha]_{400}$ −150°, $[\alpha]_{306}$ −1140°, $[\alpha]_{767}$ −1140°.

The mixture, wt 0.1 g, was dissolved in methanol–water (4:1) containing 1 g of sodium hydroxide and was allowed to stand for 38 hr. After acidification of the solution, dilution with water, extraction with ether, washing, and drying of the ether extract, there was obtained 90 mg of **34** which was recrystallized from methanol–water and then had mp 88–89°; $[\alpha]^{25}D$ −19° ($CHCl_3$, *c* 1.14); ir 1720, 1250 (ester), and 1705 cm^{-1} (ketone); nmr 3.61 (methoxyl), 1.20 (C-4 methyl), 1.08 (C-10 methyl), and 0.87 d (*J* = 5.6, isopropyl); ORD curve (*c* 0.055), $[\alpha]_{400}$ −27°, $[\alpha]_{299}$ −200°, $[\alpha]_{250}$ +364°.

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25; O, 14.35. Found: C, 75.37; H, 10.07; O, 14.46.

Registry No.—**5**, 21559-75-1; **6**, 21559-76-2; **7**, 21562-96-9; **7** (2,4-dinitrophenylhydrazone), 21559-77-3; **8**, 21559-78-4; **9**, 21559-79-5; **11**, 21559-80-8; **12**, 21559-81-9; **13**, 21559-83-0; **14**, 21559-83-1; **15**, 21559-84-2; **17**, 21559-85-3; **18**, 21559-86-4; **20**, 21559-87-5; **21a**, 21559-88-6; **21b**, 21562-60-7; **22a**, 21562-61-8; **22b**, 21562-62-9; **23**, 21562-63-0; **24**, 21562-64-1; **25**, 21562-65-2; **26**, 21562-66-3; **28a**, 21562-67-4; **28b**, 21562-73-2; **28c**, 21562-68-5; **30**, 21562-69-6; **32**, 21562-70-9; **33**, 21562-71-0; **34**, 21562-72-1.

Resin Acids. XVIII. The Lithium–Ammonia Reduction of Some Resin Acid Enones[1,2]

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The reduction of 11-oxo-13β-abiet-8(9)-en-18-oate (**3**) with lithium–liquid ammonia afforded primarily the less stable B/C *cis*-fused methyl 11-oxo-8α,13β-abiet-8(9)-en-18-oate (**5**). Methyl 7-oxo-13β-abiet-8(9)-en-18-oate (**10**) gave quite unexpectedly the B/C *cis*-fused methyl 7-oxo-8β,9β,13β-abietan-18-oate (**18b**). The lack of parallelism between the reductions of these abietanes and their steroidal counterparts which undergo conversion into the more stable B/C *trans* system is ascribed to the absence of ring D which allows ring C of abietanes to assume conformations not permitted in the steroid series. The formation of **18b** appears to result from protonation of the most stable carbanion intermediate rather than from overlap control.

Although the accompanying paper[1] describes a route to **1** which was desired as an intermediate for further synthetic work in the diterpene area, the route was somewhat circuitous and the yield of the critical intermediate **2** was low. Lithium–liquid ammonia reduction of **3** which was much more easily purified than **2** was expected to provide **1** more directly since steroidal $\Delta^{8,9}$-11-ketones afford the stable *trans*-fused 11-ketones in fair yield by this method.[4] The unexpected mode of reduction of **3** and of **10** which resulted in compounds possessing undesired B/C *cis* stereochemistry is discussed in the present paper.

Initially, a solution of **3** in dry ether was added to a solution of lithium in liquid ammonia. After 5 min the reaction was quenched by addition of ammonium chloride. Chromatography of the crude product resulted in recovery of much starting material and the formation of **1** and another saturated keto ester in a 1:9 ratio. See Scheme I. When tetrahydrofuran was employed as cosolvent and the time was extended to 2 hr, the starting material was consumed completely. However, under these conditions the carbomethoxy group was reduced to the corresponding alcohol and it was necessary to reoxidize the crude products and to methylate the resulting mixture of keto acids. Subsequent chromatography furnished only 8% **1** and 62% new saturated keto ester (ir bands at 1722 and 1689 cm^{-1}). Hence the reduction had taken an unexpected course.

The new substance was not affected by exposure to sodium methoxide, an experiment which eliminated formula **4**[5] and left as the most plausible alternative structure **5** whose *trans-anti-cis* ring system would not be expected to epimerize to the much less stable *trans-syn-trans* system.[6] Comparison of the nmr spectra of undeuterated and deuterated keto ester demonstrated that signals of three protons in the 2.0–2.5-ppm region had disappeared after deuterium exchange as expected for a substance of formula **5** and that the undeuterated compound did not exhibit the characteristically deshielded 1β-proton signal of a *trans-anti-trans* system. Figure 1 demonstrates that in an 8α,13β-11-oxoabietane the carbonyl group would be oriented so as to shield rather than deshield the 1β proton; while ring C is probably somewhat distorted from the normal chair form depicted in Figure 1, this would not be expected to induce any long-range paramagnetic shift. The ORD

(1) Part XVII: W. Herz and J. J. Schmid, *J. Org. Chem.*, **34**, 3464 (1969). (Reference 6 of this paper describes numbering and nomenclature used throughout the series.)

(2) Supported in part by National Science Foundation Grant GP-6362.

(3) National Science Foundation Fellow, 1967–1968.

(4) C. Djerassi, "Steroid Reactions," Holden-Day, Inc., San Francisco, Calif., 1963, pp 308–310.

(5) Since **1** and **4** differ only in the stereochemistry at C-9, one or the other should be epimerizable or the same equilibrium mixture should be produced from both. Since **1** is stable to base, **4** should be convertible to **1**. This was corroborated in subsequent work.

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 282–286.

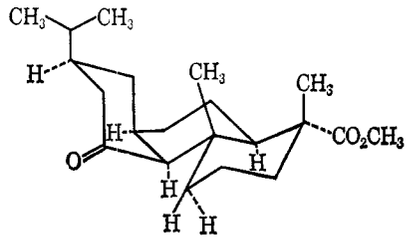


Figure 1.—Model of **5**.

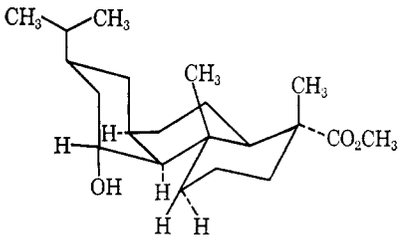
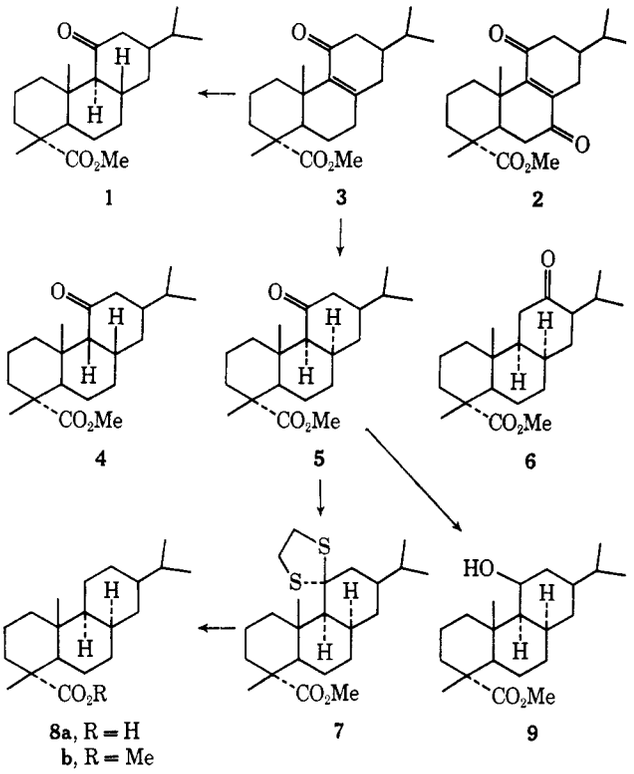


Figure 2.—Model of **9**.

SCHEME I



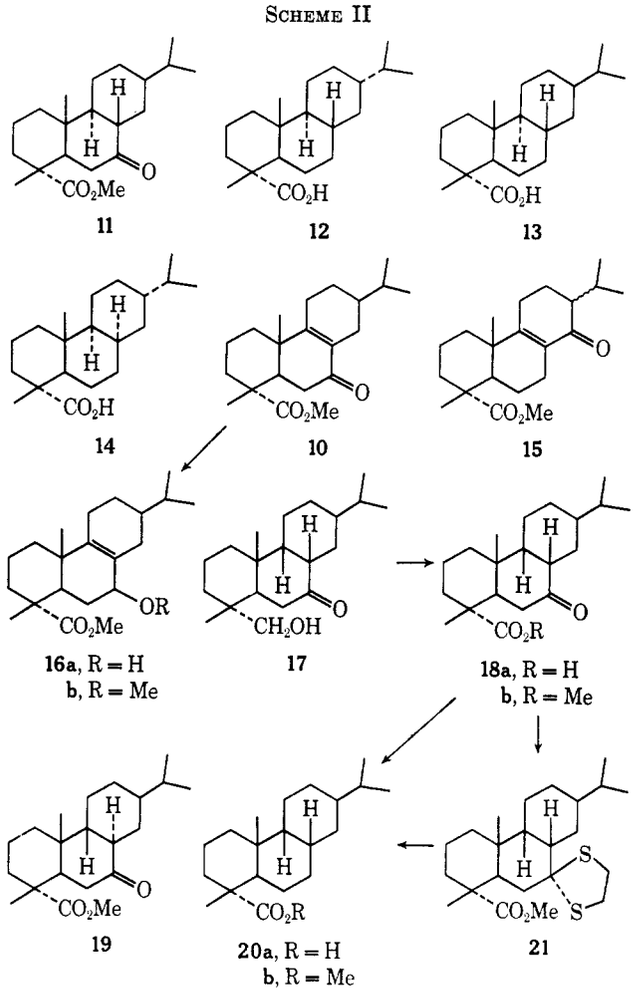
curve of the new ketone displayed a moderately strong Cotton effect in accord with that predictable for structure **5**. Distortions of ring C would not be expected to affect the sign of the Cotton effect (as, for example, in the case of **6**)[7] since ring A invariably remains in the lower left rear (negative) octant.

The model shows that the ketone group of **5** should not be hindered significantly. Indeed, **5** readily formed an ethylene thioketal **7** whose nmr spectrum displayed the signals of the methylene protons adjacent to sulfur as a complex multiplet centered at 3.27 ppm as in all other thioketals of 11-ketones[8] and a broadened one-proton doublet (J = 11 Hz) at 2.79 ppm, probably the resonance of 1β-H which is deshielded by a sulfur atom. Final evidence for the postulated stereochemistry of **5** was provided by nickel desulfurization of **7** which furnished **8b** of established configuration.[9]

The relatively unhindered nature of the 11-keto group of **5** was also demonstrated by sodium borohydride reduction in methanol (conditions under which **1** was unreactive) to the equatorial alcohol **9** [signal of axial H-11 at 3.88 ppm ($w_{1/2}$ = 17 Hz)]. A broadened doublet (J = 11.5 Hz) at 2.55 ppm was assigned to the 1β proton which is deshielded by the 11β-hydroxyl group as shown in Figure 2. The assignment was confirmed by borohydride reduction of trideuterio-**5** to the corresponding alcohol whose nmr spectrum retained the broadened doublet at 2.55 ppm. However, the signal of H-11 now appeared as broadened singlet ($w_{1/2}$ = 2.5 Hz) as would be expected for a proton coupled only to deuterium atoms.

The unforeseen mode of reduction of **3** prompted a study (see Scheme II) of the lithium–liquid ammonia

SCHEME II



reduction of the α,β-unsaturated ketone **10**[1] which, by analogy with results observed in the steroid series,[4] was expected to provide methyl 7-oxo-13β-abietan-18-oate (**11**). Chromatography of the crude product afforded in order of increasing polarity an oily keto ester A (ir bands at 1720 and 1710 cm^{-1}, yield 50%), starting material (40%), and a keto alcohol (10%). Oxidation of the keto alcohol followed by methylation gave A.

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

(8) See footnote 25 of ref 1.

(9) J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, **31**, 4128 (1966).

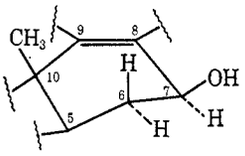


Figure 3.—Ring B of **16a**.

Wolff–Kishner reduction of A yielded a tetrahydroabietic acid, mp 189–192°, $[\alpha]$ +7°, homogeneous by all analytical criteria. Direct comparison showed that this substance differed from **8a** (mp 164°, $[\alpha]$ +21°), **12** (mp 202°, $[\alpha]$ +8°), and **13** (mp 179°, $[\alpha]$ +6°).[9] The same new tetrahydroabietic acid was formed when the thioketal of A was desulfurized and the resulting ester was hydrolyzed. Hence the reduction of A, like that of **3**, had proceeded in an entirely unexpected manner.

The nmr spectrum of the new acid whose C-10 methyl group resonated at 1.06 ppm was very different from the nmr spectra of **12** and **13** (C-10 methyl signal at 1.06 ppm),[9] an observation which would normally have suggested the presence of 8α,9α-H stereochemistry.[9] Formula **8a** having been preempted by the abietanoic acid of mp 164°,[9] acceptance of this interpretation would have led to the formulation of the new acid as **14**, an extremely unlikely possibility since it would have required epimerization of the isopropyl group to the unstable, axial position during the series of transformations beginning with methyl 13β-abiet-8(9)-en-18-oate. Compelling evidence against revision of the structure of the ketonic precursor **10** to **15** to accommodate such an epimerization has already been cited:[1] the extremely deshielded C-10 methyl resonance, and the oxidation of **10**, albeit in poor yield, to **2**. Additional proof was the sodium borohydride reduction of **10** in 90% yield to an alcohol which had to be assigned structure **16a**. In the nmr spectrum of **16a** the signal of the proton geminal to the hydroxyl group (whose proton resonated as a sharp singlet at 2.40) appeared as a broadened triplet (J = 8 Hz) at 4.04 ppm, thus clearly eliminating C-14 as a possible site of the hydroxyl group which in a reduction product of **15** should have appeared as a broadened doublet.[10]

With the structure of the enone precursor securely established as **10**, it was obvious that the keto ester A could not possess 8α,9α or 8β,9α stereochemistry[12] since

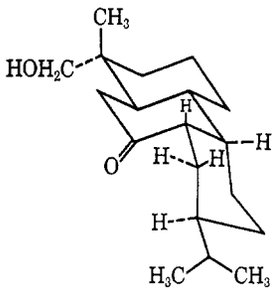


Figure 4.—Model of **17**.

subsequent removal of the ketone group would have yielded either **12** or **13** or a mixture thereof. The two remaining possibilities, methyl 9β,13β-abietan-18-oate (**18b**) and methyl 8α,9β,13β-abietan-18-oate (**19**), represent a pair of C-9 epimers of which **19** is clearly the less stable one. Since A was not affected by treatment with base, it had to be formulated as **18b**, the keto alcohol as **17**, and the abietanoic acid as **20a**.

In the nmr spectra of **18a** and **18b**, the C-10 methyl resonance was found at 1.25 ppm. This represented a paramagnetic shift of 23.5 Hz relative to **13**, a value not consistent with 9β stereochemistry (predicted[13] shift 16.5 Hz), and a shift of 12 Hz relative to **20a** and **20b**, the appropriate standards. The C-10 methyl group of **21** resonated at 1.10 ppm, a paramagnetic shift of 2.5 Hz relative to **20b** whose magnitude was in accord with that observed for other 7-thioketal derivatives[14] and could be used to confirm that epimerization at C-8 had not occurred during thioketalization. The protons of the thioketal appeared as the broadened singlet at 3.18 ppm characteristic of 7-thioketalated compounds.[8] The nmr spectra of **17** and **19** also displayed a broadened one-proton signal ($w_{1/2} \sim$ 10 Hz) at 2.83 ppm which disappeared on deuteration and could be attributed to the 8β proton since the latter (Figure 4) would experience relatively small couplings to 9β-H, 14α-H, and 14β-H and a smaller "w" coupling to 11β-H. The 8β,9β stereochemistry of **17** and **18** also accounts for the relatively large paramagnetic shift of the 8β proton. In such compounds, the 9,11 and 13,14 carbon–carbon single bonds should exert a deshielding effect on the 8β proton, the opposite effect being produced in 8β,9α-7-ketones.

The 8β,9β stereochemistry also accommodates the paramagnetic shift to 1.06 ppm of the C-10 methyl resonance of **20a** which is in accordance with the generalization[15] that as a given angular methyl group "sees" less of the remaining carbon skeleton it will resonate at lower field. Lastly, the weak negative Cotton effect of **18b** is in accord with the postulated configuration. C-2 and C-3 lie in the upper rear octant; the carbomethoxy group is partitioned between this octant and the lower right rear octant. C-11 and C-12 fall in the lower left rear octant. The isopropyl group should give a negative contribution since it is in the upper left front octant.

(10) The appearance of H-7 in the nmr spectrum of **16a** as a triplet was puzzling at first. The newly formed hydroxyl group would be expected to be β oriented and quasi-equatorial, an assignment which was supported by the J_{sum} of the quasi-axial H-7, but inspection of a model of **16a** suggested that the signal should be a doublet of doublets with a relatively large $J_{e,qa}$ to 6β-H and a somewhat smaller $J_{a,qa}$ to 6α-H (see Figure 3). However, it should be recalled that the observed splittings of the X portion of an ABX spectrum do not necessarily represent J_{AX} and J_{BX}. The X portion of the ABX system tends toward a triplet when δ_{AB} and $(J_{AX} - J_{BX})/2$ are both small compared with J_{AB}. This may be the situation in **16a**. The double bond may deshield 6β-H more than 6α-H, a circumstance which might result in near equivalence of these protons. In the absence of other effects, axial protons resonate at higher fields than β protons.

One might argue that the appearance of the signal could be explained if the hydroxyl group of the allylic alcohol were located at C-11 and β oriented. However, this would require reassignment of structure **3** which is incompatible with the evidence.[1] An attempt to reduce **3** with sodium borohydride in methanol resulted in recovery of starting material which is indicative of the presence of a hindered carbonyl group. Under forcing conditions[11] a mixture resulted which appeared to contain a significant amount of the 11β alcohol. However, on standing this substance was converted to methyl 13β-abieta-7,9(11)-dien-18-oate, a process probably catalyzed by traces of acid.

(11) W. S. Allen, S. Bernstein, and R. Littell, *J. Amer. Chem. Soc.*, **76**, 6116 (1954).

(12) The preparation of authentic methyl 7-oxo-8α,13β- and 7-oxo-13β-abietan-18-oate was achieved subsequently.[1]

(13) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963).

(14) See footnote 26 of ref 1.

(15) N. S. Bhacca and D. H. Williams, "Applications of Nmr Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 19.

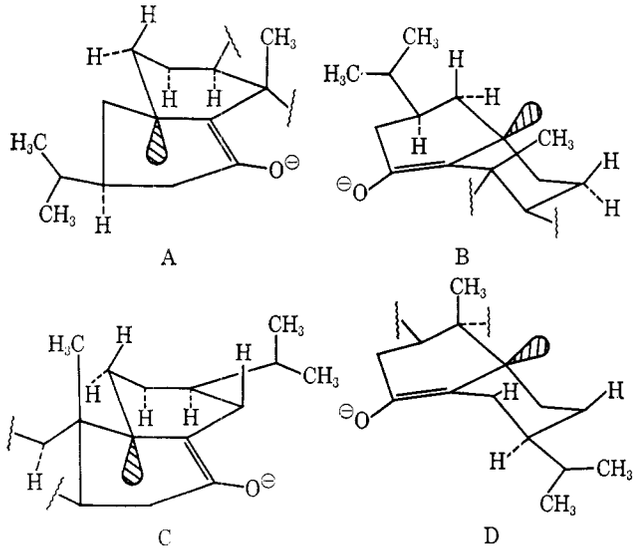


Figure 5.—Intermediates in lithium–ammonia reductions of **3** and **10**.

To explain the originally unexpected stereochemistry of the products formed during the lithium–liquid ammonia reductions of **3** and **10**, we considered the conformations of the intermediate dianions (Figure 5). The reduction of **3** produces two possible dianions possessing an equatorial isopropyl group (A and B). Conformation B would appear to be more stable since its B ring may assume the chair form whereas ring B of A must remain in a quasi-boat form, even though conformation A would be slightly favored on the basis of stereoelectronic (maintenance of overlap) considerations. Since reduction results in a 9:1 preponderance of **5** over **1**, the less favored conformation A must undergo protonation more rapidly than B. One can account for this by assuming that axial protonation of the (apparently) stereoelectronically favored A permits continuous overlap with the carbon–carbon double bond of the enolate.[16] Alternatively, inspection of the models (Figure 5) shows that proton donors could approach the electron pair of A more easily than that of B. In any event, the observed products from **3** must be the result of kinetic control.

For the reduction of **10**, the preferred conformations with an equatorial isopropyl group are C and D. Although C is slightly favored stereoelectronically, it should be less stable than D because ring C is in a quasi-boat form. Steric hindrance to approach of a proton source appears to be approximately the same. Hence, formation of **18b** is the result of protonation of the more stable intermediate D. Our observation appears to violate the principle of maintenance of overlap enunciated by Stork and Darling,[16] even though application of the latter should, from inspection of the models, result in generation of a stable *trans-anti-trans*-perhydrophenanthrene derivative instead of the *trans-syn-cis* system actually produced.

In the reduction of analogous steroidal enones, intermediates of the type favoring the stereochemistry observed in the present work are not possible since the attachment of ring D requires that ring C remain in a fixed conformation favoring elaboration of the "normal" stable *trans* B/C ring fusion.

(16) G. Stork and S. D. Darling, *J. Amer. Chem. Soc.*, **86**, 1761 (1964).

Experimental Section[17]

Reduction of 3.—A solution of 1.53 g of **3** in 125 ml of tetrahydrofuran was added to 0.4 g of lithium in 125 ml of liquid ammonia under nitrogen. Stirring was continued for 2 hr after the blue color of the solution persisted. The bulk of the liquid ammonia was allowed to evaporate and the residue was poured into water and extracted with ether. The washed and dried ether extracts were evaporated; the residue was reoxidized with Jones reagent and methylated with diazomethane. The resulting oil (1.35 g) was chromatographed over alumina. Elution with benzene–petroleum ether (1:4) gave 0.12 g of **1**. Elution with benzene–petroleum ether (1:2) gave 0.95 g of **5** which was recrystallized from petroleum ether and had mp 110–111°; $[\alpha]^{25}D$ −82° (EtOH, *c* 1.07); ir 1722, 1225 (ester), and 1689 cm^{-1} (ketone); nmr 3.61 (methoxyl), 1.20 (C-4 methyl), 1.11 (C-10 methyl), 0.91 d ppm (J = 5.9, isopropyl); ORD curve (*c* 0.46), $[\alpha]_{600}$ −80°, $[\alpha]_{322}$ −1220°, $[\alpha]_{269}$ +1740°. The substance was recovered unchanged on acidification of a refluxing solution of sodium methoxide in methanol.

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25; O, 14.35. Found: C, 75.18; H, 10.42; O, 14.51.

Attempted zinc–acetic acid reduction of **3** resulted in recovery of starting material.

Thioketal 7.—The thioketal **7**, prepared in 125 mg yield from 120 mg of **5** by the method employed for the preparation of compound **15** of ref 1, could not be induced to crystallize, but was homogeneous by tlc and nmr criteria: ir 1720, 1225 cm^{-1} (ester); nmr 3.62 (methoxyl), 3.27 m (four protons, 11-thioketal methylenes), 2.79 d (J = 11, βH-1). Raney nickel desulfurization in the usual manner produced 80 mg of a gum which solidified on standing. Recrystallization from methanol gave **8b**, mp 97–98°, identical with authentic material[9] by mixture melting point and ir and nmr spectra.

Methyl 11β-Hydroxy-8α,13β-abietan-18-oate (9).—Excess sodium borohydride was added to a methanol solution of 0.1 g of **5**. After 1.5 hr the solution was diluted with water and extracted with ether. The washed and dried ether extract was evaporated. The residue (**9**) was recrystallized from methanol and had mp 103–104°; $[\alpha]^{25}D$ −7.5° ($CHCl_3$, *c* 2.42); ir 3600 (hydroxyl), 1720, and 1245 cm^{-1} (ester); nmr 3.88 m ($w_{1/2}$ = 17, αH-11), 3.63 (methoxyl), 2.55 d (J = 11.5, βH-1), 2.09 (hydroxyl), 1.23 (C-10 methyl), 1.21 (C-4 methyl), and 0.89 d (5.7, isopropyl).

Anal. Calcd for $C_{21}H_{36}O_4$: C, 74.95; H, 10.78; O, 14.26. Found: C, 74.56; H, 10.86; O, 14.31.

Methyl 7β-Hydroxy-13β-abiet-8(9)-en-18-oate (16a).—Sodium borohydride reduction of 0.2 g of **10** in methanol and work-up as described in the previous section gave 0.2 g of gum which crystallized on trituration with hexane. Recrystallization from methanol afforded **16a** which had mp 100–101°; $[\alpha]^{25}D$ +66° (EtOH, *c* 2.03); ir 3600 (hydroxyl) and 1715, 1250 cm^{-1} (ester); nmr 4.04 t br (J = 8, αH-7), 3.62 (methoxyl), 2.40 (hydroxyl), 1.19 (C-4 methyl), 1.03 (C-10 methyl), and 0.89 d (J = 5.5, isopropyl).

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25; O, 14.35. Found: C, 75.23; H, 10.25; O, 14.51.

The acetate **16b** was prepared in 90% yield by acetylation with acetic anhydride–pyridine. It could not be induced to crystallize but had ir bands at 1725 (double intensity) and 1240 cm^{-1}; nmr signals at 5.28 t br (J = 8, αH-7), 3.62 (methoxyl), 2.02 (acetate), 1.19 (C-4 methyl), 1.05 (C-10 methyl), and 0.88 d (J = 6, isopropyl).

Reduction of 10. A.—A solution of 0.6 g of **10** in 5 ml of ether was added dropwise to excess lithium in 50 ml of liquid ammonia under nitrogen with stirring. After the addition was complete and the blue color of the solution had persisted for 5 min, ammonium chloride was added until the color was discharged. The mixture was worked up as described for the reduction of **3**. The crude product was chromatographed over alumina. Elution with petroleum ether–benzene (1:9) gave a small amount of gum, elution with benzene gave noncrystalline **18b** (35%), elution with benzene–ether (4:1) gave starting material (50%), and elution with ether gave **17** (10%).

B.—Reduction of a solution of **10** in tetrahydrofuran with lithium–liquid ammonia in the manner described for **3** gave only **17** (85%). After recrystallization from methanol it had mp 185–186°; $[\alpha]^{25}D$ +16° ($CHCl_3$, *c* 0.755); ir 3600 (hydroxyl) and 1700 cm^{-1} (ketone); nmr 3.37 d and 3.00 d (J = 11.5, AB doub-

(17) For details concerning methods see footnote 52 of ref 1.

lets of $-CH_2OH$), 2.83 m ($w_{1/2}$ = 10, βH-8), 2.61 (hydroxyl), 1.25 (C-10 methyl), 0.88 d and 0.84 d (J = 6, isopropyl), and 0.79 ppm (C-4 methyl). It was recovered unchanged from a refluxing solution of sodium methoxide in methanol.

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.31; H, 11.07; O, 10.6.

Oxidation of **17** with excess Jones reagent for 3 hr in the usual manner gave acid **18a** (80%) which was recrystallized from methanol–water and had mp 188–191°; $[\alpha]^{25}D$ −25° ($CHCl_3$, c 0.87); ir 3600–2700 (hydroxyls), 1700 (carboxyl), and 1710 cm^{-1} (ketone); nmr at 7.36 (CO_2H), 2.83 m ($w_{1/2}$ = 10, βH-8), 1.28 (C-10 methyl), 1.21 (C-4 methyl), 0.90 d, and 0.88 d (J = 6, isopropyl).

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06; O, 14.98. Found: C, 74.85; H, 10.03; O, 15.08.

Esterification of **18a** afforded **18b** identical with the material obtained in A: ir 1720, 1250 (ester), and 1710 cm^{-1}, nmr 3.65 (methoxyl), 2.83 m ($w_{1/2}$ = 10, αH-8), 1.28 (C-10 methyl), 1.21 (C-4 methyl), 0.90 d, and 0.88 d (J = 6, isopropyl); ORD curve (c 0.046), $[\alpha]_{400}$ +23°, $[\alpha]_{308}$ 0°, $[\alpha]_{260}$ +1210°.

9β,13β-Abietan-18-oic Acid (20a). A.—A mixture of 0.25 g of **18b**, 25 ml of diethylene glycol, 2.5 g of potassium hydroxide, and 2.5 ml of anhydrous hydrazine was refluxed in a nitrogen atmosphere for 1.5 hr (140°). The condenser was removed and the temperature was allowed to rise to 210°. Refluxing was continued for 2 hr; the solution was then cooled, acidified, diluted with water, and filtered. The product was recrystallized from ethanol–water (yield 0.18 g), but the nmr spectrum indicated the presence of an impurity (15%). A second recrystallization afforded pure **20a**: mp 189–192°; $[\alpha]^{25}D$ +7° ($CHCl_3$, c 0.825); ir 3600–2700 (carboxyl) and 1695 cm^{-1}; nmr signals at 1.15 (C-4 methyl), 1.07 (C-10 methyl), and 0.83 d (J = 6, isopropyl).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44. Found: C, 78.24; H, 11.09; O, 10.97.

Methylation with diazomethane gave **20b** identical with material whose preparation is described in the next paragraph.

B.—Treatment of 0.3 g of **18b** with ethanedithiol–boron trifluoride etherate in the usual manner gave, upon recrystallization of the crude product from methanol, 198 mg of the thioketal **21**. It had mp 100–101°; ir 1715 and 1220 cm^{-1} (ester); nmr 3.61 (methoxyl), 3.18 (four protons, 7-thioketal methylenes), 1.13 (C-4 methyl), 1.10 (C-10 methyl), and 0.86 d (J = 6, isopropyl). Raney nickel desulfurization of **21** produced **20b** and a small amount of another substance which appeared to be an olefin.[18] Recrystallization from methanol–water afforded pure **20b**: mp 47–49°; $[\alpha]^{25}D$ +6° ($CHCl_3$, c 0.71); nmr superimposable on that of **20b** in the methyl region.

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.75; H, 11.25; O, 10.00. Found: C, 78.59; H, 11.21; O, 10.22.

Registry No.—**5**, 21577-54-8; **7**, 21577-55-9; **9**, 21537-46-2; **16a**, 21537-47-3; **16b**, 21537-48-4; **17**, 21537-49-5; **18a**, 21537-50-8; **18b**, 21537-51-9; **20a**, 21537-52-0; **20b**, 21537-53-1; **21**, 21537-54-2.

(18) P. D. Bartlett and M. Stiles, *J. Amer. Chem. Soc.*, **77**, 2806 (1955); C. Djerassi and D. H. Williams, *J. Chem. Soc.*, 4046 (1963).

Transformations in the Resin Acid Series. Ring C

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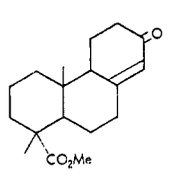
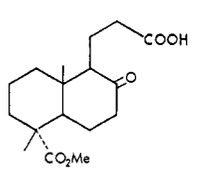
Transformations of the resin acid degradation products **1**, **2**, and **3** are discussed. The conversion of **1** into **8** by *m*-chloroperbenzoic acid has been investigated. Compound **8** undergoes a facile rearrangement to the lactone aldehyde **10**; the steric course of this arrangement is apparently different from that of the usual rearrangement of epoxy esters. Further transformations of **10** lead to a five-membered ketone **19** which also can be prepared by a route involving the benzilic acid rearrangement of the diosphenol **22**. Epoxidation of **1** afforded an epoxide **9** which was converted by boron trifluoride etherate into a mixture of **22** and **23**. The mass spectra of **22** and **23** are discussed.

In a previous communication on the oxidative degradation of resin acids[1] we focussed attention on two objectives: (1) the selective oxidation of the isopropylidene side chain of methyl neoabietate to yield the enone ester **1**, and (2) a one-step cleavage of both the double bonds in methyl neoabietate and methyl levopimarate to afford the keto acid esters **2** and **3**, respectively. This paper reports some transformations involving the degradative products **1**, **2**, and **3**.



1



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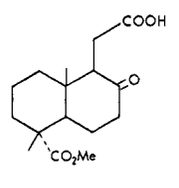
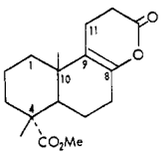


3

Lactonization of **2** with acetyl chloride–acetic acid gave exclusively the Δ^8-δ-lactone ester **4**, τ 8.93 (3 H singlet, C-10 Me), in 72% yield. Under similar conditions, however, lactonization of **3** afforded a mixture of the ene γ-lactones **5** and **6**, which under base (Et_3N) equilibration[2] gave predominantly the conjugated Δ^9-γ-lactone ester **6**. Treatment of **3** with acetic anhydride and sodium acetate also afforded a mixture of **5** and **6** which could be isomerized to **6** by treatment with ethanol and triethylamine. This isomerization to the Δ^9-γ-lactone provides a convenient handle for the cleavage of ring C of compound **6**.



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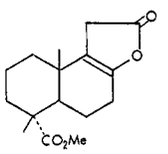

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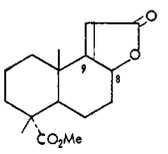
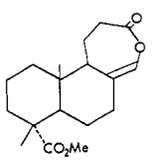


6

Oxidation of **1** with less than 2 equiv of *m*-chloroperbenzoic acid in methylene chloride resulted in a mixture of the Baeyer–Villiger products **7** and **8**. However, in



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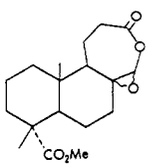

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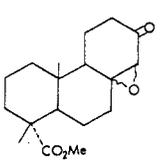

9

(1) S. W. Pelletier, K. N. Iyer, C. W. J. Chang, and A. Ogiso, *Tetrahedron Lett.*, 3819 (1968).

(2) M. P. Cava, W. R. Chan, R. P. Stein, and C. R. Willis, *Tetrahedron*, **21**, 2617 (1965).